SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED MATERIALS USING DISPERSION POLYMERIZATION

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Summary

Nanostructured materials are becoming of major significance and the technology of their production and use is rapidly growing into a powerful industry. The purpose of this work was to develop simple methods to prepare novel nanostructured materials and to explore their properties. This work focuses on three nanostructures, nanoparticle, hollow nanostructure, and core-shell nanostructure. Dispersion polymerization technique was used in the preparation of these nanostructures.

In the first part of this work, two surface-functionalized conducting nanoparticles, PANI-CS and PPy-CS were prepared. Chitosan was developed as the steric stabilizer to prevent the aggregation of polyaniline and polypyrrole. XPS spectrum proved that chitosan was present on the surface of both PANI-CS and PPy-CS nanoparticles. TEM studies showed that PPy-CS nanoparticles had the regular spherical shape while PANI-CS nanoparticles presented a non-spherical shape. TG studies showed that there exist certain chemical interaction between PANI and chitosan. The chemical structure of the PANI-CS and PPy-CS nanocomposite were characterized by FT-IR and UV-vis.

In the second part of this work, a facile method was developed for the fabrication of PPy-CS hollow nanostructures with different sizes and shapes. Two silver halides (AgCl and AgBr) were employed as templates for polymer nucleation and growth. Polymeric hollow nanospheres, hollow nanocubes and hollow plate were prepared. Control over particle dimensions (e.g. core shape, core diameter and shell thickness)
was achieved easily. These hollow nanostructures were extensively characterized using TEM, FT-IR, UV-vis, and XRD. The PPy-CS shell was found to be permeable for small molecules. The permeability of shell was controlled by the pH of the medium.

In the last part of this work, a novel photoreduction method was developed for the preparation of PPy-CS hollow nanospheres with movable Ag nanoparticles inside (Ag@PPy-CS). The formation of this novel core-shell nanostructure was a simple photoreduction process. Ag nanoparticle was formed by ultraviolet irradiation in the interior of the PPy-CS hollow nanosphere. TEM images confirmed the formation of core-shell nanostructure. XRD studies proved that the component of the core was metallic Ag. UV-vis studies showed that the surface plasmon absorption of the core-shell nanoparticle could be tuned in the range of 399.5 - 455 nm.

PANI-CS and PPy-CS nanoparticles prepared in this work may be suitable in applications such as labels, conducting coatings, electrorheology, and catalysis. The functional amine groups located at the surface of these nanoparticles are of particular useful for these applications. The pH-responsive hollow nanostructures developed in this work may find applications for the protection, delivery, and storage of chemicals with unstable properties or be used as nanoreactors. The Ag@PPy-CS core-shell nanostructures may be used as new drug delivery devices such as smart laser-responsive carrier systems.
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List of Abbreviations

AgCl  Silver chloride
AgBr  Silver bromide
AgCl@PPy-CS  Core-shell nanoparticles with AgCl core and PPy-CS shell
AgBr@PPy-CS  Core-shell nanoparticles with AgBr core and PPy-CS shell
Ag@PPy-CS  Core-shell nanoparticles with Ag core and PPy-CS shell
APS  Ammonium peroxydisulfate
CS  Chitosan
DLS  Dynamic Light Scattering
DTG,  Differential thermal analysis
FT-IR  Fourier Transform Infrared Spectroscopy
Mw  Molecular weight
PANI  Polyaniline
PANI-CS  Polyaniline-Chitosan nanocomposite
PPy  Polypyrrole
PPy-CS  Polypyrrole-Chitosan nanocomposite
SPR  Surface Plasmon Resonance
TEM  Transmission Electron Microscopy
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UV-vis  Ultraviolet-visible Spectroscopy
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Chapter 1
Introduction
1.1 Overview of Nanostructured Materials

Nanostructured materials have attracted great research interest and the technology of their production and use is rapidly growing into a powerful industry [1-3]. These fascinating materials whose sizes ranging from 1 - 100 nanometers include quantum dots, nanowires, nanotubes, nanosized metals, semiconductors, biomaterials and polymers. In the nanometer region, classic laws of physics no longer hold [2a]. In materials where strong chemical bonding is present, delocalization of valence electrons can be extensive, and the extent of delocalization can be varied with size of the system. This effect, coupled with structural changes with size variation, can lead to different chemical and physical properties, depending on size. It has now been demonstrated that a host of properties which depend on the size of such nanoscale particles, including magnetic properties, optical properties, melting points, specific heats, and surface reactivity.

Although the concept of “nanostructured material” has been put forward for only 50 years [3], some nanostructured materials have been used for more than 3,000 years. For example, colloidal gold (gold nanoparticle) was used in Egypt to make ruby glass and for coloring ceramics as early as 1,300 B.C. [4]. In modern science, heterogeneous catalysis can be considered as one of the first uses of nanoscale materials [5]. Metal nanoparticles have been widely used in this area. The research on the effect of particle size and shape has been and continues to be vigorous. Besides, the broad field of colloid chemistry can also be viewed as an early integral part of
nanotechnology [6]. The significant advance in nanomaterials is made possible due to the development of theoretical and experimental tools and techniques, which increases our understanding of matter in both the micro and the nano regimes. A typical example is the development of atomic force and scanning tunneling microscopy, which has led to sophisticated instruments that change the landscapes of surfaces atom by atom. Today nanostructured materials have attracted a great deal of attention in many areas as diverse as electronics, optics, catalysis, magnetic data storage, gene therapy, drug delivery, photography, and so on [7-8].

The main objective of this work is to develop novel strategies to synthesize functionalized nanoparticles. The fabrication of nanoparticles of controlled size, shape, and functionality is a key challenge in nanotechnology [2b-2c]. There are several established routes to nanoparticle preparation. Roughly spherical nanoparticles can be prepared by very fine milling [2d]. This route is used, for example, to prepare iron oxide nanoparticles in ferrofluid dispersions [2e]. Another more common method called colloidal method [8] produces nanoparticles with much more uniform size and shape distribution than milling. Metal and metal oxide nanoparticles have been prepared using micellar “nanoreactors” where, for example, salts are selectively sequestered in the micellar core, and then reduced or oxidized [9].

In this work, I have special interest on the preparation of conducting polymer based nanoparticles using the colloidal method. The reason for choosing conducting
polymers as the study objectives is due to their easy synthesis, good environmental stability and highly conductivities. In this work, three types of polymer nanoparticles with different shapes were prepared and studied. The first type is solid nanoparticles, which is just the ordinary nanoparticles; the second type is hollow nanoparticles, which means the interior of the nanoparticles has been removed. Sometimes, it is also named as “nanocapsule”. In order to be more accurate and avoid confusion, in this thesis, this type of nanoparticle is named as “hollow nanospheres”, “hollow nanocube”, or “hollow plate”, depending on the different shape of the hollow nanoparticles. The third type of nanoparticles is core-shell nanoparticles, which means the nanoparticles is composed of two parts, the core and the shell. They are made of different materials.

The nanoparticles studied in this work are of particular interest due to their specific properties such as special surface functionality, optical sensitivity to environmental medium, and encapsulation of large quantities of guest materials. They may have potential applications such as confined reaction vessels, drug delivery carriers, biological labels and markers. In the following sections, the state of the art in the synthesis and applications of these polymer nanoparticles will be briefly reviewed.

1.2 Conductive Polymer Nanoparticles

In the early 1970’s, Shirakawa and Ikeda prepared polyacetylene film [10], which in its pristine state was only a poor semiconductor. In 1975 polysulphur nitride (SN)₅
was discovered to become superconducting at low temperatures [11]. In 1977 MacDiarmid et al. [12] found that the treatment of polyacetylene with Lewis acids or bases can increase the conductivity by 13 orders of magnitude. Since then, a huge amount of work has been done to achieve organic conductive polymers with important electronic and optical properties of semiconductors and metal and with the attractive mechanical properties and processing advantages of organic polymers.

The most common conductive polymers are polyacetylene, polypyrrole (PPy), polyaniline (PANI), polythiophene and poly(p-phenylene) (see Table 1.1). Among them PPy and PANI have attracted the most attention due to their good stability, good conductivity without the use of toxic or highly corrosive dopant like AsF$_5$ or halogen gas, ease of preparation and promising potential application prospects. However, like most of the rest of the conducting polymers, the highly conjugated chemical structure makes PPy and PANI intractable, non-melting and insoluble, therefore unprocessable. This drawback has hindered the practical applications of these conducting polymers. Many research groups have tried various ways to improve the processability of conducting polymers. Some of the methods will now be discussed.
Table 1.1 List of some important conducting polymers

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<tr>
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<td>$10^2$ - $10^3$</td>
</tr>
<tr>
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<td>$10^2$ - $10^3$</td>
</tr>
<tr>
<td>Polythiophene</td>
<td>$10^2$</td>
</tr>
<tr>
<td>Poly(p-phenylene)</td>
<td>$10^3$</td>
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1.2.1 Methods to Improve the Processability of Conducting Polymers

Generally there are two main routes to the preparation of conductive PPy and PANI: chemical and electrochemical polymerization method. Although both methods have their own distinctive advantages over each other, the chemical method is more suitable for mass production at low costs. In this work only the chemical polymerization is covered.

The methods for improving the processability of PPy and PANI include:
(i) chemical modification of pyrrole and aniline monomers,

(ii) doping with functionalized organic acids, and

(iii) dispersion polymerization using steric stabilizers.

The first strategy which has been widely attempted in achieving solubilization involves functionalization of the starting material with suitable side chain prior to polymerization. Pyrrole and aniline molecules substituted by alkoxy, alkyl, acyl, halogen, alkylsulfonate and benzyl sulfonate groups have been reported. These side chains can be either ring-substituted [13-20] or N-substituted [21-24]. The resulting polymers can be dissolved in aqueous or certain solvent media. It was reported, however, that although ring-substituted PANI retains reasonably high conductivity, they are mainly limited to low molecular weight species [20]. On the other hand, N-substituted PANIs are soluble high molecular weight polymers, but its conductivity is greatly reduced [19].

The second synthesis route in obtaining soluble PANI has been extensively used. This involves chemical polymerization of aniline in a medium of large molecule size functionalized organic protonic acid [25-33]. The functionalized organic acid may be generally denoted as $\text{H}^+ (\text{A}^- \text{-R})$, where $\text{A}^-$ acts as counter ion which ensures overall charge neutrality of the protonated PANI, and the R functional group acts to induce compatibility with nonpolar or weakly polar organic solvents. Thus, by using appropriate R group, counter ion-induced processibility of the conducting PANI salt
can be achieved. In fact, by judicious choice of the functionalized protonic acids, one can “design” the conducting PANI-salt to be soluble in specific solvents, yet achieving conductivity comparable to those of insoluble PANI doped with inorganic acids [29-30]. On dissolution of these PANI-salts in some amine solvents, deprotonation to the emeraldine base occurs. However, materials will re-protonate when subsequently brought out of the solution. Despite of these advances, it has been generally accepted that it is impossible to dope high molecular weight PANI to the conducting form and thereafter dissolve the conductive form in common non-polar or weakly polar organic solvents.

The third method utilizes the conventional procedure for the preparation of aqueous colloids, which is to use steric stabilizers in dispersion polymerization in aqueous media. The dispersion polymerization produces particles of submicrometer size. Dispersion polymerization has several typical features:

(i) the monomer is miscible with the reaction medium (in contrast to emulsion or suspension polymerization);

(ii) the polymer produced during the polymerization is insoluble under the same conditions (like in the precipitation polymerization); and

(iii) the macroscopic precipitation of the polymer is prevented by the presence of a suitable stabilizer.

The principles of steric stabilization and the use of various types and architectures of
steric stabilizers have been studied in recent years as the interest in conducting polymers and their processing has increased. A variety of polymers, copolymers and particulate stabilizers have been used for the preparation of PANI and PPy colloids (Table 1.2 and Table 1.3). The observation that PANI colloids, unlike PPy ones, often have a non-spherical morphology opened a possibility to produce a novel class of conducting colloidal particles of varying shapes [34]. The serendipitous discovery that ultrafine colloids silica acts as a particulate stabilizer by Gill et al. [35-36] offered an alternative approach to stabilization by inorganic nanocolloids. Finally, following the paper by DeArmitt and Armes [37] in 1993, anionic low-molecular-weight surfactants have also been applied to the preparation of colloidal forms of conducting polymers [38]. The activities in the field of conducting colloids have recently reviewed by Armes [39] and Stejskal [40] and in particular for PPy dispersions by Mandal et al. [41].
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<td>Liu, J.M. [50]; Yang, S.M. [51]</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>Cooper, E.C. [52]; Innis, P.C. [53]</td>
</tr>
<tr>
<td>Poly(methyl vinyl ether)</td>
<td>Banerjee, P. [54]; Mandal, B.L. [55]</td>
</tr>
<tr>
<td>Poly(styrenesulfonic acid)</td>
<td>Sun, L. [56]; Yang [57], S.M.</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>Armes, S.P [58]; Chakraborty, M. [59]</td>
</tr>
<tr>
<td>Poly(vinyl alcohol-co-vinyl acetate)</td>
<td>Gospodinova, N. [60]; Janca, J. [61]</td>
</tr>
<tr>
<td>Poly(N-vinylpyrrolidone)</td>
<td>Eisazadeh, H. [62]; Riede, A. [63]</td>
</tr>
<tr>
<td>Proteins</td>
<td>Eisazadeh, H. [64]</td>
</tr>
<tr>
<td><strong>Tailor-made polymers:</strong></td>
<td></td>
</tr>
<tr>
<td>Graft copolymers</td>
<td>Cooper, E.C. [65]; Vincent, B. [66]</td>
</tr>
<tr>
<td>Block copolymers</td>
<td>Sapurina, I. [67]</td>
</tr>
<tr>
<td>Reactive polymers</td>
<td>Li, S. [68]; Gill, M.T. [69]</td>
</tr>
<tr>
<td><strong>Particulate stabilizers:</strong></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>Gill, M. [35]; Aboutanos, V. [70]; Riede, A. [63]</td>
</tr>
<tr>
<td>Manganese(VI) oxide</td>
<td>Biswas, M. [71]</td>
</tr>
<tr>
<td>Zirconium dioxide</td>
<td>Ray, S.S. [72]</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>Su, S.J. [73]; Feng, W. [74]</td>
</tr>
<tr>
<td>Polymer latexes</td>
<td>Xie, H.Q. [75]; Lei, T. [76]</td>
</tr>
<tr>
<td><strong>Surfactants:</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>Yang, S. [77]; Kim, B.-J. [78]</td>
</tr>
<tr>
<td>Dodecylbenzenesulfonic acid</td>
<td>Haba, Y. [79]; Segal, E. [80]</td>
</tr>
<tr>
<td>Other surfactants</td>
<td>Gan, L.M. [81]; Lchinoche, D. [82]</td>
</tr>
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Table 1.3 Stabilizers for PPy Colloids

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>First author, reference</th>
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</thead>
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<tr>
<td><strong>Water-soluble polymers:</strong></td>
<td></td>
</tr>
<tr>
<td>Ethyl(hydroxyethyl)cellulose</td>
<td>Mandal, T.K.[83]; Mandal, T.K.[84]</td>
</tr>
<tr>
<td>Hydroxypropylcellulose</td>
<td>Epron, F.[85]; Armes, S.P. [86]</td>
</tr>
<tr>
<td>Methylcellulose</td>
<td>Bjorklund, R.B.[87]; Epron, F.[85]</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>Mrkic, J.[88]</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>Cawdery, N.[89]; Goodwin, J.W.[90]; Barisci, J.N.[91]</td>
</tr>
<tr>
<td>Poly(methyl vinyl ether)</td>
<td>Digar, M.L.[92]; Mandal, T.K.[84]</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>Eizazadeh, H.[93]; Chen, Z.[94]</td>
</tr>
<tr>
<td>Poly(vinyl alcohol-co-vinyl acetate)</td>
<td>Armes, S.P. [95]; Cooper, E.C.[65]</td>
</tr>
<tr>
<td>Poly(N-vinylpyrrolidone)</td>
<td>Armes, S.P. [86]; Chen, Z.D.[96]</td>
</tr>
<tr>
<td>Proteins</td>
<td>Barisci, J.N.[91]</td>
</tr>
<tr>
<td><strong>Tailor-made polymers:</strong></td>
<td></td>
</tr>
<tr>
<td>Block copolymers</td>
<td>Beadle, B.M.[97]; Selvan, S.T.[98]</td>
</tr>
<tr>
<td>Reactive polymers</td>
<td>Armes, S.P. [86]; Simmons, M.R.[99]</td>
</tr>
<tr>
<td>Statistical copolymers</td>
<td>Mrkic, J.[88]</td>
</tr>
<tr>
<td><strong>Particulate stabilizers:</strong></td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>Armes, S.P. [100]; Neoh, K.G.[101]</td>
</tr>
<tr>
<td>Iron (III) oxide</td>
<td>Gangopadhyay, R.[102]</td>
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<tr>
<td>Tin (IV) dioxide</td>
<td>Maeda, S.[103]; Saoudi, B.[104]</td>
</tr>
<tr>
<td>Polymer latexes</td>
<td>Yassar, A.[105]; Liu, C.F.[106]</td>
</tr>
<tr>
<td><strong>Surfactants:</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium dodecylbenzenesulfonate</td>
<td>DeArmitt, C.[37]</td>
</tr>
<tr>
<td>Other surfactants</td>
<td>Zelenev, A.[107]</td>
</tr>
</tbody>
</table>

Dispersion polymerization of aniline (or pyrrole) is an efficient way to prepare conducting nanoparticles with different morphologies. Clearly, in the various examples quoted, control of the particle morphology is very desirable. In the case of the thin polymeric films, for example, the use of rod or needle-like particles ensures that electrical conductivity is maintained, at relatively low volume fractions of the conducting particles, by a percolation mechanism [108]. On the other hand, in the
case of chromatographic beads, spherical particles would be more desirable. For encapsulation, drug delivery, development of artificial cells, and protection of biologically active agents (e.g., proteins, enzymes or DNA) [109-110], hollow spheres of functional materials are preferred.

Different morphologies of PANI (or PPy) nanoparticles have been reported by the dispersion polymerization method. Vincent et al. [66] used poly (ethylene oxide) as steric stabilizer to yield needle-like PANI particles. When graft-copolymer stabilizer based on poly (ethylene oxide) was used, PANI spheres were produced. Hydroxypropylcellulose was used by Stejskal [45] as a steric stabilizer in the dispersion polymerization of aniline. The morphology of the particles can be varied from well-defined spheres to coral-like objects by increasing the polymerization temperature from 0 °C to 40 °C. A micelle solution composed of hydrophobically end-capped poly (ethylene oxide) was employed by Kim et al. [111] to prepared PANI particles. “Ringlike” shape of PANI particles was observed. The crystallinity and the conductivity were found to strongly depend on the size of the micelle.

1.2.2 Applications of Conducting Polymers

Numerous applications of conducting polymers have been proposed. These include electromagnetic shielding, batteries, analytical electrodes and sensors, transparent electrodes for light-emitting diodes, electrochromic devices, gas-separation membranes, antistatic coatings, electronic components and circuitry, anticorrosion
protection, heating elements and many others [112-113]. Here I illustrate some uses directly associated with the colloidal forms of PANI and PPy.

1.2.2.1 Conducting coatings

Conducting polymer coatings are obtained after evaporation of PANI or PPy dispersions. Conductivity and mechanical properties are tuned by varying the composition of the film and the type of stabilizer. Eisazadeh et al. [114] prepared PANI and PPy dispersion electrochemically. Colloids were electrocoagulated at negative potentials and both PANI and PPy-based coatings on metallic surfaces were obtained in this way. Kasicka et al. [115] investigated the control of electroosmotic flow in capillary zone electrophoresis. They used PANI dispersion stabilized with hydroxypropylcellulose [45] to produce conducting coating on the outer capillary surface. Application of external electric field along the capillary length proved to be an efficient tool for the regulation of electroosmotic flow and for the optimization of oligopeptide separations.

1.2.2.2 Analytical and Separation Uses

Nagaoka et al. [116] investigated PANI dispersions stabilized with poly(vinyl alcohol) (PVA). Colloids were electrochemically active and adsorbed various anions. PANI dispersion was proposed to be applied as an ion exchanger or to be used to concentrate analytes from solutions. Emeraldine base selectively uptakes various anionic substrates. The adsorption ability of PANI-PVA colloid increased with the
increasing size of anions [117]. Anionic species were released and collected after electrochemical reduction of PANI to leucoemeraldine or after deprotonation [118-119]. The sorption of palladium and gold with silica-stabilized PANI and PPy colloids from aqueous solution has been investigated by Huang and Neoh [101,120]. While palladium chloride became complexed with microparticles, the reduction of chloroauric acid to gold with conducting polymers took place. The particles were proposed for used in the recovery of precious metals and for organic catalysis.

1.2.2.3 Diagnostics

It has been demonstrated that PPy colloids can be utilized in diagnostic assays for the human pregnancy hormone (hCG), HIV antibody, and hepatitis B surface antigen [121]. The colloidal immunoreagents used in these tests were made by adsorption of the appropriate ligands to the unmodified surface of the latex particles. In this application the electroactivity of the conducting polymer is irrelevant: the “value-added” properties are its intense, intrinsic chromogenicity and its well-defined (narrow size distribution) colloidal dimensions.

The potential requirement for the marker particles in visual diagnostic assays were summarized by Armes [121b]:

( i ) intense coloration (preferably intrinsic one);

( ii ) facile synthesis;

(iii) compatibility with biological ligands;
(iv) small particle size (< 200 nm);
(v) high degree of dispersion (no aggregates);
(vi) good colloidal stability at physiological pH; and
(vii) surface functionalization (e.g., with carboxyl or amino groups).

Carboxyl groups have been introduced into PPy particles with copolymerization of pyrrole with pyrrole-1-propanoic acid [122]. Goller et al. [123] demonstrated the introduction of amino groups by functionalization of PPy-silica particles with 3-aminopropyltriethoxysilane or by dispersion copolymerization of pyrrole and 1-(3-aminopropyl)-pyrrole. Such dispersions were used as novel marker particles for immuno-diagnostic assays. Human serum albumin and human-globulin immobilization on PPy-polyacrolein core-shell particles 150 nm in diameter was investigated by Miksa and Slomkowski [124]. Functionalized PPy particles were used as polymer supports for the controlled adsorption of proteins in potential diagnostic applications. Kim et al. [125] introduced a conducting polymer, PANI, as a conductivity modulating agent on the gold surface after immobilizing an antibody specific to human albumin used as a model analyte. The conductometric signal was substantially improved.

### 1.2.2.4 Catalysis

Paramagnetic materials are often observed to have catalytic activities. For example, PANI promotes decomposition of hydrogen peroxide [126] or it can be used in place
of synthetic metal catalyst in dehydrogenation oxidation [127]. Polyaniline protonated with hexachloroplatinic acid was applied in the catalytic hydrogenation of alkynes to alkanes [128]. In particular, PANI colloids can be used due to their high active surface area and feasible separation from the system by centrifugation. Introduction of small quantities of PANI dispersion was found to accelerate the polymerization of aniline both in precipitation and dispersion mode [129]. Huang et al. [130] prepared PANI and PPy colloids stabilized with colloidal silica. These colloids were able to uptake palladium from aqueous solutions. PANI colloids offer a large specific surface area compared to other forms of PANI and can act as a catalyst carrier. The catalytic activity of palladium-containing electroactive-polymer microparticles was demonstrated by the removal of the dissolved oxygen from water and in hydrogenation of nitrobenzene to aniline. Even in the absence of palladium, the leucoemeraldine colloid reduced the content of dissolved oxygen in water but its catalytic activity in the reduction of nitrobenzene was negligible. The combination of PANI and palladium has been shown to be effective in the catalysis of 2-ethylanthraquinone hydrogenation [131].

1.3 Polymeric Hollow Nanospheres

It is well-known that nanometer-sized containers, e.g., micelles and vesicular structures are used widely by nature in biological systems. However, due to the non-covalent interactions responsible for their formation these objects have only a limited stability and may undergo structural changes [132]. This leads, for example, to a rapid clearance of conventional lipid vesicles from the blood after their intravasal
administration. Many applications (e.g., in drug delivery), however, require more stable particles. To solve this, polymeric hollow nanospheres have received considerable research attention. Such hollow spheres are of particular interest due to their potential for encapsulation of large quantities of guest molecules within their empty core domain and high structural stability toward complicated physiological environments [133]. These materials could be useful in applications in areas as diverse as biological chemistry, synthesis and catalysis. In fact a multitude of different applications have already been proposed for polymeric hollow spheres, such as confined reaction vessels, drug carriers [134], protective shells for cells or enzymes [135], transfection vectors in gene therapy [136], carrier systems in heterogeneous catalysis [137], dye dispersants or as materials for removal of contaminated waste [138].

Size- and shape-persistent hollow spheres can be prepared using a variety of techniques, each of them having its special advantages (and also disadvantages). In the following sections, an overview of the current state of the art in the field of hollow polymer particles preparation will be given. Both strengths and weakness of the respective preparative methods will be evaluated critically.

1.3.1 Self-assembly Strategy

In nature, lipid molecules can aggregate in dilute aqueous solution into spherically closed bilayer structures, so-called vesicles or liposomes. It is quite reasonable that
the hollow morphology of these aggregates should render them suitable as precursors for the preparation of more stable hollow nanospheres. For example, lipids that are functionalized with polymerizable groups can be polymerized within such vesicular structures [139]. As a result of the polymerization, individual lipid molecules are interconnected via covalent bonds which stabilize the shell-forming membrane considerably.

Similarly, amphiphilic block copolymers can also aggregate in aqueous solution to form micellar structures [140]. Block copolymer micelles may be significantly more stable than those formed from conventional lipids due to the larger size and the lower dynamics of the underlying polymer molecules [140c]. However, they can disintegrate under certain conditions (e.g., dilution or presence of surfactants) into individual block copolymer molecules because they are held together only by non-covalent interactions. To solve this, block copolymer molecules could be modified with polymerizable groups. A subsequent polymerization of the resulting “macromonomers” interconnects them through covalent bonds which stabilize the whole particle. Such block copolymer based hollow nanospheres can be expected to possess great potential for encapsulation and controlled release from their interior. This is especially so, since the physical properties of their polymer shells can be controlled to a large extent by the block lengths, the block length ratio or the chemical constitution of the underlying polymer molecules. One example is the formation of vesicles from a poly(isoprene)-block-poly(2-cinnamoyl methacrylate) (PI-PCEMA)
diblock copolymer in hexane-THF mixtures [141-142]. But converting these vesicles into stable, water-soluble polymer nanospheres required a rather costly procedure [141]. The PCEMA blocks were first photocrosslinked and then the PI blocks had to be hydroxylated to make these hollow nanospheres water-soluble. The radii of the nanocapsules were about 50 - 60 nm and changed only very slightly during these conversions.

In the context of possible applications, it would be desirable to have detailed information about the permeability of these polymer hollow spheres. It is expected that besides the chemical constitution of the polymer backbone, the meshsize, i.e., the crosslinking density of the polymer network structure, also plays an important role. Only molecules that are smaller than this mesh-size should be able to diffuse across the polymer shell. Molecules which are larger cannot pass through the polymer membrane of the hollow spheres for geometrical reasons.

1.3.2 Emulsion / Suspension Polymerization Approach

Hollow polymer particles can be prepared applying suspension and emulsion polymerization techniques [143]. Although in most cases these methods have been shown to lead to particles with diameters of several micrometers, nanometer-sized polymer hollow spheres are also possible.

For example the polymerization of divinylbenzene in toluene/divinylbenzene swollen
polystyrene latex particles or in polystyrene containing toluene droplets leads to the formation of hollow PDVB particles [143a]. This is because the microphase separation limits the compatibility of chemically different polymers in solution, which leads to the formation of a PDVB shell around a toluene-polystyrene core. After evaporation of the toluene a cavity remains in the center of the particles.

Another rather convenient method leading to hollow polymer particles proceeds through emulsion polymerization [143b-143d]. First the core particles are synthesized by conventional emulsion polymerization. A different monomer is then added and a cross-linked shell is polymerized around the core particle. The synthesis of such core-shell latexes is simple in concept but rather difficult in practice. This holds particularly if one is interested in well-defined and homogeneous particle morphology which is desirable for the preparation of hollow polymer particles. It has been demonstrated that both thermodynamic and kinetic factors are of crucial importance here. Additionally, to end up with a hollow polymer sphere one needs to remove the core of the particles at the end. Since core and shell are frequently chemically rather similar this is another critical step of the preparation procedure. Usually rather aggressive reaction conditions, like a prolonged alkali and acid treatment at high temperature, are required to degrade the particle core [143b-143c]. Although hollow polymer particles can be formed using such methods, the question remains to what extent do the polymer shells survive intact under these conditions?
An elegant approach to remove the core under very mild conditions has recently been demonstrated [143d]. The authors report the synthesis and characterization of nanometer sized hollow organosilicon particles. The synthesis followed a two-step procedure similar to that described above. The core of the particles was formed by a low molecular weight poly(dimethylsiloxane) (PDMS) around which a crosslinked organosilicon shell was formed in a second step. The PDMS from the interior of the particles could be removed quantitatively by ultrafiltration. The preparation procedure is summarized in Figure 1.1. The remaining organosilicon nanocapsules were characterized by GPC, DLS, XRD and AFM. The nanocapsules had typical diameters of 50 nm and a shell thickness of about 6 nm. Interestingly, they could be refilled with poly(dimethylsiloxane) chains with a molecular weight of about 6000 Da, i.e., rather large molecules, which reflects an obviously rather high porosity of the polymer shells. Hence, typical low molecular weight substances are expected to be released very fast from such particles. These organosilicon capsules represent a very promising system for applications in various areas.
1.3.3 Template Strategy

Template is widely used to prepare hollow nanospheres [9g]. This strategy allows the formation of a polymer shell around a preformed template particle that can subsequently be removed. Due to its relative ease of operation, this method has become the most promising approach in the production of polymeric hollow nanospheres. Two main methods have been developed along this line.

The first method is called layer-by-layer deposition, a convenient way to exploit the well-known polyelectrolyte self-assembly at charged surfaces. This chemistry uses a series of layer-by-layer deposition steps of oppositely charged polyelectrolytes [144].
One starts with colloidal particles carrying surface charges (e.g., a negative surface charge). Polyelectrolyte molecules having the opposite charge (i.e., polycations) are readily adsorbed to such a surface due to electrostatic interactions. As a result the original surface charge is usually overcompensated by the adsorbed polymer. Hence, the surface charge of the coated particle changes its sign and is now available for the adsorption of a polyelectrolyte of again opposite charge (i.e., a polyanion). As sketched in Figure 1.2, such sequential deposition produces ordered polyelectrolyte multilayers, the thickness of which can be exactly controlled by the number of deposition steps. But the disadvantage is that the tedious adsorption procedure normally takes a long time to complete.

![Figure 1.2 Illustration of the procedure for preparing hollow spheres using layer-by-layer deposition of oppositely charged polyelectrolytes on colloidal particles. (Reproduced from Chem. Mater., 1999, 11, 1048)](image)

As template particles, weakly crosslinked melamine–formaldehyde particles have been used. Exposure of the coated particles to an acidic solution of pH < 1.6 dissolves
the melamine–formaldehyde core without affecting the layered polyelectrolyte shells. The resulting polyelectrolyte shells are shape persistent and clearly preserve their hollow sphere morphology after removal of the template. Nevertheless it is expected that their long-term stability depends very much on the surrounding environment of the particles. In biological fluids (e.g., in blood plasma), or in media of high ionic strength which may screen the ionic interactions responsible for maintaining their integrity, the long-term stability of such polyelectrolyte shells may be rather limited.

Functionalized polystyrene latex particles carrying surface charges are also suitable substrates for the polyelectrolyte self assembly technique. In one case inorganic particles were incorporated into the adsorbed shells by a sequential adsorption of nanometer-sized SiO$_2$ particles with negative surface charge and cationic poly(diallyldimethylammonium chloride) (PDADMAC) [145]. Layers with a thickness ranging from tens to hundreds of nanometers could be prepared by this procedure. Removing the polystyrene core leaves the SiO$_2$/PDADMAC nanocomposite shells, which are subsequently removed by calcinating at high temperature to leave behind only the SiO$_2$ shells. [145]. Both the composite and the purely inorganic capsules are shown to have interesting physical properties such as enhanced mechanical stability or exceptional permeability behavior.

The second method is to use inorganic nanoparticles as the templates. This is also one of the most frequently employed methods to achieve polymer coatings on solid
particles. The polymerization reaction can be either catalyzed by an initiator or by the colloidal particles themselves. Matijevic et al. reported the coating of aluminum hydrous oxide-modified silica particles with poly(divinylbenzene) (PDVB) layers by pre-treatment of the inorganic cores with coupling agents such as 4-vinylpyridine or 1-vinyl-2-pyrrolidone, followed by subsequent admixing of divinylbenzene and a radical initiator [146]. Polymer layers of poly(vinylbenzyl chloride) (PVBC), copolymers of PDVB-PVBC, and double shells of PDVB and PVBC were also synthesized around inorganic particles using a similar approach [147]. The surface characteristics of the silica cores were substantially altered, as evidenced by electrophoresis measurements. It is possible to mix a dye into the silica particle so that the dye can be retained in the core as the polymer shell is permeable to small inorganic ions but not to the dye molecules [146].

Gold nanoparticles have successfully been used as templates for nucleation and growth of surrounding PPy and poly(N-methylpyrrole) shells [148]. This approach begins with gold nanoparticles being filtered into a porous Al₂O₃ support membrane with a pore size of 200 nm. Initiator (Fe(ClO₄)₃) was then poured into the top of the membrane and several drops of the monomer (pyrrole or N-methylpyrrole) were placed underneath the membrane (see Figure 1.3). Polymerization is effected when the monomer vapor makes contact with the initiator. The deposition of the polymer preferentially occurred on the surface of the gold particles. This resulted in the formation of hybrid polymer-encapsulated gold nanoparticles that were conveniently
isolated by dissolution of the membrane material in basic solution. It was shown that PPy and composite poly(N-methylpyrrole) / PPy multilayers of a predetermined thickness can be formed on gold nanoparticles of 30 nm diameter. Controlling the thickness and the composition of the polymer coatings are attractive features of this strategy. The thickness is dependent on the polymerization time and can be varied from 5 to 100 nm. Obviously the ions of the gold etchant were able to diffuse through the polymer shell, the permeability of which could even be tuned by the oxidation state of the polymer. This method shows promise for the coating of various template particles with a range of polymers and can be extended to biomacromolecules [148].

*Figure 1.3* Schematic diagram of the method for synthesizing Au@PPy core-shell nanoparticles. The particles are first trapped and aligned in the membrane pores by vacuum filtration and subsequently coated with PPy, which occurs via polymerization of the monomer vapor when it diffuses into the membrane and interacts with the initiator (Fe(ClO₄)₃). The membrane is then dissolved, leaving behind nanoparticle composites. The gold can also be etched first and the membrane then dissolved, resulting in hollow PPy nanospheres. (Reproduced from *J. Am. Chem. Soc.* 1999, 121, 8518)
1.4 Objectives

From the above discussion, it can be seen that the current state of the art provides a reasonable basis for developing such polymer nanoparticles further towards various applications especially in biomedical science. However most of the stabilizers shown in Table 1.2 and 1.3 are polymers which are either incompatible with the human body or their toxicology studies are not yet evaluated. New biocompatible steric stabilizers are required to be developed. Control of particle size, particle charge, and surface hydrophobicity of the nanoparticles are very important since these directly affect their performance inside the body. The present preparation methods do not provide a satisfactory means to exhibit total control. In addition, the permeability of the shell of the hollow nanospheres plays a crucial role in controlled drug delivery but it is often difficult to control the permeability of shell.

The main objective of this work was to solve these problems. I have focused on developing simple strategies to produce conducting polymer based nanoparticles with controllable properties. Several methods have been developed to prepare three different polymer nanoparticles (solid nanoparticles, hollow nanoparticles and core-shell nanoparticles). All these methods are based on the dispersion polymerization of monomers (i.e., aniline and pyrrole) in the presence of a novel biocompatible stabilizer.
1.4.1 Surface-functionalized PANI-CS and PPy-CS nanoparticles

In this part, chitosan (CS) was developed as a novel biocompatible steric stabilizer to prepare surface-functionalized conducting nanoparticles. Chitosan is a natural poly(aminosaccharide) [2-amino-2-deoxy-(1-4)-β-D-glucopyranosamine] which has been used extensively for various industrial and medical applications [149]. The structure of a poly(aminosaccharide) segment of chitosan is shown in Figure 1.4. The driving force in the development of applications for chitosan is not only that it is naturally abundant, but it is also non-toxic and biodegradable. Chitosan has been successfully used to stabilize polymer nanoparticles such as poly(methyl methacrylate) [150], poly(butyl cyanoacrylate) [151] and polystyrene [152]. In this work, two surface-functionalized conducting nanoparticles, PANI-CS and PPy-CS have been prepared. The structures and morphologies of these nanoparticles will also be characterized extensively using various tools. The functional conducting nanoparticles prepared in this part have potential applications in biomedical science. They can be used as carriers in controlled drug delivery or be used as “marker” particles in immunodiagnostic assays.

Figure 1.4 Chemical structure of chitosan
1.4.2 PPy-CS hollow nanostructures

In this part, I focus on the preparation and characterization of polymer hollow nanostructures (hollow nanosphere, hollow nanocubes and hollow plate). A facile template-assisted method was developed to produce novel core-shell nanostructures. This method is derived from the dispersion polymerization technique described in Section 1.4.1. Using silver halides (AgCl and AgBr) as the cores respectively, two novel core-shell nanostructures, AgCl@PPy-CS and AgBr@PPy-CS, were prepared and characterized. PPy-CS hollow nanostructures were prepared by removing core nanoparticles from the above core-shell nanostructures. Three polymeric hollow structures (hollow nanospheres, hollow nanocubes and hollow nanoplates) were obtained by using AgBr nanoparticles with different morphologies as the core template. The core-shell nanoparticles may be useful in designing new heterogeneous catalytic systems because the light-sensitivity of the silver halides could be prevented using the core-shell structure [153].

1.4.3 PPy-CS Hollow Nanospheres Containing Movable Ag Cores

Recently hollow nanospheres functionalized with movable inorganic nanoparticle cores have been explored as novel nanostructures by several groups [154-155]. Inorganic nanoparticles (e.g. gold or silica) have been incorporated into the interior of hollow nanospheres. Novel optical or electronic properties can be introduced to the hollow nanospheres by this method. In this work, a novel photoreduction method was developed for the preparation of PPy-CS hollow nanospheres with movable Ag
nanoparticles inside (Ag@PPy-CS). TEM will be used to study the formation of these nanostructures. UV-vis spectra will be used to study the optical properties of these nanostructures. These nanostructures are suitable as drug carriers or gene carriers [156]. The inserted Ag nanoparticles may provide an ideal optical probe for monitoring the chemicals to diffuse into and out of the hollow nanospheres.

In the next chapter, the synthesis and characterization of PANI-CS nanocomposite will be discussed. Chitosan will be employed as a steric stabilizer for the dispersion polymerization of aniline. The morphology and chemical structure of the PANI-CS nanocomposite together with the colloidal properties of the PANI-CS dispersion will be studied in detail.
Chapter 2
Synthesis and Characterization of Surface-Functionalized Conducting Polyaniline-Chitosan Nanocomposite
2.1 Introduction

Surface-functionalized nanoparticles are one type of nanoparticles having functional groups (such as –NH₂, -COOH or -OH) on their surfaces. Compared with the ordinary nanoparticles, they have some novel applications. Surface-functionalized nanoparticles are good candidates for constructing core-shell structured particles by the layer-by-layer self-assembly strategy [145,157]. Composite particles that contain an inner core covered by a shell (core-shell particles) exhibit significantly different properties from those of the core itself, with the surface properties governed by the characteristics of the coating. Surface-engineered colloids are widely exploited in the areas of coating, electronics, photonics, and catalysis. Surface-functionalized nanoparticles are very useful in biomedical science. They are well suited as site-specific drug carriers [150]. The functional groups on the surface often make these nanoparticles either positively charged or negatively charged. Research shows that positively charged particles have an improved stability in the presence of biological cations [158] and are gaining increasing importance for drug delivery following intravenous, oral, or ocular administration [159].

It is well known that colloidal dispersions of intrinsically conducting polymers such as polyaniline or polypyrrole can be prepared by dispersion polymerization [50,66,160-163]. This method provides a facile way to the preparation of conducting nanoparticles with different morphologies such as spherical, rice-grain, and needle-like [50,66,160]. During the dispersion polymerization, a steric stabilizer (usually a
water soluble polymer or an inorganic colloid) may be attached to the precipitating conducting polymer. After the formation of dispersion particles, the stabilizer produces a shell of soluble chains over the particle surface, which sterically prevents the particles from forming aggregates [161]. This method can be employed to prepare surface-functionalized conducting nanoparticles [164]. For example, surface functionalization of PPy-SiO$_2$ nanoparticles by amino or carboxyl groups have been extensively studied because of their potential applications in diagnostic assays [122-123,165-166]. They may minimize the ubiquitous nonspecific binding problems which often result in reduced specificity and/or sensitivity for the interested analyzes [167]. In principle there are two strategies to prepare these nanoparticles. One is the copolymerization of pyrrole and 1-(2-carboxyethyl) pyrrole in colloidal SiO$_2$ (20 nm) dispersions [122]. But the amount of functional groups incorporated into the copolymer is limited. The copolymer also has a lower doping level than that of the homopolymer [168]. The other strategy is to use aminopropyltriethoxysilane to add amino groups to the surface of silica and silica gel particles prior to the deposition of PPy on them [169]. However, functionalization in this case mainly occurs on silica surface and the colloid suffers from a lower degree of amination and irreversible on prolonged storage. Improved strategies are thus needed to prepare surface-functionalized nanoparticles.

In this work I have prepared novel surface-functionalized polyaniline-chitosan (PANI-CS) conducting nanoparticles by dispersion polymerization. Chitosan is chosen as the
steric stabilizer because it has been successfully used to stabilize polymer nanoparticles such as poly(methyl methacrylate) [152] and poly(butyl cyanoacrylate) [150]. Chitosan is a natural poly(aminosaccharide) [2-amino-2-deoxy-(1-4)-β-D-glucopyranosamine] which has been used extensively for various industrial and medical applications [151]. The structure of a poly(aminosaccharide) segment of chitosan is shown in Figure 1.4 (see page 28). The amine groups are known to behave normally with respect to protonation in aqueous solution. Chitosan plays two roles during the dispersion polymerization of aniline. Firstly, it acts as a steric stabilizer to form stable colloidal dispersion of PANI-CS. Secondly, according to the steric stabilization mechanism [161], PANI-CS nanoparticles will be formed when aniline is polymerized in chitosan solution with the outer layer of the nanoparticle covered by chitosan. Thus the surface functionalization of PANI-CS nanoparticles can be realized by the amino groups on the chain of chitosan. Compared with other functional groups, amino group functionalized particles may perform better on the adsorption of biomolecules such as DNA [170]. Many water-soluble polymers such as poly(ethylene oxide) [66], polyacrylamide [162], and poly(vinyl alcohol) [163] have been used as steric stabilizers to produce stable PANI dispersions but little work has been done on the polymerization of aniline in aqueous chitosan solution [171]. The colloidal stability of the PANI-CS dispersion and the morphology of the PANI-CS nanocomposite have never been reported before. In this work, the structural, thermal, electrical properties and morphology of the novel surface-functionalized conducting nanoparticles will be discussed.
2.2 Experimental

2.2.1 Chemicals

Aniline (99.9%, monomer), ammonium peroxydisulfate (APS, oxidant) and chitosan (Mw: 70 kDa, 150 kDa and 300 kDa. Degree of deacetylation: 85 %, 72 %, and 80 %) were purchased from Aldrich. The deacetylation degree of chitosan determines the content of the amido groups still present after hydrosis, which ultimately affects the polymer’s reactivity. The deacetylation degree was determined by Infrared spectroscopy [172]. Aniline was purified by distillation in vacuum before polymerization. Other reagents were used as received without further purification.

2.2.2 Synthesis of surface-functionalized PANI-CS nanoparticles

The polymerization was carried out in double-walled glass vessels under magnetic stirring and nitrogen atmosphere. Cold water was circulated through the outer jacket of the vessel to maintain a constant temperature. Different concentrations of aqueous chitosan solutions were prepared by dissolving chitosan in 0.2 M HCl solution. For a typical reaction, aniline (0.144 mL) was added to 40 mL of the chitosan solution (1.0 w/v %) before it was cooled to the desired temperature (12.5 °C). The polymerization began when the oxidant (APS, 0.285 g) was poured into the mixture and the reaction was maintained for 12 h. After that the reaction mixture was centrifuged at 5000 rpm for 20 mins, and the resulting sediment was redispersed in deionized water using an ultrasonic bath. This centrifugation-redispersion cycle was repeated three times in order to remove the excess chitosan and other byproducts completely. The green
composite mass was washed with acetone and dried under reduced pressure. For the experiment to determine the colloidal stability of the PANI-CS dispersion, the dispersion was purified by dialysis in water using a dialysis membrane bag with a molecule weight cut-off of 10,000. Pure doped PANI was also prepared at the same conditions without chitosan for comparison. PANI-CS prepared from different aqueous chitosan solutions (0.25 wt %, 0.5 wt %, 1.0 wt % and 1.5 wt %, respectively) and temperatures (-20 °C, 1.5 °C, 12.5 °C and 35 °C, respectively) were used in a series of experiments. The molar ratio of APS to aniline was maintained at 1.0.

2.2.3 Characterizations

2.2.3.1 Ultraviolet-Visible Spectroscopy

Possible changes in electronic structure of PANI being formed with the support of chitosan were subjected to UV-vis spectrophotometric characterizations over 250-1100 nm using a Shimadzu (UV1601PC) UV-vis spectrophotometer. The cell temperature was kept at room temperature (24 °C).

2.2.3.2 Transmission Electron Microscopy

The morphology and size of PANI-CS nanoparticles was studied by a JEOL (JEM 100) transmission electron microscope with an accelerating voltage at 100 kV. Each suspension was diluted to an appropriate solid content and a drop of it was placed onto a formvar support on copper grids (150 meshes) for TEM observation. The mean diameter was calculated by counting more than 100 nanoparticles.
2.2.3.3 Colloidal stability

The colloidal stability of the PANI-CS dispersion was examined by leaving the dispersion at 25 °C for a fixed time to observe whether there formed turbidity or precipitate. Meanwhile TEM was used to monitor the change of the size and shape of the nanoparticles, and UV-vis spectrophotometric characterization was conducted to examine the change of UV absorbance of the dispersion.

2.2.3.4 X-ray Photoelectron Spectroscopy

The XPS experiments were performed using a VG ESCALAB 220i-XL instrument equipped with a monochromatic Al K$_\alpha$ (1486.6 eV photons). The pressure in the chamber was maintained at $10^{-10}$ mbar during the analysis. The instrument was calibrated with pure gold, silver and copper standard samples by setting the Au 4f$_{7/2}$, Ag 3d$_{5/2}$ and Cu 2p$_{3/2}$ peaks at binding energies of 83.98 ± 0.02, 368.26 ± 0.02 and 932.67 ± 0.02 eV respectively. The dried samples were mounted onto standard VG sample holders using double-sided adhesive tape.

2.2.3.5 Elemental Analysis

Elemental analysis of the PANI-CS composites were carried out using a Perkin-Elmer 240C CHN analyzer for carbon, hydrogen, and nitrogen determinations. The amount of chitosan in PANI-CS was calculated on the basis of the difference in C/N ratio of the composite relative to that of pure polyaniline (5.14) and chitosan (5.49, degree of deacetylation: 80%).
2.2.3.6 Electrical Conductivity Measurement

The conductivity of PANI-CS samples were measured with a standard four-probe technique at room temperature [173]. A Keithley 220 programmable current source and a Keithley 2000 were employed to provide the electrical current and the voltage, respectively. The PANI-CS powder dried under vacuum and ground with pestle in a mortar was then pressed to prepare disk with a diameter of 1.2 cm and thickness of 2 mm.

2.2.3.7 Zeta Potential Measurement

The zeta potential of PANI-CS nanoparticles was determined from electrophoretic mobility measurements with a Zetasizer 3000 HS (Malvern, UK) electrophoresis meter. All the samples were dispersed in 10 mM NaCl and the measurements were conducted at 25 °C.

2.2.3.8 Fourier Transform Infrared Spectroscopy

FT-IR spectra were acquired on a Bio-Rad Merlin (FTS3000) FT-IR spectrophotometer, with the frequency range from 4000 cm\(^{-1}\) to 450 cm\(^{-1}\) using 30 scans per spectrum at 4 cm\(^{-1}\) resolution. The spectra were measured at room temperature (24 °C). The dried samples were dispersed in KBr pellets for characterization. About 0.4 mg of the polymer was ground with 300 mg of KBr and pressed under vacuum with several increments in pressure to 3.5 × 10\(^5\) psi. The sample was kept at each intermediate pressure for 5 min.
2.2.3.9 Thermogravimetry analysis

Thermogravimetric (TG) analysis was done on a Du Pont Thermal Analyst 2200 system with a TGA 2960 Simultaneous Differential Thermal Analyser module. Samples were heated from 40 °C to 700 °C at a heating rate of 20 °C / min. Approximately, 5-8 mg of finely divided polymer sample was heated from room temperature to 800 °C at a linear rate of 20 °C / min. Heating was done in dry air with a flow-rate of 75 cm³ / min.

2.3 Results and Discussion

2.3.1 Formation of the colloidal dispersion of PANI-CS nanoparticles

The formation of the colloidal dispersion of nanoparticles can be monitored by UV-vis spectroscopy. UV-vis spectroscopy is particularly suitable for the study of electronic structure of conducting polymer, which contains extended π-conjugated chains and exhibit unusual color changes [174].

Figure 2.1 shows the UV-vis spectra of the PANI-CS dispersion at different extent of polymerization. At the beginning of the polymerization, aniline in aqueous solution of chitosan gives a flat absorption spectra, showing no peaks in the range of 300 nm - 1000 nm (spectrum a). After about 50 mins of polymerization, the solution turned blue slowly, which indicates the formation of protonated pernigraniline in equilibrium
Figure 2.1 UV-vis spectra of PANI-CS composite on different polymerization stage (0.144 mL of aniline in 40 mL of 1.0 wt% acidic chitosan solution, temperature: 12.5 °C).

with a small proportion of the corresponding unprotonated base form (spectrum b) [174]. An absorption peak at 310 nm and a broad absorption peak at 550 nm are observed in the spectra. The peak at 310 nm is assigned to the $\pi-\pi^*$ transition of benzenoid rings, while the peak at 550 nm is assigned to the $\pi-\pi^*$ transition of quinoid rings on the PANI chains. As time goes on, the intensity of the above two peaks increases (spectrum c). When the polymerization time exceeds 190 mins, the solution turns green quickly which is associated with the progressive shift of the two
absorption peaks to higher wavelength region (spectrum d). This indicates the formation of protonated emeraldine. There is no precipitate observed during the polymerization. The reaction medium is in the form of an optically transparent colloidal dispersion, which suggests chitosan effectively prevents the formation of macroscopic precipitate. The colloidal PANI-CS dispersion is formed.

2.3.2. Morphologies and formation mechanism of the PANI-CS nanoparticles

The morphologies of the PANI-CS nanoparticles were studied by transmission electron microscopy (TEM). TEM is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film, or can be detected by a CCD camera. The morphology, composition, and crystallographic information of the studied material can be obtained from this technique.

TEM images (Figure 2.2) show the presence of PANI-CS nanoparticles. The images reveal that when APS is used as the oxidant, the dispersion polymerization of aniline in aqueous solution of chitosan yields fairly monodispersed nanoparticles with rice-grain morphologies. A summary of particle sizes of the surface-functionalized PANI-CS nanoparticles is given in Table 2.1.
Figure 2.2 Morphologies of PANI-CS nanoparticles synthesized in (a) 1.0 wt.% chitosan solution, $T = -20^\circ C$ (sample No. 5); (b) 1.0 wt.% chitosan solution, $T = 1.5^\circ C$ (sample No. 6); (c) 1.0 wt.% chitosan solution, $T = 12.5^\circ C$ (sample No. 3); (d) 0.25 wt.% chitosan solution, $T = 12.5^\circ C$ (sample No. 1); (e) in 1.5 wt.% chitosan solution, $T = 12.5^\circ C$ (sample No. 4). Refer to Table 2.1 for details of the reaction parameters.
Table 2.1 Effect of reaction parameters on the mean size of surface-functionalized PANI-CS nanoparticles

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Aniline/chitosan Feed ratio (g/g)</th>
<th>Mw of chitosan (kDa)</th>
<th>Temperature (°C)</th>
<th>TEM particle size (nm) Length</th>
<th>Width (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14 / 0.1</td>
<td>300</td>
<td>12.5</td>
<td>260 - 310</td>
<td>85 - 95</td>
</tr>
<tr>
<td>2</td>
<td>0.14 / 0.2</td>
<td>300</td>
<td>12.5</td>
<td>240 - 280</td>
<td>80 - 90</td>
</tr>
<tr>
<td>3</td>
<td>0.14 / 0.4</td>
<td>300</td>
<td>-20</td>
<td>145 - 170</td>
<td>60 - 70</td>
</tr>
<tr>
<td>4</td>
<td>0.14 / 0.4</td>
<td>300</td>
<td>1.5</td>
<td>145 - 155</td>
<td>60 - 70</td>
</tr>
<tr>
<td>5</td>
<td>0.14 / 0.4</td>
<td>300</td>
<td>12.5</td>
<td>180 - 200</td>
<td>60 - 70</td>
</tr>
<tr>
<td>6</td>
<td>0.14 / 0.4</td>
<td>70</td>
<td>12.5</td>
<td>185 - 205</td>
<td>75 - 85</td>
</tr>
<tr>
<td>7</td>
<td>0.14 / 0.4</td>
<td>300</td>
<td>12.5</td>
<td>155 - 170</td>
<td>55 - 65</td>
</tr>
<tr>
<td>8</td>
<td>0.14 / 0.4</td>
<td>150</td>
<td>12.5</td>
<td>175 - 190</td>
<td>60 - 70</td>
</tr>
</tbody>
</table>

\(^a\) As determined by the widest part of the PANI-CS nanoparticle

The formation of PANI-CS nanoparticles could be explained as a result of the interaction between chitosan and PANI chains by a steric stabilization mechanism [161]. At the beginning of the polymerization, the particle nucleation begins in the aqueous phase with the generation of oligomers containing the initiators. These oligomers agglomerate and nucleate a particle when the polymerization has extended their size to the point where they become water-insoluble. At the same time chitosan physically absorbs onto PANI by hydrogen bonding to prevent precipitation. If the initiation occurs around the core particles and the produced oligomers deposited on their surfaces, the further reaction would also mainly taken place on the surfaces of core particles rather than in the aqueous bulk phase because the dimer and succeeding...
oligomers have lower oxidation potentials than aniline [175]. As a result, the polymerization of aniline proceeds preferably close to nucleated particles, which explains a relatively low polydispersity of dispersion particles. When the polymerization is completed, the PANI-CS nanoparticles are formed as depicted in Figure 2.3. The inner part of the particles is composed of both PANI and chitosan, while the outside is covered by a shell of chitosan.

![Figure 2.3 Schematic illustration of the surface-functionalized PANI-CS nanoparticle. The core is composed of both PANI and chitosan while the surface of the core is coated with chitosan.](image)

The presence of chitosan at the surface of PANI-CS nanoparticle is further confirmed by the XPS. Figure 2.4 shows the high resolution C 1s core level spectra of the PANI-CS nanocomposite. In the spectra there are three peaks at 285.6, 287.2 and 288.9 eV, respectively. The peak at 285.6 eV is assigned to the C-C bondings which belong to polyaniline and chitosan [176]. The peak at 287.2 eV is assigned to C-N, C-O or
C-O-C bonding that belongs to chitosan. The last peak at 288.9 eV is assigned to C=O or O-C-O bonding that also belongs to chitosan [176b], because chitosan usually contains some of the acetamido groups that come from the original chitin. It should be noted that for PANI sample, there is often a small peak located at about 287 eV which was due to the oxidation of the PANI sample under ambient conditions [176c]. But this peak is usually very small and only presented as a small shoulder. In our spectrum this peak has been developed as a separate peak which can be observed even without deconvolution. XPS technique is highly surface-specific, so we conclude that chitosan must be present at the surface (or within the first few nanometers) of the functionalized PANI-CS nanoparticles.
Figure 2.4 C 1s core level X-ray photoelectron spectrum of the surface-functionalized PANI-CS nanoparticles (Sample No. 3, see Table 2.1 for reaction parameters). The peaks at 287.2 and 288.9 eV are due to chitosan which is at the surface of the nanoparticles.

The dispersion polymerization of aniline in the presence of a steric stabilizer often yields particles with different morphologies such as sphere, rice-grain or needle-like [161]. Particles with rice-grain morphology has been reported when poly(acrylic acid) was used as a steric stabilizer [50,177]. The morphology of the particle is believed to be controlled by three factors [161]:

(i) the formation rate of PANI;

(ii) the interaction efficiency of PANI with the stabilizer; and

(iii) the diffusion and transport processes involved in the growth of dispersion
particles. When the formation rate of PANI is much faster than the diffusion of the stabilizer (chitosan), a local depletion of the free chitosan may occur at PANI surfaces where the polymerization takes place. More and more primary particles without steric stabilizer are thus produced. In this case the particle growth is expected to give rise to non-spherical morphologies.

The reaction temperature had a profound effect on the morphology of PANI-CS nanoparticles. Figure 2.2a, 2.2b and 2.2c (see page 42) show the morphology of PANI-CS nanoparticles synthesized at -20 °C, 1.5 °C and 12.5 °C, respectively. Nanoparticles synthesized at low temperatures are more irregular than those synthesized at a higher temperature. As the reaction temperature increases, the surface of the nanoparticles becomes more “smooth”. Stejskal [178] reported that when hydroxypropylcellulose was used as the steric stabilizer in the dispersion polymerization of aniline, the morphologies of the particles could be varied from well-defined spheres to coral-like objects by increasing the polymerization temperature. Formation of coral-like objects means that hydroxypropylcellulose cannot prevent the aggregation of PANI due to the increase of the polymerization rate. In this work, nanoparticles of rice-grain shape can be prepared in the temperature range from -20 °C to 35 °C.

2.3.3 Effect of reaction parameters on the size of PANI-CS nanoparticles

The mean size of the nanoparticles can be controlled by adjusting the reaction
parameters. The effect of the chitosan concentration on the mean size of PANI-CS nanoparticles was studied and the results show that the mean size of PANI-CS nanoparticles decreases with an increase in chitosan concentration. As the concentration of chitosan increases from 0.25 % to 1.5 %, the width of the nanoparticle decreased from 85 nm to 55 nm while the length decreases from 260 nm to 150 nm (Figure 2.2d and 2.2e, Table 2.1). This is because at low concentration of chitosan solution the amount of stabilizer is insufficient to effectively cover the available surface, resulting in an unstable colloidal system. The smaller particles therefore agglomerated until the total surface area decreased to a point where the amount of chitosan available was sufficient to produce a stable suspension.

The effect of molecular weight of chitosan on the mean size of PANI-CS nanoparticles was studied by using three chitosan having different molecular weight (Mw = 70 kDa, 150 kDa and 300 kDa, respectively) as the stabilizer. The results indicate that, for the same chitosan concentration (1.0 w/v %) and temperature (12.5 °C), the mean size of PANI-CS decreases with increasing chitosan molecular weight. As the molecular weight of chitosan increases from 70 kDa to 300 kDa, the width of the nanoparticle decreases from 80 nm to 65 nm while the length decreases from 200 nm to 150 nm (see Table 2.1, page 43).

2.3.4 Effect of reaction parameters on the colloidal stability of PANI-CS dispersion

The problem of colloidal stability is one of the most challenging subjects from both
the industrial and the academic point of view [3]. It is demonstrated in the previous section that chitosan is effective in the prevention of precipitation of PANI-CS nanoparticles to form optically transparent dispersions with excellent stability. The stabilization of PANI in the aqueous solution of chitosan is possible over a wide range of reaction conditions. The effect of reaction conditions on the formation of colloidal dispersions of surface-functionalized PANI-CS nanoparticles is discussed below.

It shows that an increase in the initial chitosan concentration (w/v %) produces more stable PANI-CS dispersions. When the initial chitosan concentration is as low as 0.25 %, the dispersion is only stable for 7 days and precipitation occurred. When chitosan concentration reaches 1.0 % and beyond, the dispersion remains stable and no precipitation is observed. TEM study showed that the size and shape of the nanoparticles remained unchanged on 1 year of storage. The dispersion also showed no change in UV absorbance. As discussed earlier, the outer layer of PANI-CS nanoparticles is mostly cover by chitosan. The thickness of the chitosan layer attached to PANI-CS nanoparticles increases with increasing concentration of chitosan, which results in an increase in the stability of the PANI-CS dispersion.

The effect of the molecular weight of chitosan on the stability of PANI-CS dispersion was studied. When chitosan having low molecular weight (Mw = 70 kDa) is used in the polymerization while other conditions keep unchanged, the PANI-CS dispersion is not stable and precipitate occurs after 3 days. When chitosan with higher molecular
weight (Mw = 150 kDa) is used, the dispersion could be stable for 1 month. Further increase the molecular weight of chitosan (Mw = 300 kDa) produces more stable PANI-CS dispersions. Chitosan is a cationic polymer at acidic pH and is rich at the surface of PANI-CS nanoparticle to stabilize it through electrosteric stabilization mechanism. The thickness of the chitosan layer increases with increasing molecular weight, which result in an increase in the steric repulsive energy and the electrostatic repulsive energy and finally in an increase in the total potential energy between two particles. So the increase of molecular weight of chitosan will cause the stabilization efficiency to increase as well. Similar results and explanations have been given for dextran [179] and many other polymeric surfactants [180].

High reaction temperatures are required to form stable PANI-CS dispersion. When the polymerization was conducted at -20 °C, the colloidal dispersion was only stable for 6 hours. When the temperature was increased to 1.5 °C, the colloidal dispersion formed was stable for 3 days. As the reaction temperature was further raised to 12.5 °C, the dispersion of PANI-CS nanoparticles was very stable and no precipitate was observed. It is commonly known that PANI prepared at lower temperature usually has higher molecular weights [181-182]. PANI of high molecular weights with longer chains is more likely to precipitate during the polymerization. On the other hand, the stabilization efficiency of chitosan will decrease at low temperatures. XPS analysis shows that there is less amount of chitosan on the surface of PANI-CS particles produced at -20 °C than those produced at 12.5 °C. As a result, high molecular weight
PANI chains together with lower content of chitosan on the surface of the particles account for the colloidal instability of the PANI-CS dispersion produced at low temperatures.

The pH value is also found to affect the stability of the PANI-CS dispersion. The pH value of the obtained PANI-CS dispersion was determined to be in the range of 3 to 4. This low pH is due to the presence of HCl, which is used in the preparation of PANI. The dispersion is found to be stable until the pH value of the dispersion is increased to 6 by adding 0.5 M NaOH. Further increase the pH will cause the colloid to precipitate. It is well known that chitosan is insoluble in water, alkali and organic solvents, but is soluble in most solution of organic acid when the pH of the solution is less than 6.5. The amino groups of chitosan play a vital role for its solubility in water. Adjusting the dispersion to a neutral pH will cause the $\text{–NH}_3^+$ cations on the surface of PANI-CS nanoparticles to convert to $\text{–NH}_2$, rendering the nanoparticles unstable in water.

2.3.5 Conductivities

The elemental analysis of doped PANI and PANI-CS nanocomposites with different PANI loadings and the conductivities of these nanocomposites are shown in Table 2.2. The mass loading of PANI can be estimated from the weight percent of the C/N ratio reported for doped PANI and for PANI-CS. It can be seen that the ratio of PANI (weight percent) in PANI-CS composite is always higher than the initial feed ratio. This is due to the loss of chitosan in the preparation process. Here chitosan acts as the
stabilizer to prevent the precipitation of PANI. Not all of chitosan interact with PANI to form the PANI-CS nanoparticle. Some of them remained in the dispersion after the polymerization of aniline. The presence of chitosan is confirmed by the IR spectrum of the supernatant of the reaction mixture obtained by centrifuge.

Table 2.2 The composition and conductivity of the PANI-CS nanoparticles (Temperature = 12.5 °C, [APS]/[aniline] = 1.2, Mw of chitosan = 300 kDa, Reaction volume = 40 mL)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>aniline / chitosan Feed ratio (g / g)</th>
<th>PANI loading (theoretical) wt %</th>
<th>PANI loading (actual) wt %</th>
<th>Conductivity (S / cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.144 / 0</td>
<td>100</td>
<td>100</td>
<td>6.10 ± 0.4</td>
</tr>
<tr>
<td>2</td>
<td>0.14 / 0.1</td>
<td>58</td>
<td>65</td>
<td>0.25 ± 0.05</td>
</tr>
<tr>
<td>3</td>
<td>0.14 / 0.2</td>
<td>41</td>
<td>46</td>
<td>2.03(±0.4) × 10⁻³</td>
</tr>
<tr>
<td>4</td>
<td>0.14 / 0.3</td>
<td>32</td>
<td>38</td>
<td>1.92(±0.4) × 10⁻⁴</td>
</tr>
<tr>
<td>5</td>
<td>0.14 / 0.4</td>
<td>26</td>
<td>29</td>
<td>7.06 (±0.4) × 10⁻⁴</td>
</tr>
<tr>
<td>6</td>
<td>0.14 / 0.6</td>
<td>19</td>
<td>22</td>
<td>3.05 (±0.4) × 10⁻⁵</td>
</tr>
</tbody>
</table>

The room temperature conductivity of the PANI-CS nanocomposite is lower than those of PANI prepared under the same conditions in the absence of chitosan (see Table 2.2). The conductivity of PANI-CS nanocomposite lies in the range of 3.05 × 10⁻⁵ to 0.25 S / cm, which is similar to those reported for other sterically stabilized PANI nanocomposite [66,160]. It shows that the conductivity of the PANI-CS nanocomposite increases with the increasing weight percentage of PANI. An increase
in the content of PANI from 22 % to 65 % results in an enormous increase in conductivity by four orders of magnetite. Such conductivities are remarkable in view of the adsorbed layer of insulating chitosan which must have completely coated the PANI particles in order to account for the long-term colloidal stability of the dispersion.

2.3.6 Zeta potential

Zeta potential is the charge that develops at the interface between a solid surface and its liquid medium. This potential, which is measured in millivolts, arises from one of several mechanisms [183]. Zeta potential is a function of the surface charge of the particle, any adsorbed layer at the interface, and the nature and composition of the surrounding suspension medium. It can be experimentally determined and, because it reflects the effective charge on the particles, is related to the electrostatic repulsion between them. The zeta potential has proven to be extremely relevant to the practical study and control of colloidal stability and flocculation processes.

The zeta potentials of PANI-CS nanoparticles in 10 mM NaCl solution are shown in Table 2.3. The results indicate that PANI-CS nanoparticles carry positive charge. This is easy to understand since both chitosan and PANI are polycationic polymers. The zeta potential of these nanoparticles were in the range of 4.8 - 17.2 mV. It was also found that the zeta potential increases as the chitosan concentration increases. This is an indication of the strong repulsion between the particles. Similarly results have been
reported on other positively charged polyester nanocapsules [158,184], nanoparticles [185], microcapsules [186] and liposomes [187] that were produced by coating or interacting them with chitosan. Some investigators have succeeded in improving the stability of liposomes [187], emulsions and nanocapsules [158] using chitosan and its derivatives.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>PANI loading (wt %)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>65</td>
<td>+ 4.8</td>
</tr>
<tr>
<td>3</td>
<td>46</td>
<td>+ 8.5</td>
</tr>
<tr>
<td>5</td>
<td>29</td>
<td>+ 11.4</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>+ 17.2</td>
</tr>
</tbody>
</table>

*Refer to Table 2.2 for reaction parameters of the samples

2.3.7 Structural characterizations of the PANI-CS nanocomposite

The FT-IR spectra of chitosan, doped PANI and PANI-CS nanocomposite are shown in Figure 2.5. For chitosan (spectrum a), the absorption peak at 1649 cm\(^{-1}\) can be assigned to the carbonyl stretching of secondary amides (amide I band) and the peak at 1590 cm\(^{-1}\) is assigned to the N–H bending vibration of primary amines [188]. The IR spectrum of doped PANI (spectrum c) exhibits several typical bands at 1559 cm\(^{-1}\) (C=C stretching of quinoid rings), 1476 cm\(^{-1}\) (C=C stretching of benzenoid rings), 1300 cm\(^{-1}\) (C-N stretching of secondary amine of PANI backbone) and 810 cm\(^{-1}\) (C-H aromatic out-plane bending), respectively [189]. When the IR spectrum of PANI-CS (spectrum b) is compared with these two spectra, it can be seen that PANI-CS has the
characteristics of both chitosan and PANI. The bands at 820 cm$^{-1}$ and 1307 cm$^{-1}$ in PANI-CS are due to PANI, for they are absent in the spectrum of chitosan. The absorption band structure of PANI-CS in the region of 1400 to 1700 cm$^{-1}$ is quite complex. The strong band at 1649 cm$^{-1}$ which is assigned to chitosan and two strong bands at 1559 cm$^{-1}$ and 1474 cm$^{-1}$ that are assigned to PANI are all disappeared. Two new bands appeared at 1614 cm$^{-1}$ and 1523 cm$^{-1}$ strongly suggest a possible chemical interaction between the PANI and the chitosan, rather than just a physical mixture.

![FT-IR spectra](image)

**Figure 2.5** FT-IR spectra of (a) chitosan, (b) PANI-CS nanocomposite (PANI loading: 35%) and (c) doped PANI.
2.3.8 TG studies of the PANI-CS nanocomposite

Thermogravimetry (TG) involves the continuous monitoring the weight change of a sample with temperature at a constant rate of change of temperature or with time isothermally. The most common use for TG is in measuring the thermal and oxidative stability of polymers under stringent working conditions. Since all organic molecules have a limiting thermal stability and will ultimately decompose either completely or to a limiting extent, to a more or less stable residue, the technique is applicable to all polymers.

For a polymer composite to be useful in many applications, it must have good thermal stability. It is known that HCl-doped PANI loses their dopants when heated at 190 - 350 °C [18]. The resultant polymers have diminished conductivity. Also, the evolution of the corrosive dopant is not desirable, as the acid can do harm to the environment. Thus, it is important to study the thermal decomposition pattern of polymers to determine if they possess the thermal stability required in the intended applications.

The TG thermocurves of doped PANI, chitosan and PANI-CS nanoparticles are shown in Figure 2.6. For PANI (curve a), the initial weight loss between 40 °C and 100 °C is attributed to the loss of moisture and unbound HCl [190]. After that PANI does not show any substantial weight loss until the thermal degradation of the main chain that begins at about 300 °C and continues until 610 °C. For chitosan (curve b), the first
weight loss takes place between 40 °C and 140 °C, which is due to the release of absorbed moisture and bounded (H-bond) water. The sharp loss peak between 270 °C and 370 °C is due to the oxidation degradation of the chitosan [191]. The following less sharp weight loss zone over the temperature range of 370 °C - 700 °C may be attributed to further structural degradation with the liberation of small molecules such as H₂ and NH₃. The thermocurve of PANI-CS (curve c) includes weight loss features of both PANI and chitosan. Compared with PANI or chitosan, PANI-CS has the highest onset weight loss temperature of about 220°C. The second weight loss between 190 °C and 330 °C is assigned to the degradation of chitosan and release of dopant HCl. The third mass loss zone appears between 480 °C and 680 °C is due to the decomposition of the PANI main chain. Compared with doped-PANI, the decomposition temperature of the PANI main chain in PANI-CS nanocomposite is substantially increased by 200 degrees. This enhanced thermal stability may be attributable to the chemical interaction between PANI and chitosan, which is also confirmed to exist by FT-IR spectrum of PANI-CS nanocomposite.
Figure 2.6 TG curves of a) doped PANI, b) chitosan and c) PANI-CS nanocomposite ((PANI loading: 35%).

This novel surface-functionalized PANI-CS nanoparticle can be considered for applications in biomedical science. The amino groups of chitosan are nucleophilic and reactive at higher pH values. They are suitable sites for chemical modification and for enzyme immobilization. Recent research shows that chitosan and DNA may form complexes which have a greater protection from degradation by nucleases. This is attracting much interest in the development of vaccines [192]. The cationic characteristic of chitosan is a crucial parameter for the complex formation. The nature of the interaction involved in the nanoparticle formation is predominantly electrostatic.
2.4 Conclusions

A novel surface-functionalized PANI-CS conducting nanocomposite has been synthesized and characterized. TEM study shows that surface-functionalized PANI-CS nanoparticles have uniform rice-grain morphologies. As the concentration of chitosan increases, the mean size of the PANI-CS nanoparticles decreases. Increasing the molecular weight decreases the mean size of the PANI-CS nanoparticles. As the reaction temperature increases, the surface of the nanoparticles becomes more “smooth”. The colloidal dispersion of the PANI-CS nanoparticles has excellent storage stability which is due to the steric stabilization provided by chitosan. The stability is affected by the concentration of chitosan, its molecular weight, and the reaction temperature. The PANI-CS dispersion is stable in acid media (pH < 6.5) and unstable in alkali media. XPS spectrum shows that chitosan is present on the surface of PANI-CS nanoparticles. Zeta potential studies show that PANI-CS nanoparticles carry positive charges, which can be attributed to the presence of chitosan at the surfaces. The chemical structure of the PANI-CS composite is confirmed by FT-IR and UV-vis. FT-IR and TG studies show that there exist certain chemical interaction between PANI and chitosan, which caused the decomposition temperature of the PANI main chain in PANI-CS nanocomposite to be 200 degrees higher compared with PANI.

In this chapter, chitosan is proved to be an excellent stabilizer that could efficiently prevent the precipitation of PANI. In the next chapter, chitosan is further developed as
the steric stabilizer for the dispersion polymerization of pyrrole. The structure of the PPy-CS nanocomposite will be characterized by various characterization tools.
Chapter 3
Synthesis and Characterization of Surface-Functionalized Conducting Polypyrrole-Chitosan Nanocomposite
3.1 Introduction

Polypyrrole (PPy) is one of the most promising conducting polymers because under certain circumstances it has high electrical conductivity [193], good environmental stability [194] and is easily synthesized. But most conducting polymers suffer from the processability problem, inasmuch as they are insoluble and infusible. It has been realized that one of the ways to improve the processability would be to prepare the polymer in colloidal form [161]. For PPy, this is best achieved by the dispersion polymerization route, in which pyrrole is oxidatively polymerized in the presence of a polymeric stabilizer. In such polymerization the reaction mixture is homogeneous to start with. As polypyrrole forms, it begins to separate out from the medium, being insoluble in the latter. However, this macroscopic precipitation is prevented by the adsorption of the polymeric stabilizer on the surface of the PPy particles. A number of such stabilizers have been reported in the literature (see Table 1.3, page 11).

In Chapter 2, chitosan was developed as a novel steric stabilizer for the dispersion polymerization of aniline. Chitosan successfully prevents the precipitation of polyaniline, and PANI-CS nanoparticles with rice-grain shape were prepared and characterized. The dispersion containing PANI-CS nanoparticles show good colloidal stability. Besides, the amine groups of the chitosan would provide surface-functionalization to these nanoparticles. Surface-functionalization, particularly with certain hydrophilic groups such as carboxylic acids or amines, can be highly desirable in diagnostic assays since it can sometimes minimize the ubiquitous nonspecific
binding problems which often result in reduced specificity and/or sensitivity for the analyte of interest [167]. These nanoparticles carry positive charges in acid media. It has been shown that positively charged nanoparticles may have improved stability in the presence of biological cations [158] and may be favorable for drug molecules due to their interaction with negatively charged biological membranes and site-specific targeting in vivo [159]. In this chapter chitosan is further developed as the stabilizer for the dispersion polymerization of pyrrole. The use of chitosan as the stabilizer allows unique control over the colloidal stability of the dispersions, which may prove to be useful in the large-scale preparation necessary for commercial applications of the processable form of PPy. The synthetic conditions will be optimized in order to obtain stable colloidal dispersions containing PPy-CS nanoparticles. The structure of the formed PPy-CS nanoparticles will be explored in detail.

3.2 Experimental

3.2.1 Chemicals

Pyrrole (99.9%), anhydrous ferric chloride (99%), ammonium persulfate (99%), chitosan (Mw: 300 kDa, 150 kDa, and 70 kDa, degree of deacetylation: 85 %, 72 %, and 80 %, as determined by IR) were purchased from Aldrich. Pyrrole was distilled at 60 - 70 mm Hg. The middle fraction of the distillate was collected, transferred into a number of small tubes, degassed in a vacuum line (1 × 10⁻⁵ torr), sealed, and stored in the dark at -10 °C. Other reagents were used as received without further purification.
3.2.2 Synthesis of surface-functionalized PPy-CS nanoparticles

The polymerization was carried out in double-walled glass vessels under magnetic stirring and nitrogen atmosphere. Cold water was circulated through the outer jacket of the vessel to maintain a constant temperature. Aqueous chitosan solutions (1.0 w/v %) were prepared by dissolving the required amount of chitosan in 0.2 M HCl solution. For a typical reaction, pyrrole (0.2 mL) was added to 40 mL of the chitosan solution (1.0 w/v %) before it was cooled to the desired temperature (2 °C). The polymerization began when the oxidant (FeCl₃, 1.13 g) was poured into the mixture and the reaction was maintained for 12 h. After that the reaction mixture was purified by centrifuging at 11,000 rpm for 20 mins, and the resulting sediment was redispersed in deionized water using an ultrasonic bath. This centrifugation-redispersion cycle was repeated three times in order to remove the excess chitosan and other byproducts completely. The black composite mass was washed with acetone and dried under reduced pressure. In the experiment to determine the colloidal stability of the PPy-CS dispersion, the dispersion was purified by dialysis in water using a dialysis membrane bag with a molecule weight cut-off of 10,000. A series of PPy-CS were prepared at different temperatures (2 °C, 12.5 °C and 25 °C, respectively) to study the effect of temperature on the stability of the colloid dispersions. The molar ratio of FeCl₃ to pyrrole was maintained at 2.4 [195].

3.2.3 Characterizations

The characterizations of the PPy-CS nanocomposite are similar to those of PANI-CS
nanocomposite which were described in Chapter 2. Changes in the electronic structure of PPy-CS nanocomposite were studied by UV-vis spectrophotometry over 250 - 1100 nm using a Shimadzu (UV1601PC) UV-vis spectrophotometer. The morphology and size of the PPy-CS nanoparticles were studied by a Philips (CM 10) transmission electron microscope with an accelerating voltage at 100 kV. XPS experiments were performed using a VG ESCALAB 220i-XL instrument equipped with a monochromatic Al Kα (1486.6 eV photons). Elemental analysis of the PPy-CS composite was carried out using a Perkin-Elmer 240C CHN analyzer for carbon, hydrogen, and nitrogen determinations. Conductivities of PPy-CS samples were measured with a standard four-probe technique at room temperature. The zeta potential of PPy-CS nanoparticles was determined from electrophoretic mobility measurements with a Zetasizer 3000 HS (Malvern, UK) electrophoresis meter. FT-IR spectra were acquired on a Bio-Rad Merlin (FTS3000) FT-IR spectrophotometer, with the frequency range from 4000 cm⁻¹ to 450 cm⁻¹ using 30 scans per spectrum at 4 cm⁻¹ resolution. Thermogravimetry analysis (TG) was carried out on a Du Pont Thermal Analyst 2200 system with a TGA 2960 Simultaneous Differential Thermal Analyser module.

3.3 Results and Discussion

3.3.1 UV-vis spectra of PPy-CS colloid dispersions

The formation of the colloidal dispersion of PPy-CS was monitored by UV-vis spectroscopy as is shown in Figure 3.1. At the beginning of the polymerization (e.g.
before the addition of FeCl$_3$), pyrrole in aqueous chitosan solution gave a flat absorption spectra, showing no peaks in the range of 250-1100 nm (Figure 3.1, spectrum a). After the addition of FeCl$_3$ for 5 minutes, an intense sharp band appeared at 295 nm (Figure 3.1, spectrum b). This absorption band could be attributed either to the $\pi$-$\pi^*$ singlet-triplet transition of pyrrole monomer [196], or to the bandgap transition of pyrrole oligomers [197]. As the polymerization proceeded, the intensity of this band decreased and it fully disappeared at the end of polymerization, which meant the exhaustion of pyrrole monomers or oligomers. After 50 minutes of polymerization, three new absorption bands centered at 460 nm, 757 nm and 970 nm were observed (Figure 3.1, spectrum c) which could be attributed to the presence of polarons and bipolarons in PPy chain [198]. The presence of these peaks meant the formation an oxidized, conducting PPy. Similar absorption bands have been observed in other conducting polymer colloids [199]. As the polymerization proceeded, the intensity of these bands continued to increase until the polymerization completed after 6 h (Figure 3.1, spectrum e).
Figure 3.1 UV-vis spectra of PPy-CS nanocomposite on different polymerization stage (0.2 mL of pyrrole in 40 mL of 1.0 wt % acidic chitosan solution, reaction temperature: 2.0 °C).

3.3.2. Morphologies and Formation Mechanism of PPy-CS nanoparticles

The morphology of the PPy-CS nanoparticles was studied by TEM. TEM images (Figure 3.2) shows that the nanoparticles are spherical in shape and the size of the PPy-CS nanoparticles can be varied in the range of 40 – 120 nm. This is different to the morphology of the PANI-CS particles prepared in Chapter 2, in which PANI-CS nanoparticles with rice-grain shape were prepared. It was reported that the polymerization of pyrrole in the presence of the stabilizer often produces nanoparticles with spherical shapes [161]. This may be due to the fact that the polymerization of PANI is not an autoaccelerated process. The autoacceleration of the
Figure 3.2 Morphologies of PPy-CS nanoparticles. (a) [pyrrole]/[chitosna] = 0.02/0.4 (sample No. 1); (b) [pyrrole]/[chitosna] = 0.1/0.4 (sample No. 2); (c) [pyrrole]/[chitosna] = 0.2/0.4 (sample No. 4); (d) [pyrrole]/[chitosna] = 0.3/0.4 (sample No. 5); (e) [pyrrole]/[chitosna] = 0.4/0.4 (sample No. 6); (f) [pyrrole]/[chitosna] = 0.2/0.4, Mw of Chitosan = 150 kDa (sample No. 7). Refer to Table 3.1 for reaction parameters.
polymerization is responsible for the formation of non-spherical morphology in PANI dispersions. A summary of particle size of the surface-functionalized PPy-CS nanoparticles is given in Table 3.1.

Table 3.1 Effect of synthetic conditions on the particle size of surface-functionalized PPy-CS nanoparticles

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Pyrrole / Chitosan Feed ratio (g / g)</th>
<th>Mw of Chitosan (kDa)</th>
<th>Oxidant</th>
<th>Temperature (°C)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02&lt;sup&gt;a&lt;/sup&gt; / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>42 - 48</td>
</tr>
<tr>
<td>2</td>
<td>0.1 / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>55 - 59</td>
</tr>
<tr>
<td>3</td>
<td>0.15 / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>58 - 63</td>
</tr>
<tr>
<td>4</td>
<td>0.2 / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>62 - 65</td>
</tr>
<tr>
<td>5</td>
<td>0.3 / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>75 - 78</td>
</tr>
<tr>
<td>6</td>
<td>0.4&lt;sup&gt;b&lt;/sup&gt; / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>110 - 113</td>
</tr>
<tr>
<td>7</td>
<td>0.2 / 0.4</td>
<td>150</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>68 - 71</td>
</tr>
<tr>
<td>8</td>
<td>0.2 / 0.4</td>
<td>70</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0</td>
<td>72 - 80</td>
</tr>
<tr>
<td>9</td>
<td>0.2 / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>12.5</td>
<td>62 - 65</td>
</tr>
<tr>
<td>10</td>
<td>0.2 / 0.4</td>
<td>300</td>
<td>FeCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>25.0</td>
<td>63 - 66</td>
</tr>
<tr>
<td>11</td>
<td>0.2 / 0.4</td>
<td>300</td>
<td>(NH₄)₂S₂O₈</td>
<td>2.0</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

<sup>a</sup> Minimum quantity needed to polymerize  
<sup>b</sup> Maxima quantity that forms stable dispersion

The formation of PPy-CS nanoparticles can be explained by a steric stabilization [161] mechanism which is similar to the formation mechanism of PANI-CS nanoparticles. At the beginning of the polymerization, the particle nucleation began in the aqueous
phase with the generation of oligomers containing the initiators. These pyrrole oligomers agglomerated and nucleated into a particle when they became water-insoluble due to the increase in size. At the same time chitosan physically absorbed onto the PPy by hydrogen bonding and this in turn prevented precipitation. If the initiation occurred around the seed particles and the produced oligomers deposited on their surfaces, the further reaction mainly took place on the surfaces of core particles rather than in the aqueous bulk phase because the dimer and succeeding pyrrole oligomers had lower oxidation potentials than pyrrole [197]. As a result, the polymerization of pyrrole proceeded preferably close to nucleated particles, which explained a relatively low polydispersity of dispersion particles. When the polymerization was completed, the shape and size of PPy-CS nanoparticles formed and depicted in Figure 3.3. The inner part of the particles contained both PPy and chitosan while the outside was covered by a shell of chitosan.
Figure 3.3 Schematic illustration of the surface-functionalized PPy-CS nanoparticle. The core is composed of both PPy and chitosan while the surface of the core is coated with chitosan. Free stabilizers accompany dispersion particles.

The presence of chitosan at the surface of the PPy-CS nanoparticles is further confirmed by the XPS results. Figure 3.4 shows the high resolution C 1s core level spectrum of the PPy-CS nanocomposite. The highly resolved C 1s spectrum may be divided into three component peaks at 285.4, 287.0 and 288.5 eV, respectively. The peak at 285.4 eV is assigned to the C-C bondings formed in PPy and chitosan [178]. The peak at 287.0 eV is assigned to C-N, C-O or C-O-C bonding attributed to chitosan. The last peak at 288.5 eV is assigned to C=O or O-C-O bonding formed in chitosan [178b], because chitosan usually contains some of the acetamido groups that come from the original chitin. It should be noted that for pure PPy sample, there is
often a small peak located at about 287 eV which is due to the oxidation of the PPy sample under ambient conditions [200]. But this peak is usually very small and only presented as a small shoulder. In Figure 3.4, this peak has been developed as a separate peak which can be observed even without deconvolution. Since XPS technique acknowledges to be highly surface-specific, we conclude that chitosan must be present at the surface (or within the first few nanometers) of the functionalized PANI-CS nanoparticles.

**Figure 3.4** C 1s core level X-ray photoelectron spectrum of the surface-functionalized PPy-CS nanoparticles (sample No. 4, see Table 3.1 for reaction parameters). Peaks at 287.0 and 288.5 eV are assigned to chitosan which is at the surface of the nanoparticles.
3.3.3 Effect of Reaction Parameters on the Size of PPy-CS Nanoparticles

The size of PPy-CS nanoparticles can be controlled by adjusting reaction parameters such as the amount of pyrrole and the molecular weight of chitosan. The results showed that the particle size increases with an increase of amount of pyrrole (Table 3.1 and Figure 3.2). When 0.02 mL (0.27 mmol) of pyrrole is used in the polymerization, the particle size of PPy-CS is about 42 - 48 nm. Increase the amount of pyrrole (0.1 mL, 1.3 mmol) while keeping the concentration of chitosan unchanged results in bigger PPy-CS nanoparticles with sizes in the range of 55 - 59 nm. The maximum amount of pyrrole that can be used was found to be 0.4 mL (5.4 mmol), size of PPy-CS nanoparticle: 110 - 113 nm). Further increase of the amount of pyrrole would give unstable dispersions. With the increase of the amount of pyrrole, the amount of stabilizer is insufficient to effectively cover the available surface of nuclei, resulting in an unstable colloidal system. The smaller particles therefore agglomerated until the total surface area decreased to a point where the amount of chitosan available was again sufficient to produce a stable suspension.

The particle size increases with the decrease in molecular weight (Mw) of chitosan for the same chitosan concentration, as shown in Table 3.1 (Sample No. 4, 7, and 8). This may result from the coverage of a greater area of the particle surface with a higher Mw polymer. Assuming a loop-train-tail configuration of the adsorbed stabilizer molecule [201] and assuming further that the sizes of these portions viz. tails, trains, loops, et al. remain unchanged with changes in Mw, it follows that the higher the Mw of the
stabilizer, the larger the surface area of the particles covered. On the other hand, the number of stable particles in a dispersion polymerization is determined by the relative rate of homocoalescence of nuclei/particulates vs. stabilizer adsorption before stable particles that have their whole surface covered with stabilizer form, the stage being called “primary stabilization” [202]. Thus, using a stabilizer of higher molecular weight one may expect a greater number of primary particles unless the stabilizer adsorption is adversely decreased with an increase in molecular weight of the stabilizer. The greater the number of primary particles so formed, the smaller the size of the finally formed particles. In Chapter 2 the similar result was reported when chitosan is used as the stabilizer for the dispersion polymerization of aniline. Mandal et al. also reported the similar result for the dispersion polymerization of pyrrole when ethylhydroxy-ethylcellulose was used as the stabilizer [203].

3.3.4 Effect of Reaction Parameters on the Colloidal Stability of PPy-CS Dispersion

The problem of colloidal stability is one of the most important topics from both the industrial and the academic point of view. It has been demonstrated in Chapter 2 that chitosan effectively prevented the precipitation of PANI. The colloidal stability of the PANI-CS dispersion depended on many reaction parameters such as the concentration of chitosan, the reaction temperature, the Mw of chitosan and so on. In this chapter it was found that the stabilization of PPy in the chitosan solution is possible over a wide range of reaction conditions.
In our experiment, the concentration of chitosan used in the reaction was kept unchanged (40 mL of 1 % chitosan solution) and the reaction temperature was 2 °C. The minimum amount of pyrrole that can polymerize under this condition was found to be 0.02 mL. Below this level, the polymerization of pyrrole cannot proceed. The maximum amount of pyrrole which can be used was found to be 0.4 mL. Above this level, chitosan cannot effectively prevent the aggregation of PPy and precipitation occurred.

The effect of the molecular weight of chitosan on the stability of PPy-CS dispersion was studied. When chitosan having a low molecular weight (Mw = 70 kDa) was used in the polymerization while other conditions remain unchanged, the PPy-CS dispersion was not stable and precipitation occurred after 5 days. When chitosan with a higher molecular weight (Mw = 150 kDa) was used, the dispersion was stable for 2 months. Further increase in the molecular weight of chitosan (Mw = 300 kDa) produced more stable PPy-CS dispersions. Chitosan is a cationic polymer at acidic pH that operates at the surface of PPy-CS nanoparticles to stabilize them through electrosteric stabilization mechanism. The thickness of the chitosan layer increases with increasing molecular weight, which results in an increase in the steric repulsive energy and the electrostatic repulsive energy and finally in an increase in the total potential energy between two particles. So the increase of molecular weight of chitosan will cause the stabilization efficiency to increase as well. Similar results and explanations have been given for dextran [179] and many other polymeric surfactants.
The pH value of the reaction medium was also found to affect the stability of the PPy-CS dispersion. The PPy-CS dispersion was found to be stable when the pH was below 6.5. Further increase the pH by the addition of a base caused the precipitation of the colloid system. The destabilization induced by the addition of a base could be reversed simply by the addition of excess acid. This weak, reversible flocculation behavior strongly suggest that destabilization is due to the reduced solvation of chitosan (which is quickly restored on reprotonation) rather than actual desorption of the stabilizer. It is well known that chitosan is insoluble in water, alkali and organic solvents, but is soluble in most solution of organic acid when the pH of the solution is less than 6.5. The amino groups of chitosan play a vital role for its solubility in water. Adjusting the dispersion to a neutral pH will cause the $-\text{NH}_3^+$ cations on the surface of PPy-CS nanoparticles to convert to $-\text{NH}_2$, rendering the nanoparticles unstable in water. Besides, it was also observed that PPy-CS dispersion would be unstable and slatted-out (flocuulated) by the addition of sufficient quantities of inorganic electrolyte such as NaCl.

The reaction temperature has no obvious effect on the colloidal stability of the PPy-CS dispersion. The reaction proceeded at three different temperatures (2.0 °C, 12.5 °C, and 25 °C) and stable PPy-CS dispersions were prepared under these conditions. This is different with that of PANI-CS dispersion prepared under different temperatures. In
Chapter 2 it was shown that reaction temperature affected significantly the stability of PANI-CS dispersion.

Another oxidant APS has been used to replace FeCl$_3$ to initiate the polymerization of pyrrole. The polymerization can proceed but the dispersion formed was unstable which led to precipitation. Since APS has a higher oxidation potential ($E^\circ = +2.05$ V) than that of FeCl$_3$ ($E^\circ = +0.75$ V), this high oxidation potential accelerated the polymerization rate of pyrrole. The result is an uncontrolled fast nucleation which caused macroscopic precipitation [195].

3.3.5 Conductivities

The elemental analysis of doped PPy and PPy-CS nanocomposite with different PPy loadings and the conductivities of these nanocomposites are shown in Table 3.2. The mass loading of PPy was estimated from the weight percent of the C/N ratio reported for doped PPy and for PPy-CS. It can be seen that the ratio of PPy (weight percent) in the PPy-CS composite is always higher than the initial feed ratio. This may be due to the loss of chitosan in the preparation process. Chitosan acts as the stabilizer to prevent the precipitation of PPy. Not all of chitosan interact with PPy to form the PPy-CS nanoparticle. Some of them are present in the dispersion after the polymerization of pyrrole. This is similar to the case of those of PANI-CS nanoparticles that reported in Chapter 2. The presence of chitosan is confirmed by the IR spectrum of the supernatant of the reaction mixture obtained by centrifuge.
Table 3.2 The composition and conductivity of the PPy-CS nanoparticles (Temperature = 2.0 °C, [FeCl₃] / [pyrrole] = 2.4, Mw of chitosan = 300 kDa, Reaction volume = 40 mL)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pyrrole / Chitosan Feed ratio (g / g)</th>
<th>PPy loading Theoretical wt %</th>
<th>PPy loading Actual wt %</th>
<th>Conductivity (S / cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02 / 0.4</td>
<td>5</td>
<td>8</td>
<td>Too low</td>
</tr>
<tr>
<td>2</td>
<td>0.1 / 0.4</td>
<td>20</td>
<td>24</td>
<td>$2.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>0.15 / 0.4</td>
<td>27</td>
<td>30</td>
<td>$3.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>0.2 / 0.4</td>
<td>33</td>
<td>39</td>
<td>$8.4 \times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>0.3 / 0.4</td>
<td>43</td>
<td>45</td>
<td>$4.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>6</td>
<td>0.4 / 0.4</td>
<td>50</td>
<td>58</td>
<td>$4.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>Pure PPy</td>
<td>0.2 / 0</td>
<td>100</td>
<td>100</td>
<td>2.5</td>
</tr>
</tbody>
</table>

*a Refer to Table 3.1 for the reaction parameters of sample 1-6.
*b As determined from elemental analysis.

The room temperature conductivities of the PPy-CS nanocomposites are always lower than that of PPy prepared under the same conditions in the absence of chitosan (see Table 3.2). The conductivity of PPy-CS nanocomposite lies in the range of $2.1 \times 10^{-6}$ to $4.6 \times 10^{-2}$ S / cm, which is similar to those reported for other sterically stabilized PPy nanocomposite [204]. It shows that the conductivity of the PPy-CS nanocomposite increases with the increasing weight percentage of PPy. An increase in the content of PPy from 24 % to 58 % results in an enormous increase in conductivity by four orders of magnetite. Such conductivities are remarkable in view of the considerable amount of non-conducting chitosan in the PPy-CS nanoparticles.
3.3.6 Zeta Potential

The zeta potentials of PPy-CS nanoparticles in 10 mM NaCl solution are shown in Table 3.3. The results show that all PPy-CS nanoparticles carry positive charge, which suggest the presence of chitosan at the surface of the nanoparticles. Chitosan are polycationic polymers and the free amino groups on it are responsible for the measured positive zeta potential [205]. The zeta potential of the PPy-CS nanoparticle was found to be in the range of 4.3 - 25.3 mV. The highest zeta potential was obtained for sample No. 2, which has the highest chitosan loading. It was found that zeta potential of the PPy-CS nanoparticles decreased with the increase of PPy loading. Similar results have been reported for other positively charged polyester nanocapsules [158,184], nanoparticles [185], microcapsules [186] and liposomes [187] that were produced by coating or interacting them with chitosan. Some investigators have succeeded in improving the stability of liposomes [187], emulsions and nanocapsules [158] using chitosan and its derivatives.

<table>
<thead>
<tr>
<th>Sample NO.</th>
<th>PPy loading (wt %)</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>24</td>
<td>+ 25.3(±0.5)</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>+ 18.4(±0.5)</td>
</tr>
<tr>
<td>4</td>
<td>39</td>
<td>+ 10.2(±0.4)</td>
</tr>
<tr>
<td>6</td>
<td>58</td>
<td>+ 4.3(±0.2)</td>
</tr>
</tbody>
</table>

* Refer to Table 3.1 for the reaction parameters of the samples
3.3.7 Structural Characterizations of the PPy-CS Nanocomposite

FT-IR spectra of PPy bulk powder (synthesized by precipitation polymerization in the absence of chitosan), chitosan, and PPy-CS nanocomposite are depicted in Figure 3.5. The IR spectrum of PPy bulk powder (spectrum a) is in good agreement with literature and confirms that this material is highly doped, as expected [204a, 206]. A number of characteristic broad bands are observed in the range of 700 - 1800 cm\(^{-1}\). The bands at 1640, 1535, and 1455 cm\(^{-1}\) are assigned to C–C ring vibrations of pyrrole; the bands at 1162 and 1033 cm\(^{-1}\) are assigned to =C-H in-plane vibrations of PPy backbone; the bands at 964 and 768 cm\(^{-1}\) are assigned to =C-H out-of-plane vibrations of PPy backbone. In the case of chitosan (spectrum c), the main absorption peak at 1655 cm\(^{-1}\) is be assigned to the carbonyl stretching of secondary amides (amide I band) and the peak at 1590 cm\(^{-1}\) is assigned to the N–H bending vibration of primary amines [188]. The spectrum of PPy-CS shell (spectrum b) comprised the main peaks of both chitosan and PPy. A number of characteristic peaks of these two polymers are observed, particularly in the 1000 - 1800 cm\(^{-1}\) region. For example, the band at 894 cm\(^{-1}\) in spectrum is due to the presence of chitosan, because it is absent in the spectrum of PPy. Similarly, the bands at 1160 cm\(^{-1}\) and 962 cm\(^{-1}\) are due to the presence of PPy since they are absent in the spectrum of chitosan. This shows that the PPy-CS shell is a hybrid material. The absorption band structure of PPy-CS in the region of 1700 to 1400 cm\(^{-1}\) is quite complex. In this region chitosan have two strong bands at 1649 cm\(^{-1}\) and 1590 cm\(^{-1}\) while PPy have two bands at 1640 cm\(^{-1}\) and 1535 cm\(^{-1}\). In spectrum b, two bands appeared at 1630 cm\(^{-1}\) and 1544 cm\(^{-1}\), which suggest a
possible chemical interaction between PPy and chitosan, rather than just a physical mixture.

![FT-IR spectra of (a) PPy, (b) PPy-CS (sample No. 4) and (c) chitosan. Refer to Table 3.1 for sample numbers.](image)

**Figure 3.5** FT-IR spectra of (a) PPy, (b) PPy-CS (sample No. 4) and (c) chitosan. Refer to Table 3.1 for sample numbers.

Thermal analysis of PPy-CS nanocomposite was carried out by TG and DTG. The results were compared with those of the pure PPy and chitosan as shown in Figure 3.6. For pure PPy (Figure 3.6a), the initial fraction of weight loss between 40 °C and 150 °C was attributed to the loss of moisture and unbound HCl [190]. After that PPy did not show any substantial weight loss until the thermal oxidation decomposition of the main chain happened in the range of 250 °C and 590 °C. Two steps as indicated by the two peaks of the derivative weight curve for pure PPy around 310 °C and 495 °C are depicted in Figure 3.6a. For chitosan (Figure 3.6b), the first weight loss zone was
observed between 40 °C and 150 °C, which was due to the release of absorbed moisture and bounded (H-bond) water. Then two steps as indicated by the two peaks of the derivative weight curve around 310 °C and 525 °C were observed. The first sharp step was due to the oxidation decomposition / degradation of the chitosan [191] while the following less sharp peak may be attributed to further structural degradation with the liberation of small molecules such as NH$_3$. The thermocurve of PPy-CS (Figure 3.6c) includes weight loss features of both PPy and chitosan. The initial weight loss between 40 °C and 160 °C was attributed to the loss of moisture and unbound HCl. After that, the second weight loss fraction was observed between 180 °C and 300 °C, which was assigned to the degradation of chitosan and release of dopant HCl. The third weight loss was observed between 310 °C and 490 °C, which was due to the decomposition of the PPy main chain. It was found that decomposition temperature of chitosan main chain in PPy-CS nanocomposite (180 °C) was lower than that of pure chitosan (240 °C). This may be attributable to the chemical interaction between PPy and chitosan, which is also confirmed to exist by FT-IR spectrum of PPy-CS nanocomposite.
Figure 3.6 TG and DTG curves of (a) pure PPy, (b) Chitosan and (c) PPy-CS composite (sample No. 4. See Table 3.1 for reaction parameters of the sample.)
3.4 Conclusions

A novel surface-functionalized PPy-CS conducting nanocomposite has been synthesized and characterized in this chapter. TEM study shows that surface-functionalized PPy-CS nanoparticles have a uniform spherical shape. The size of the PPy-CS nanoparticles can be controlled in the range of 40 - 120 nm. As the concentration of chitosan increases, the mean size of the PPy-CS nanoparticles decreases. Increasing the molecular weight of CS decreases the mean size of the PPy-CS nanoparticles. The colloidal dispersion of the PPy-CS nanoparticles has excellent storage stability which is due to the steric stabilization provided by chitosan. The stability is affected by the concentration of chitosan, its molecular weight, and the reaction temperature. The PPy-CS dispersion is stable in acidic media (pH < 6.5) and it precipitates in alkaline media. XPS confirms that chitosan is present on the surface of PPy-CS nanoparticles. Zeta potential studies show that PPy-CS nanoparticles carry positive charges, which is due to the presence of chitosan at the surfaces. The chemical structure of the PPy-CS nanocomposite is characterized by FT-IR, UV-vis and TG studies.

In this Chapter and Chapter 2, chitosan was successfully developed as the steric stabilizer for the dispersion polymerization of aniline or pyrrole. This dispersion polymerization technique is easy to control, and reaction condition is mild. In the next chapter, the dispersion polymerization technique will be developed further to produce polymeric hollow nanospheres.
Chapter 4
Facile Fabrication of AgCl@ Polypyrrole-Chitosan Core-Shell Nanoparticles and Polymeric Hollow Nanospheres
4.1 Introduction

The ability to obtain, control, manipulate, and modify structures at nanometer scale is of great scientific and technological interests to scientist [207]. Recently there has been increasing interest in the fabrication of core-shell nanomaterials. These nanomaterials may have better performance compared with those of the individual core or shell material. For example, Klabunde et al. [208] demonstrated that core-shell nanoparticles such as Fe$_2$O$_3$@MgO and Fe$_2$O$_3$@CaO had greatly enhanced efficiencies over pure MgO and CaO catalysts for SO$_2$ adsorption, H$_2$S removal, and chlorocarbon destruction. Generally there are two major routes to synthesize core-shell nanomaterials [4]. The first one consists of the in-situ synthesis of nanoparticles in the polymer matrix. The second one involves the polymerization of the monomers around the nanoparticles. Core-shell nanoparticles such as Au@PPy [148], Fe$_2$O$_3$@Polystyrene [209] and Au@HCMS [154c] have been reported using these approaches. A recent example of materials design via self-assembly is the fabrication of core-shell particles by the Layer-by-Layer adsorption of different materials [157a, 207, 210]. Fine control of the shell can be achieved using this method.

It is described in Chapter 1 that different morphologies of PPy particles could be obtained easily by changing the synthetic methods. For instance, PPy particles with spherical shapes could be obtained by dispersion polymerization in the presence of polymeric stabilizers or low molecular weight surfactants [161]. PPy nanotubes have been synthesized by using an alumina membrane template or by a self-assembled
method in the presence of β-naphthalene sulfonic acid. But to the best our knowledge, there is little report on the core-shell and hollow nanostructure of PPy [148].

In this chapter, a facile one-step pathway to the synthesis of AgCl@ Polypyrrole-Chitosan (AgCl@PPy-CS) core-shell nanoparticles is provided. AgCl is the core material while PPy-CS acts as the polymeric shell. Chitosan is chosen as the steric stabilizer for the polymerization of pyrrole. As is shown in Chapter 3, chitosan can efficiently prevent the aggregation of PPy. The formed PPy-CS nanoparticles dispersed very well in aqueous media. It is thus envisioned that in the presence of AgCl nanoparticles, the polymerization of pyrrole process may occur at the surface of AgCl nanoparticle to form AgCl@PPy-CS core-shell nanoparticles. AgCl is chosen as the core because silver halides are important semiconductors. If certain conditions are controlled to avoid photo-decomposition, silver halides can also be used in heterogeneous catalysis [211]. Although silver halide nanoparticles have been extensively investigated, there are few examples describing the synthesis and properties of core-shell nanoparticles containing silver halides. Besides, our AgCl@PPy-CS nanoparticles could also be used as templates to produce PPy-CS hollow nanospheres. Polymeric hollow spheres have recently been used as novel carriers and nanoreactors with designed properties because they exhibit controllable permeability and surface functionality [212]. This should enable many applications such as the controlled release of drugs [213] or gene therapy [136].
4.2 Experimental

4.2.1 Chemicals

Pyrrole (99.9%), ferric chloride (FeCl₃, 99%), chitosan (Mw: 300 kDa, extent of deacetylation: 80 %, as determined by IR), silver nitrate (99.5%), sodium chloride (NaCl, 99.5%), ammonium hydroxide (NH₄OH), nitric acid (HNO₃) were purchased from Aldrich. Pyrrole was purified by distillation in vacuum, stored under nitrogen and refrigerated in the dark. Other reagents were used as received without further purification. Water purified with cartridges from a Millipore purification system (NANOPure, Barnstead, USA) to a resistivity of 18.0 MΩ·cm was used in the preparation of all samples.

4.2.2 Synthesis of AgCl@PPy-CS Core-shell Nanoparticles

The reaction was carried out in a double-walled glass vessel under magnetic stirring and nitrogen atmosphere. Cold water was circulated through the outer jacket of the vessel to maintain a constant temperature. 0.01 g of AgNO₃ and 0.025 mL of pyrrole was first added to 20 mL of chitosan solution (300 kDa, 1.0 wt %, in 0.05 M HNO₃). 0.14 g of oxidant FeCl₃ (dissolve in 5 mL of water) was introduced to the above dispersion. The polymerization was conducted at 2 °C for 12 h. After polymerization, the reaction mixture was purified by dialysis using a membrane bag (Spectrum Medical Industries, Inc. Mw cut-off: 3,500 Da) in 0.05 M HNO₃. The dispersion after dilution was used for TEM and UV-vis characterization studies. Finally, the AgCl@PPy-CS core-shell material was obtained by precipitating with acetone and
4.2.3 Synthesis of PPy-CS Hollow Nanospheres

0.005 g of AgCl@PPy-CS core-shell material was first dispersed in 20 mL of distilled water by ultrasonication. The pH of the dispersion was then adjusted to 13 by 5 M NH₄OH and stirred for 24 h. The formed silver ammonia ions were removed by dialysis with a membrane bag (molecule weight cut-off: 3,500) in 0.1 M NH₄OH. After dialysis the pH of the dispersion was adjusted to 4 with 2 M HNO₃. The PPy-CS hollow nanospheres was obtained by precipitating in acetone and dry in vacuum at 40 °C for 24 h.

4.2.4 Characterization

4.2.4.1 Transmission Electron Microscopy

The morphologies and sizes of AgCl@PPy-CS core-shell nanoparticles were recorded on a Philips CM10 electron microscope at an accelerating voltage of 100 kV. The dispersion containing AgCl@PPy-CS core-shell nanoparticles was diluted to an appropriate solid content and a drop of it was placed onto a formvar support on copper grids (150 meshes) for TEM observation. The mean diameter was calculated by counting more than 100 nanoparticles.

4.2.4.2 Ultraviolet-visible Spectroscopy

A Shimadzu (UV1601PC) UV-vis spectrophotometer was used to measure the
absorption of the dispersions containing core-shell nanoparticles or hollow nanospheres. The scan covered from 250 - 1100 nm and the cell temperature was kept at room temperature (24 °C).

4.2.4.3 X-ray Diffraction Pattern

The XRD pattern of the samples were recorded on a Siemens D5005 diffractometer equipped with a Cu kα (1.5405 Å) X-ray source. The powders were mounted by double-sided adhesive tape on plastic sample holders.

4.3 Results and Discussion

4.3.1 Illustration of the reaction route

The overall procedure for the synthesis of AgCl@PPy-CS core-shell nanoparticles and PPy-CS hollow nanospheres is illustrated in Figure 4.1. AgNO₃ and pyrrole were first introduced to a solution of chitosan before the introduction of FeCl₃, which was selected to be an initiator to oxidize pyrrole. The formation of AgCl core and PPy-CS shell took place in the same reaction medium but the formation rates were different. AgCl nanoparticles formed instantly due to the rapid reaction rate between silver and chlorine ions. When FeCl₃ aqueous solution was added to the reaction medium, a white emulsion formed at once. This is an indication of the formation of AgCl nanoparticles. The polymerization of pyrrole initiated by Fe³⁺ began at the same time but it was a relatively slow process [161]. The polymerization proceeded for about 12 h and the reaction medium turned black gradually, as a result of the formation of PPy.
After polymerization, a shell of PPy-CS composite was formed on the surface of each AgCl nanoparticle. The AgCl could further be removed by treating the nanoparticles with NH₄OH:

$$\text{AgCl (s) + NH}_4\text{OH} \rightarrow \text{Ag[(NH}_3\text{)}_2]^{+} + \text{Cl}^-$$

Since the polymer shell was permeable to ions and small organic molecules [214], silver ammonia ions could easily be removed by dialysis.

![Diagram of the preparation process](image)

**Figure 4.1** Schematic illustration of the preparation of AgCl@PPy-CS core-shell nanoparticles and PPy-CS hollow nanospheres.

### 4.3.2 Morphologies

TEM images presented in Figure 4.2 illustrate the nanostructures prepared at various stages of the preparation. Figure 4.2a shows the image of AgCl nanoparticles immediately after FeCl₃ had been added to the reaction medium. At this stage, the polymerization of pyrrole had just started and no polymeric shell was observed. Stabilized by chitosan, AgCl nanoparticles dispersed very well in aqueous media with
diameters of $20 \pm 2$ nm.

**Figure 4.2** TEM images of (a) AgCl nanoparticles; (b) AgCl@PPy-CS nanoparticles; (c) PPy-CS hollow nanospheres. Reaction condition: 20 mL of chitosan (1 wt%, in 0.05 M of HNO$_3$), 0.01 g of AgNO$_3$, 0.025 mL of pyrrole, 0.14 g of FeCl$_3$. The reaction temperature is 2 $^\circ$C.

Figure 4.2b shows a representative image of core-shell nanoparticles after the polymerization of pyrrole for 12 h. AgCl nanoparticles surrounded by a spherical polymer shell (PPy-CS) are evident in the image. Well defined particles are readily observed with light contrast shells and the dark contrast cores (AgCl). The mean
diameter of core-shell nanoparticles is around $50 \pm 5$ nm (diameter of core: $20 \pm 3$ nm, thickness of shell: $15 \pm 4$ nm). The polymer appears to have nucleated on and grown outward from the AgCl particles. Most of the cores are spherical in shapes which are just the same size as those nanoparticles shown in Figure 4.2a. It is not clear why PPy formed preferably on AgCl nanoparticles. One possible explanation is that the surface of AgCl nanoparticle has lower oxidation potentials than pyrrole itself. As a result, the reaction would mainly take place on the surfaces of core particles rather than in the aqueous bulk phase. There may also be insoluble PPy-Chitosan nanoparticles formed in the solution, but the total amount is very small (less than 5 %) according to the TEM observation.

Figure 4.2c is a typical TEM image of PPy-CS hollow nanospheres. The image shows strong contrast between the dark ring and the pale center of the spherical particles, which indicates the formation of hollow nanostructures. The diameter of the hollow nanospheres is about $50 \pm 5$ nm while the diameter of the hole is about $20 \pm 3$ nm. The inner diameter of the hollow nanosphere matched the diameter of the template particle, only a little reorganization, collapse, or shrinkage occurs when the hollow nanospheres are dried for TEM observation.

The diameter of AgCl core depends on the concentration of AgNO$_3$ and the amount of chitosan in the reaction medium. The thickness of the shell, on the other hand, depends on the concentration of pyrrole, the amount of chitosan and the
polymerization time. Figure 4.3a shows the core-shell nanoparticles with enlarged cores (30 ± 2 nm) compared with Figure 4.2b. Figure 4.3b shows core-shell nanoparticles with even bigger cores (60 ± 5 nm) and thinner shells (10 ± 2 nm) compared with Figure 4.2b. The reaction temperature should be low enough (2 °C) in order to get uniform nanoparticles. At higher polymerization temperature (15 °C), multiple AgCl nanoparticles inside one polymer shell are observed (Figure 4.3c). Slow polymerization rate favors the formation of single core-shell nanostructures.

Figure 4.3 TEM images of AgCl@PPy-CS nanoparticles prepared at different reaction conditions: 20 mL of Chitosan (1 wt%, in 0.05 M of HNO₃), x g of AgNO₃, y mL of pyrrole, where x = 0.02, y = 0.025 for (a), x = 0.05, y = 0.01 for (b), and x = 0.01, y = 0.025 for (c). The reaction temperature is for (a) and (b) is 2 °C while for (c) is 15 °C.
4.3.3 Formation Mechanism

Choosing an effective stabilizer is very important for the synthesis of core-shell nanoparticles. According to the results from Chapter 2 and 3, chitosan was proven to be an excellent steric stabilizer for the conducting polymers, e.g., PANI and PPy. In this chapter, chitosan also behaved very well as a stabilizer. No precipitation of PPy was observed after the reaction. The structure of a representative poly-(aminosaccharide) segment of chitosan is shown in Figure 4.1. Amine groups are known to behave normally with respect to protonation in aqueous solution. In our case, chitosan has two roles: (i) to stabilize AgCl nanoparticles; and (ii) to prevent the aggregation of polypyrrole. After the formation of AgCl nanoparticles, chitosan would be adsorbed onto the surface of AgCl nanoparticles by interactions between the metal ions and amino and/or hydroxyl groups of chitosan. At the same time, pyrrole monomers are oxidized by FeCl₃ to form polycationic PPy chains, which lags behind the formation of AgCl. The polymer appears to have nucleated on the adsorbed chitosan, forming core-shell nanoparticles finally. Meanwhile, FeCl₃ also plays two roles during the formation of AgCl@PPy-CS. One is that chlorine ions provide building blocks to form AgCl nanoparticles; and the other is that ferric ions act as the oxidant for the polymerization of pyrrole.

Several reports on the polymerization mechanism of pyrrole have been suggested. However, the mechanism is not clearly understood. Figure 4.4 shows one of the most widely accepted mechanisms of polymerization of pyrrole [195]. In the initial step,
radical cations ($C_4NH_5^+$) are produced by the oxidation of pyrrole monomer. Two of these radical cations then couple to a dimer with deprotonation, leading to a bipyrrrole. After the deprotonation, the bipyrrrole is reoxidized and couples with another radical cation. The process continues to form PPy chains. The termination step is known to occur owing to the nucleophilic attack of water molecules or impurities on the polymer chains.

Figure 4.4 One possible polymerization mechanism of pyrrole [195].
4.3.4 Stability of PPy-CS Hollow Nanospheres

PPy-CS hollow nanospheres are stable in acid solution but not in alkaline solution. In acidic solution where the pH is smaller than 6.5, PPy-CS hollow nanospheres could disperse very well. If the pH of the medium is larger than 6.5, the dispersion containing PPy-CS hollow nanospheres would be unstable and precipitate out after a few hours. This can be explained as the presence of chitosan in the shell [215]. The PPy-CS hollow nanospheres redispersed very well in the medium if the pH is readjusted to acidic condition. This “precipitate-dispersion” cycle can be repeated for many times without affecting the properties or morphologies of the PPy-CS hollow nanospheres.

The mechanical stability of the hollow nanospheres is a critical question that needs to be studied. From practical considerations, these capsules should be stable enough to withstand a wide range of pH change, solvent etching, and shear stress. The PPy-CS hollow nanospheres exhibited very high stability against strong alkaline condition (NaOH solution, pH = 14) or strong acidic condition (HNO₃ solution, pH = 1.0) even for 4 h. They are still well dispersed in weak acid media and able to keep their intact structures. For hollow spheres prepared by layer-by-layer method, some additional pathways are often needed to strengthen the shells. For example, by incorporation of the photosensitive diazoresin in a layer-by-layer manner, the charge interaction in the multilayers can be converted into covalent bonding via UV irradiation [216]. In another example, hollow multilayer poly(allylamine hydrochloride)/poly(acrylic acid)
(PAH/PSS) microcapsules are treated with glutaraldehyde (GA) to manipulate the stability and mechanical strength. The amino groups of PAH molecules in the capsule shells readily react with aldehyde groups of GA at very mild conditions [217]. Consequently, aqueous GA reacts with the amino groups as an unsaturated polymer to yield stabilized bonds (Schiff base) by resonance [218]. PPy-CS hollow nanospheres prepared in this work shows better stability compared with those of hollow spheres prepared by the layer-by-layer technique. No additional pathways are needed to strengthen the PPy-CS shells. The good stability of the shell may be caused by the strong physical / chemical interactions existed between PPy and CS.

4.3.5 Structure Characterizations

4.3.5.1 UV-vis Absorption Spectroscopy

The UV-vis absorption spectra of the formation of AgCl and AgCl@PPy-CS nanoparticles at different stage are presented in Figure 4.5 (Spectrum a and b). Spectrum a was taken immediately after FeCl₃ was added to the reaction medium. An absorption peak appears at 256 nm is observed, which is assigned to the direct exciton absorption bands of AgCl NPs. This peak corresponds to an energy gap value of 4.8 eV. Compared with the bulk AgCl value of 3.2 eV, it reveals that this material is nanosized. [219-220]. No additional peaks related to PPy were observed at this stage. Spectrum b was taken when the polymerization was completed. In addition to the surface plasmon band related to AgCl, a broad absorbance at 446 nm corresponds to the π-π* transition of the polypyrrole chain was observed [98]. UV-vis spectra not
only confirm the formation of AgCl and polypyrrole, but also suggest that AgCl was formed first followed by polypyrrole. Even after long periods of sunlight exposure, no additional optical absorption was developed in the 300 - 500 nm range, where silver metal had been reported to absorb [221]. This is because the polymer shell may act as an electron-hole scavenger to offer an efficient pathway for their recombination, thus avoiding electron-silver ion formation [155]. The UV-vis absorption spectrum of PPy-CS hollow nanospheres is shown in Figure 4.5 (Spectrum c). The peak at 252 nm that is related to the direct exciton absorption bands of AgCl nanoparticles had disappeared. The broad band centered at 460 nm confirms the presence of polypyrrole [98].
Figure 4.5 UV-vis absorption spectra of (a) AgCl nanoparticles; (b) AgCl@PPy-CS core-shell nanoparticles and (c) PPy-CS hollow nanospheres. The reaction conditions are the same as those of nanoparticles prepared in Figure 4.2.

4.3.5.2 Powder X-Ray Diffraction Pattern

The crystalline structure of the AgCl@PPy-CS nanoparticles was analyzed using XRD (Figure 4.6). The XRD spectrum of AgCl@PPy-CS (spectrum a) shows several sharp diffraction peaks together with a broad peak. The sharp peaks at $2\theta = 27.9^\circ$, $32.3^\circ$, $46.4^\circ$, $55.0^\circ$ and $57.6^\circ$ are assigned to (111), (200), (220), (311) and (222) planes of FCC structure of AgCl crystal [222]. Positions of the peaks are in excellent agreement with JPCDS data. The broad peak centered at $2\theta = 25.5^\circ$ corresponds to amorphous structure of polypyrrole-chitosan composite [223]. No diffraction peak
characteristic of Ag₂O or Ag is observed, which confirms that the component of the core of the nanoparticle is AgCl only. The XRD pattern of the polymer hollow nanospheres is shown in Figure 4.6b. Spectrum b shows a broad band centered at $2\theta = 25.5^\circ$, which is consistent with amorphous structure of PPy-CS [223]. Compared with the XRD pattern of AgCl@PPy-CS, the sharp peaks that correspond to AgCl crystals are absent. This means that AgCl has been completely removed from the nanoparticles.

![XRD patterns](image)

**Figure 4.6** XRD patterns of (a) AgCl@PPy-CS nanoparticles and (b) PPy-CS hollow nanospheres. Reaction conditions are the same as those prepared in Figure 4.2.

### 4.4 Conclusions

A novel one-step sequential method to prepare AgCl@PPy-CS core-shell
nanoparticles with a typical diameter of $50 \pm 5$ nm was reported in this chapter. The novelty of this method lies in that it does not need to prepare AgCl nanoparticles or PPy-CS composite in advance. The formation of core and shell is simple and can be performed sequentially in the same reaction medium. The size of the core and thickness of shell could be controlled by adjusting the reaction parameters. AgCl@PPy-CS nanoparticles may find applications in photography or the development of new catalysts. The AgCl core can further be removed to form PPy-CS hollow nanospheres. These polymeric hollow nanospheres may have applications in drug delivery, cell transplantation and waste removal.

Although the method provided in this chapter can be used to prepare PPy-CS hollow nanospheres in large scale, it still have some limitations. Firstly, it is relative difficult to control the size of the AgCl nanoparticles in a larger range of sizes. The biggest size of AgCl nanoparticles that could be prepared in this method is found to be 60 nm, beyond which, macroscopic precipitate will occur. Secondly, the process to remove the core is conducted in alkali conditions by using NH$_4$OH. This will cause certain aggregation of the hollow nanospheres (see Figure 4.1c). To address these problems, it is necessary to develop better core material that could be prepared in a large range of sizes and better etching reagent that could easily remove the core material without causing aggregation. In the next chapter, we will report the improved strategy for producing core-shell nanoparticles and hollow nanospheres.
Chapter 5
Fabrication of pH-Responsive Polymeric Hollow Nanospheres, Hollow Nanocubes and Hollow Plates
5.1 Introduction

Recently there has been a great deal of interests on the study of polymeric hollow spheres [212]. These hollow spheres can be utilized widely in areas of medicine, pharmaceutics, agricultures, and cosmetics [224]. The vast majority of the applications are associated with the controlled release of encapsulated active ingredients (e.g., drugs, vaccines, antibodies, hormones, pesticides, and fragrances) under well-defined conditions. Many techniques such as layer-by-layer deposition technique [145], in-situ polymerization on template particles [148,225], pH-induced micellization of grafted copolymer [226], and core-free-template strategy [227] have been developed to prepare hollow spheres whose size ranges from ten of nanometers to a few micrometers. It is even possible to prepare hollow structures with different shapes such as hollow cubes [228] or star-like capsules [229].

The techniques mentioned above can only be used to prepare hollow spheres with a specific size range. For example, using layer-by-layer deposition technique, the size of the hollow spheres could be fabricated at sub-micrometer and micrometer scale [230] but not in the nanometer regime. This is because the common template (melamine formaldehyde latex particle) used in the process become less efficient at the nanometer scale. To prepare hollow nanospheres, smaller templates (e.g., gold nanoparticles [231]) or other methods (e.g., in-situ polymerization on template particles [148,225]) have to be used instead. Similarly, it is not feasible to prepare hollow structures with other shapes such as hollow cubes using the common template.
Other template material (e.g., CdCO₃ particle with cubic shape) has been used to prepare polyelectrolyte hollow cubes [228].

It has been reported that the properties of the shell strongly depend on the fabrication process [228a]. Although the composition of the shell is the same, the template used and template removal process also affect the properties of the shell. For example, CaCO₃, CdCO₃, and MnCO₃ crystals were used as templates for the fabrication of polymeric hollow spheres by the layer-by-layer technique [228a]. It was found that the texture of the particle surface determined the morphology of the derived hollow spheres. The surface of the hollow spheres varied from smooth in the case of MnCO₃ and CdCO₃ to very rough and inhomogeneous for CaCO₃. In applications, it is often necessary to evaluate the performance of a series of hollow spheres with different sizes or shapes. The difference in the nature of the shells holds the key to the properties exhibited by the hollow nanostructures. Thus it is desirable to develop a general method that can prepare hollow structures with a wide range of sizes and variable shapes while retaining the same property (such as permeability and morphology) of the shell.

A simple method to realize this is to use a single template material to prepare these hollow structures. It has been demonstrated in Chapter 4 that AgCl can be used as template to produce PPy-CS hollow nanospheres. In this chapter, I further develop this method to fabricate polymeric hollow nanostructures of different shapes (sphere,
cube and plate) and sizes (from 30 nm to 500 nm). Silver bromide, a light-sensitive material widely used in photographic industry [232], was employed as templates to prepare AgBr@Polypyrrole-Chitosan (AgBr@PPy-CS) core-shell nanoparticles. Subsequent removal of AgBr formed PPy-CS hollow nanostructure. Three polymeric hollow nanostructures, PPy-CS hollow nanosphere, PPy-CS hollow nanocube and hollow plate can be fabricated using this template material. The same template material and the same fabrication procedure afford the shell of these hollow structures the similar permeability. Meanwhile, the encapsulated AgBr nanoparticles provide us with a convenient optical probe to measure the permeability of the polymeric shell. The transport behavior of –SCN ions through the shell in response to changes in pH of the medium has been studied. Our long-term goal is to design smart polymeric hollow nanostructures which response to environmental changes. In the present work, I mainly focused on the preparation and characterization of these hollow nanostructures.

5.2 Experimental

5.2.1 Chemicals

Pyrrole (99.9 %), Ferric chloride (FeCl₃, 99%), Silver nitrate (AgNO₃, 99+ %), Calcium bromide (CaBr₂, 99 %), Ammonium thiocyanate (NH₄SCN, 99%) and Chitosan (Mw: 300 kDa, degree of deacetylation: 85 %, determined by FT-IR) were purchased from Sigma-Aldrich. Pyrrole was purified by distillation in vacuum before polymerization. Other reagents were used as received without further purification.
Water purified with cartridges from a Millipore purification system (NANOPure, Barnstead, USA) to a resistivity of 18.0 MΩ·cm was used in the preparation of all samples. Precautions were taken to ensure the cleanliness of the distilled water, reagents and the glass vessels used. The presence of traces of silver might subsequently serve as unwanted nucleation centers.

5.2.2 Preparation of AgBr@PPy-CS core-shell nanoparticles

AgBr nanospheres, nanocubes and plates were prepared according to a well-known method [232] with modifications. At the nucleation phase, the AgBr emulsion was made by a controlled addition of solutions of AgNO₃ and CaBr₂ to a stirred reactor, which contained aqueous chitosan solution at room temperature. AgBr nanoparticles formed at this stage are small nanoparticles. The emulsion was then heated at 60 °C for 1h, in a process known as ripening phase. Small AgBr nanoparticles are transformed to bigger nanocubes or plates. In this process the concentration of bromide ion controls the nanoparticle morphology. Low bromide ion concentrations favor cubic morphologies with (100) bounded surfaces, whereas higher bromide ion concentrations afford the formation of parallel twin planes that engender a tabular morphology with (111) surfaces.

5.2.2.1 AgBr@PPy-CS core-shell nanosphere

The reaction was carried out in double-walled glass vessels under magnetic stirring and nitrogen atmosphere. Cold water was circulated through the outer jacket of the
vessel to maintain a constant temperature. AgNO\(_3\) (0.1 g, 1 equiv.) and CaBr\(_2\) (0.07 g, 1 equiv.) were added simultaneously to 20 mL of chitosan solution (1 wt %, in 0.05 M HNO\(_3\)) to form AgBr emulsion. Pyrrole (0.025 mL) was then introduced to the emulsion followed by FeCl\(_3\) (0.14 g) to initiate the polymerization. The polymerization was conducted at 2 °C for 12 h. The product was purified by dialysis using a membrane bag (Spectrum Medical Industries, Inc. Mw cut-off: 3,500 Da) in 0.05 M HNO\(_3\). Finally, the AgBr@PPy-CS core-shell material was obtained by precipitating with acetone and dry in vacuum at 40 °C for 24 h.

5.2.2.2 AgBr@PPy-CS core-shell nanocube.

AgNO\(_3\) (0.1 g, 1 equiv.) and CaBr\(_2\) (0.07 g, 1 equiv.) were added to 20 mL of chitosan solution (1 wt %, in 0.05 M HNO\(_3\)) to form AgBr emulsion. The emulsion was ripened at 60 °C for an hour. Pyrrole (0.025 mL) was then introduced to the emulsion followed by FeCl\(_3\) (0.14 g) to initiate the polymerization. The polymerization was conducted at 2 °C for 12 h. The reaction mixture was purified by centrifuge at 6,000 rpm to remove small core-shell particles. The precipitate was mainly composed of nanocubes. It was collected and dried for further characterizations.

5.2.2.3 AgBr@PPy-CS core-shell plate.

AgNO\(_3\) (0.1 g, 1 equiv.) and CaBr\(_2\) (0.10 g, 1.2 equiv.) were added to 20 mL of chitosan solution (1 wt %, in 0.05 M HNO\(_3\)) to form AgBr emulsion. The emulsion was then ripened at 60 °C for an hour. Pyrrole (0.025 mL) was then introduced to the
emulsion followed by FeCl$_3$ (0.14 g) to initiate the polymerization. The reaction mixture was purified by centrifuge at 6,000 rpm to remove small core-shell particles. The precipitate was mainly composed of nanoplates. It was collected and dried for further characterizations.

5.2.3 Preparation of PPy-CS hollow nanostructure

0.005 g of AgBr@PPy-CS core-shell material (core-shell nanospheres, core-shell nanocube or core-shell plate) was first dispersed in 20 mL of distilled water by ultrasonication. The NH$_4$SCN solution (0.61 %, 3 mL) was then added to the dispersion. The reaction was continued for 6 h at room temperature. After that, the formed [Ag(SCN)$_2$] ions were removed by dialysis with a membrane bag (Mw cut-off: 3,500 Da) in water. The PPy-CS hollow nanoparticles was obtained by precipitating in acetone and dry in vacuum at 40°C for 24 h.

5.2.4 Characterization

The characterizations of the AgBr@PPy-CS nanocomposite are similar to those of AgCl@PPy-CS nanocomposite which were described in Chapter 4. TEM images of the samples were recorded on a Philips CM10 electron microscope at an accelerating voltage of 100 kV. The nitrogen content of PPy-CS shell was measured using a Perkin-Elmer 240C C, H, N analyzer. The amount of chitosan in PPy-CS shell was calculated on the basis of the difference in C/N ratio of the composite relative to that of pure polypyrrole (3.43) and chitosan (5.49 %, degree of deacetylation: 80 %). FT-
IR spectroscopy studies were carried out on a Bio-Rad Merlin (FTS3000) IR spectrophotometer (30 scans per spectrum at 4 cm\(^{-1}\) resolution). XRD pattern of the samples were recorded on a Siemens D5005 diffractometer equipped with a Cu k\(\alpha\) (1.5405 Å) X-ray source. A Shimadzu (UV1601PC) UV-vis spectrophotometer was used to measure the absorption of the dispersions and the transport rate of -SCN\(^-\) ions through the polymer shell. For the measurement of the transport rate, the absorption data was collected in-situ using the “Time course” mode provided by the software equipped with the spectrophotometer.

5.3 Results and Discussion

5.3.1 Formation of PPy-CS Hollow Nanostructures

The overall procedure for producing PPy-CS hollow nanostructures involves several steps as illustrated in Figure 5.1. The first step is the formation of AgBr nanoparticles using chitosan as the stabilizer. AgBr is chosen as the template because it is not only cheap and readily available, but also it is easy to control the shape of AgBr nanoparticles [232]. Using the method commonly used in the photographic industry, AgBr nanoparticles were prepared with different shape (nanosphere, nanocube and plate) as templates (see Experimental for details). The subsequent step involves the formation of a PPy-CS polymeric shell on each AgBr nanoparticle. Chitosan acts as the steric stabilizer which efficiently prevents the precipitation of PPy [215,233]. An electro-steric stabilization mechanism accounts for the formation of this PPy-CS nanocomposite [161,233] Previous results showed that the PPy-CS shell was a stable,
permeable shell which dispersed very well in aqueous media [234]. Both PPy and chitosan are biocompatible materials [235], which make it easy to find applications in biomedical area. The final step was the removal of AgBr template. This is achieved easily by treating the core-shell nanoparticles with NH₄SCN solution. AgBr core is dissolved by forming silver thiocyanide complexes [236]. The shell keeps the original structure after removing the core.

5.3.2 Morphologies of PPy-CS Hollow Nanostructures

TEM images presented in Figure 5.2 illustrate the formation of the nanostructures
obtained using the above procedure. Figure 5.2a shows the image of AgBr@PPy-CS core-shell nanospheres (core size: 35 ± 3 nm, shell thickness: 15 ± 3 nm). Well defined particles which contained the light contrast PPy-CS shell and the dark contrast AgBr core were readily observed. It was found that pyrrole preferred to polymerize around AgBr nanoparticle to form PPy-CS shell instead of self-polymerize to form PPy-CS nanoparticle. One possible explanation is that the surface of AgBr nanoparticle may have a lower oxidation potential than pyrrole itself [161]. There were also some PPy-CS nanoparticles formed in the solution, but the total amount was very small (≤ 5 %) according to TEM observation. Figure 5.2b shows the image of PPy-CS hollow nanospheres, which were obtained by treating the core-shell nanoparticles with NH₄SCN solution. The image showed strong contrast between the dark ring (PPy-CS shell) and the pale center of the cores. Compared with the contrast of the core in Figure 5a, the contrast of the core in Figure 5.2b become lighter, which was caused by the removal of the AgBr nanoparticle. This means the formation of the hollow structure. Besides, it can be seen that although AgBr had been removed, the dimensional stability of the shell is maintained.

Figure 5.2c is the image of AgBr@PPy-CS core-shell nanocubes using AgBr nanocubes as the template. Core-shell structures were evident due to the light contrast of the shell and dark contrast of the core. The mean edge length of the AgBr nanocubes was in the range of 140 ± 15 nm while the mean thickness of the PPy-CS shell is 18 ± 1 nm. Figure 5.2d shows the image of PPy-CS hollow nanocubes, which

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Figure 5.2 TEM images of (a) AgBr@PPy-CS nanosphere; (b) PPy-CS hollow nanosphere; (c) AgBr@PPy-CS nanocube; (d) PPy-CS hollow nanocube; (e) AgBr@PPy-CS nanoplate; and (f) PPy-CS hollow nanoplate. Reaction condition: 20 mL of chitosan (1 wt%, in 0.05 M of HNO$_3$), $x$ g of AgNO$_3$, $y$ mL of pyrrole, where $x = 0.5$, $y = 0.025$ for (a), $x = 1.0$, $y = 0.025$ for (c), and $x = 1.0$, $y = 0.025$ for (e). For (c), the AgBr emulsion was ripened (heat at 60 °C for 1h) before the polymerization. For (a) and (c), the [Ag]/[Br] molar ratio is 1:1; for (e), the [Ag]/[Br] molar ratio is 1:1.2. The reaction temperature is 2 °C.
were obtained by treating the core-shell nanocubes with NH$_4$SCN solution. The thickness of the shell (20 ± 1 nm) kept unchanged compared with that of the shell before removing the core. At the same time, the shell kept the original cubic structure intact. This means the removal process did not affect the dimensions of the resulting hollow structure. The formation of polymeric hollow microcubes has been reported by Antipov [228a] and Silvano [228b]. They prepared polyelectrolyte hollow cubes with mean edge length at 3 μm using the lay-by-layer deposition technique. CdCO$_3$ cubic microparticles were used as the template. In this work, we successfully reduced the size of the polymeric hollow cubes to a smaller scale (less than 200 nm).

Figure 5.2e is the TEM image of AgBr@PPy-CS hollow plate using AgBr plate as the template. These core-shell particles have the irregular tabular structure. The mean equivalent circular diameter of the AgBr plates was in the range of 450 ± 20 nm while the mean thickness of the PPy-CS shell was about 20 ± 1 nm. The image of the PPy-CS hollow plate is presented in Figure 5.2f. It clearly shows the formation of hollow structure. Compared with the sizes of hollow nanosphere and hollow nanocube, the size of hollow plate is much bigger. Our method not only controls the shape of the hollow structure (sphere, cube and plate), but also the size of the hollow structure (from nanometer to sub-micrometer). The same template material was used in all of the preparation process.

The dimensions (e.g. core size and shell thickness) of the hollow nanostructure can be
controlled by adjusting reaction parameters. The size of AgBr nanoparticles was affected by the concentration AgBr and the concentration of chitosan in the reaction media. The thickness of the PPy-CS shell was dependent on the concentration of pyrrole, the concentration of chitosan, and the polymerization time. Figure 5.3a shows the image of PPy-CS hollow nanosphere with the smallest core (core size: 12 ± 2 nm, shell thickness: 10 ± 1 nm) that could be prepared. Figure 5.3b shows the image of PPy-CS hollow nanocubes with the smaller size (edge length of cube: 100 ± 10 nm, shell thickness: 24 ± 2 nm) compared with that Figure 5.2d. Figure 5.3c shows the image of PPy-CS hollow nanocubes with thicker shell (edge length of cube: 145 ± 15 nm, shell thickness: 30 ± 3 nm).

Figure 5.4 show the average size changes of the core of PPy-CS hollow nanospheres and hollow nanocubes as a function of the feeding amount of AgBr. If other conditions are fixed, the average core diameter of PPy-CS hollow nanospheres was tunable from 12 nm to 50 nm by changing the amount of AgBr from 1.6 to 6.4 mmol (Figure 5.4a). For hollow nanocubes, the average edge length was tunable from 70 nm to 135 nm by changing the amount of AgBr from 2.7 to 8.0 mmol (Figure 5.4b). For hollow plates, the mean equivalent circular diameter was tunable in the range from 450 nm to 600 nm. The reaction temperature should be kept at about 2 °C in order to obtain uniform core-shell nanoparticles. As higher temperatures, pyrrole would likely to self-polymerize to form PPy-CS nanoparticles instead of forming a shell around AgBr.
Figure 5.3 TEM images of PPy-CS hollow nanostructures prepared at different reaction conditions: 20 mL of Chitosan (1 wt%, in 0.05 M of HNO₃), x g of AgNO₃, y mL of pyrrole, where x = 0.3, y = 0.025 for (a), x = 0.7, y = 0.025 for (b), and x = 1.0, y = 0.05 for (c). The reaction temperature is 2 °C. For (b) and (c), the AgBr emulsion was ripened (heat at 60 °C for 1h) before polymerization of pyrrole.
Figure 5.4 (a) Diameter of the core of PPy-CS hollow nanospheres with increasing AgBr amount (Other conditions: 20 mL of 1 wt % chitosan; 0.025 mL of pyrrole; the reaction temperature was 2 °C; the AgBr emulsion was used without the ripening process; the shell thickness the hollow nanospheres were between 10-13 nm). (b) The average edge length of PPy-CS hollow nanocubes prepared with the increase of AgBr amount (Other conditions: 20 mL of 1 wt % chitosan; 0.025 mL of pyrrole; the reaction temperature was 2 °C; the AgBr emulsion was heated at 60 °C for 1h before polymerization and the [Ag]/[Br] molar ratio is 1:1; the shell thickness the hollow nanocubes were between 18-24 nm)

5.3.3 Structural Characterization

The chemical structure of the PPy-CS shell was characterized by FT-IR. Figure 5.5 is
the FT-IR spectra of the polypyrrole powder (synthesized by precipitation polymerization in the absence of chitosan and AgBr), chitosan, and PPy-CS hollow nanocubes. For PPy (spectrum a), the spectrum is in good agreement with literature [204]. A typical peak is observed at 1537 cm\(^{-1}\). This is due to the \(\nu\) ring vibration of pyrrole. In the case of chitosan (spectrum c), the main absorption peak at 1655 cm\(^{-1}\) is assigned to the carbonyl stretching of secondary amides (amide I band) and the peak at 1590 cm\(^{-1}\) is assigned to the N–H bending vibration of primary amines [188]. The spectrum of PPy-CS shell (spectrum b) comprised the main peaks of both chitosan and PPy. A number of characteristic peaks of these two polymers are observed, particularly in the 1000–1700 cm\(^{-1}\) region. This clearly shows that the PPy-CS shell is a hybrid material. For PPy-CS hollow nanospheres and hollow plates, the FT-IR spectra are the same as that of hollow nanocube.
Figure 5.5 FT-IR spectra of (a) chitosan, (b) PPy-CS hollow nanocubes, and (c) polypyrrole.

The similar elemental analysis method used in Chapter 3 was employed to determine the composition of the PPy-CS shell. For PPy-CS nanocube, the shell contains 89.6 % of chitosan and 10.4 % of PPy. In the case of PPy-CS hollow nanospheres (87.2 % of Chitosan) and hollow plate (88.3 % of chitosan), almost the same percentage of chitosan was obtained. The shell of the three hollow nanostructures has nearly the same composition. All of the core-shell nanoparticles and hollow nanostructures disperse very well in acidic aqueous media and start to aggregate at pH value larger than 7. This is due to the solubility of CS under these conditions [235b].

UV-vis absorption spectra of AgBr nanocubes, AgBr@PPy-CS core-shell nanocubes and PPy-CS hollow nanocubes are shown in Figure 5.6. Spectrum a is a typical UV-vis absorption spectrum of AgBr emulsion. The peak at 310 nm is assigned to the
direct excitation absorption of AgBr NPs. Its position, corresponding to an energy gap of about 4.0 eV is blue-shifted with respect to that of bulk AgBr (2.7 eV, 475 nm). This behavior is a well-known quantum size effect affecting semiconductor nanoparticles and is itself an evidence that AgBr is nanosized. The second and more intense broad absorption band centered at 275 nm is assigned to the spin-orbit interaction splitting of the direct exciton absorption of AgBr nanoparticles [155,220,237]. Since experimental and theoretical investigations showed that $(\text{AgBr})_n$ with $n \leq 4$ do not show split excitonic bands, this peculiar absorption feature suggests that nanoparticles are composed by at least four AgBr molecular units.

**Figure 5.6** UV-vis absorption spectra of (a) AgBr nanocube; (b) AgBr@PPy-CS core-shell nanocube; and (c) PPy-CS hollow nanocube. The reaction conditions are the same as those of nanocubes prepared in Figure 5.2.
Spectrum b was taken at the end of the polymerization. There is a high-intensity tail center at about 800 nm which extends into the near-IR region. This can be explained as a characteristic of an oxidized PPy [235]. The absorption band that belongs to the \( \pi-\pi^* \) transition of PPy chain (about 440 nm) [98] is not clear because this band overlaps with the absorption bands that is attributed to AgBr. One might expect certain shifts in the absorption bands of AgBr following polymerization on the basis of the effective medium theories [239]. But our results show that AgBr nanoparticles together with PPy-CS have little effect on the optical properties of the AgBr nanoparticles. Similar results had been reported on other inorganic / organic core-shell systems such as Au@PPy [240a] and Au@Poly(N-isopropyl acrylamide) [240b] core-shell nanoparticles.

Spectrum c is the UV-vis absorption spectrum of PPy-CS hollow nanocubes. It was found that after treating AgBr@PPy-CS with NH\(_4\)SCN solution, the two bands that related to the presence of AgBr nanoparticle disappeared. A broad band centered at 440 nm together with a high-intensity tail centered at about 800 nm confirms the presence of PPy [98,238]. This shows that NH\(_4\)SCN can efficiently remove AgBr from the interior of the core-shell nanoparticles. Considering the results of both FT-IR and UV-vis spectra, it is clear that the shell is a hybrid material which contains both polypryyole and chitosan. For AgBr particles with different shapes, there is little difference between the UV-vis absorption characteristics of these core-shell particles (see Figure 5.7).
Figure 5.7 UV-vis absorption spectra of AgBr@PPy-CS core-shell nanosphere, PPy-CS hollow nanosphere (1), and AgBr@PPy-CS core-shell nanoplate, PPy-CS hollow nanoplate (2). The reaction conditions are given in experimental section.

The crystalline properties of the AgBr@PPy-CS core-shell nanocubes and PPy-CS hollow nanocubes was studied by XRD (Figure 5.8). The XRD spectrum of AgBr@PPy-CS (spectrum a) shows several sharp diffraction peaks together with a broad peak. The sharp peaks at $2\theta = 30.9^\circ$, $44.5^\circ$, $55.1^\circ$, and $64.5^\circ$ are assigned to
(200), (220), (222) and (400) planes of FCC structure of AgBr crystal [211]. Positions of the peaks are in excellent agreement with JPCDS data (File No.: 00-001-0950). The broad peak centered at $2\theta = 26.5^\circ$ corresponds to amorphous structure of PPy-CS composite [223]. No diffraction peak characteristic of AgCl or Ag is observed, which confirms that the component of the core is AgBr. The XRD pattern of the polymer hollow nanocubes is shown in Spectrum b. There is only a broad band centered at $2\theta = 26.5^\circ$, which is consistent with amorphous structure of PPy-CS. The sharp peaks that correspond to AgBr crystals are absent. This further confirms that AgBr has been completely removed.

![XRD patterns of (a) AgBr@PPy-CS nanocubes, and (b) PPy-CS hollow nanocube. Reaction conditions are the same as those of nanocubes prepared in Figure 5.2.](image)

**Figure 5.8** XRD patterns of (a) AgBr@PPy-CS nanocubes, and (b) PPy-CS hollow nanocube. Reaction conditions are the same as those of nanocubes prepared in Figure 5.2.
5.3.4 Permeability of the Shell

A unique feature of the PPy-CS hollow nanostructures is that the permeability of the shell is pH-responsive. The encapsulated AgBr nanoparticles provide us with a convenient probe to measure the permeability. To study this, an etching solution containing NH$_4$SCN (0.61 wt %) was added to a series of dispersions which contain AgBr@PPy-CS core-shell nanocubes at different pH values (2.2, 3.3, and 6.4). The UV-vis absorption band of AgBr centered at 310 nm was monitored over time to detect the transport rate of -SCN$^-$ ions through the PPy-CS shell. The intensity of this absorption band decreased as –SCN$^-$ ions come through the shell to dissolve AgBr. Figure 5.9 is the transport profiles of -SCN$^-$ ions through the PPy-CS shell. It showed that decreasing the pH caused the transport rate to slow down. The fastest transport rate appeared at pH = 6.4.
Figure 5.9 UV absorbance of the AgBr@PPy-CS nanocube (at 310 nm) vs etching time at different pH values (2.2, 3.3, and 6.4). PPy-CS nanocubes used are the same as those of nanocubes prepared in Figure 5.2.

These results could be rationalized by considering the cationic characteristics of PPy-CS shell since both chitosan and polypyrrole are cationic polymers. For PPy-CS hollow nanocube, the main component of the shell is chitosan (89.6 %). Thus the shell behaves more like chitosan. The structure of a representative poly(aminosaccharide) segment of chitosan is given in Figure 5.1 (see page 113). Chitosan is a weak alkaline with a $pK_a$ of 6.5 [241]. When the pH of the medium is lower than 6.5, chitosan carries a positive charge along its backbone. Decreasing the pH causes an increase of $-\text{NH}_3^+$ ions on chitosan molecules [242]. This brings strong electrostatic attractive force between the positive $-\text{NH}_3^+$ ion and the negative $-\text{SCN}^-$ ion. It would retard the
transportation of -SCN’ ion through the shell. This accords with the fact that the transport rate at pH = 3.3 was faster than that of pH = 2.2. As the pH value of the medium increases, chitosan will be less charged. The electrostatic attraction force becomes weaker which makes -SCN’ ion easier to go through the shell. This explains why the transport rate at pH = 6.4 is faster than those of pH = 2.2 and 3.3. Thus it is able to control the permeability of the PPy-CS shell by simply adjusting the pH of the medium. The permeability of other two hollow structures in the same conditions as that of hollow nanocubes were also measured. All of the three hollow structures have the same permeabilities. This means the shape of the template does not affect the properties of the hollow structures formed in the later stage.

5.4 Conclusions

In this chapter a facile method for the fabrication of PPy-CS hollow nanostructures of different sizes and shapes by using silver bromide as a single template material is described. This method is easy to carry out and all the materials used are low cost and readily available. Control over particle dimensions (e.g. core shape, core diameter and shell thickness) can be achieved easily. The permeability of polymeric shell can be controlled by the pH of the medium. The fastest transport rate of the -SCN’ ions through PPy-CS shell, which measures the permeability of the shell, was observed at weak acidic condition (pH = 6.4). These pH-responsive hollow nanostructures may find applications as drug carriers or as nanoreactors.
In the next chapter, we attempt to increase the functionality of the PPy-CS hollow nanospheres. Silver nanoparticles with different sizes will be introduced into the interior of the hollow nanospheres. The encapsulated silver nanoparticle may act as an optical probe to monitor the chemical to come in or go out of the interior of the hollow nanospheres.
Chapter 6
Preparation of PPy-CS Hollow Nanospheres Containing Silver Cores with Different Sizes
6.1 Introduction

Recently polymeric hollow nanospheres have attracted considerable research attention due to their large variety of applications in chemistry, biotechnology and materials science [9g,109,135b,212,243-246]. The advantages of polymeric hollow nanosphere include its encapsulation property, controllable permeability and surface functionality [133]. Many methods [145,213,226,227] have been developed to prepare these hollow nanostructures.

An important aspect about hollow nanospheres is that their functionalization could be achieved by encapsulating guest species, which would endow them with diverse properties. Hollow nanospheres functionalized with movable inorganic nanoparticle cores have been explored as novel nanostructures by several groups [154,247]. Nanoparticles such as tin, gold or silica could be incorporated into the interior of hollow nanospheres. Novel properties can be introduced to the hollow nanospheres by this method. Lee et al. [247] prepared tin-encapsulated hollow carbon spheres as an anode material in lithium secondary batteries. The encapsulation of Sn nanoparticles with hollow carbon spheres improved the cycle performance of metal Sn as an anode material. Kamata et al. [154a] reported that the incorporation of Au nanoparticle as a movable core into a polymeric hollow sphere could provide an optical probe for monitoring the diffusion of chemical reagent into and out of the shell. Skirtach et al [248] showed that under laser illumination, the capsules containing Ag nanoparticles could be deformed or cut, thus providing a venue for remote release of encapsulated
The usual method for the preparation of hollow nanospheres with movable cores is based on a template-assisted approach [154b,154c]. Firstly, the core (e.g., Au nanoparticle) particle is prepared and then it is coated with a polymeric shell. The shell is further functionalized with certain reactive groups to grow another polymer layer. By removing the middle polymer layer using a solvent or calcination, hollow spheres with movable cores are formed. This method often needs complicated organic synthetic technique to grow another polymer layer. It is also difficult to control the size of the core nanoparticle.

In this chapter, an easy photoreduction method will be described for producing a novel core-shell nanostructure: Polypyrrole-Chitosan hollow nanospheres containing movable Ag nanoparticles (Ag@PPy-CS). Compared with the usual approach, this method does not require the preparation of two polymer layers. In this method, hollow nanospheres were prepared first before the introduction of the core material. The formation of Ag core is achieved by an ultraviolet irradiation technique. No reduction reagent is needed because chitosan (one component of the PPy-CS hollow sphere) acts as the reducing reagent. The size of the Ag nanoparticles can be controlled easily by varying the concentration of AgNO3, which enables the optical property (surface plasmon resonance) of the core-shell nanostructure to be tuned. This method affords a convenient platform for building novel core-shell nanostructures with controllable
properties.

6.2 Experimental Section

6.2.1 Chemicals

Pyrrole (99.9 %), ferric chloride (FeCl₃, 99%), silver nitrate (AgNO₃, 99+ %), calcium bromide (CaBr₂, 99 %), ammonium thiocyanate (NH₄SCN, 99%) and chitosan (Mw: 300kDa, degree of deacetylation: 80 %, determined by FT-IR) were purchased from Sigma-Aldrich. Pyrrole was purified by distillation in vacuum before polymerization. Other reagents were used as received without further purification. Water purified with cartridges from a Millipore purification system (NANOPure, Barnstead, USA) to a resistivity of 18.0 MΩ·cm was used in the preparation of all samples. Precautions were taken to ensure the cleanliness of the distilled water, reagents and the glass vessels used.

6.2.2 Preparation of PPy-CS hollow nanospheres

AgBr nanospheres were prepared first according to a well-known method [232] with necessary modifications. AgNO₃ (0.1 g, 1 equiv.) and CaBr₂ (0.07g, 1 equiv.) were added simultaneously to 20 ml of chitosan solution (1 wt %, in 0.05 M HNO₃) to form AgBr emulsion. Pyrrole (0.025 mL) was then introduced to the emulsion followed by FeCl₃ (0.14g) to initiate the polymerization. The polymerization was conducted at 2 °C for 12 h. The product was purified by dialysis using a membrane bag (Spectrum Medical Industries, Inc. Mw cut-off: 3,500 Da) in 0.05 M HNO₃. Finally, the
AgBr@PPy-CS core-shell material was obtained by precipitating with acetone and dry in vacuum at 40 °C for 24 h.

0.005 g of AgBr@PPy-CS core-shell nanoparticles was first dispersed in 20 ml of distilled water by ultrasonication. The NH₄SCN solution (0.61%, 3 ml) was then added to the dispersion. The reaction was continued for 6 h at room temperature. After that, the formed [Ag(SCN)₂]⁻ ions were removed by dialysis with a membrane bag (Mw cut-off: 3,500 Da) in water. It should be noted that Fe²⁺ ions must be removed completely using this process. Otherwise they will directly react with Ag⁺ ions to form metallic Ag in the next step. The PPy-CS hollow nanoparticles was obtained by precipitating in acetone and dry in vacuum at 40 °C for 24 h.

6.2.3 Preparation of Ag@PPy-CS core-shell nanoparticles

0.005 g of PPy-CS hollow nanosphere was first dispersed in 5 ml of AgNO₃ solution (Five different AgNO₃ solutions were used in a series of experiments. The concentrations are 3.8 × 10⁻³ M, 5.7 × 10⁻³ M, 7.6 × 10⁻³ M, 9.5 × 10⁻³ and 1.1 × 10⁻² M, respectively.) The pH of the dispersion was adjusted to 6.4 using diluted NaOH solution (0.5 M). The pH of the dispersion was then adjusted to 2.2 after it was stirred for 1 h. The unwanted Ag⁺ ions outside the hollow spheres were then removed by dialysis with a membrane bag (Mw cut-off: 3,500 Da) in water. After that, the mixture was irradiated using a column like, low-pressure mercury lamp (Vilber Lourmat, France, 40W, λ = 365 nm) for 3 h to reduced the Ag compound to metallic Ag.
6.2.4 Characterization

The characterizations of the Ag@PPy-CS nanostructures are similar to those of AgBr@PPy-CS nanocomposite which were described in Chapter 5. TEM images of the samples were recorded on a Philips CM10 electron microscope at an accelerating voltage of 100 kV. The optical absorption spectrum of the dispersions containing PPy-CS nanospheres or Ag@PPy-CS core-shell nanoparticles was conducted on a Shimadzu (UV1601PC) UV-vis spectrophotometer. XRD patterns of the samples were recorded on a Siemens D5005 diffractometer equipped with a Cu kα (1.5405 Å) X-ray source. The powders were mounted by double-sided adhesive tape on plastic sample holders.

6.3 Results & Discussion

The schematic procedure to produce Ag@PPy-CS nanostructure contains three main steps which are illustrated in Figure 6.1. Our approach starts from Polypyrrole-chitosan (PPy-CS) hollow nanosphere, which is prepared according to the method described in Chapter 5. In the first step, PPy-CS hollow nanospheres was dispersed in AgNO₃ solution for some time to allow Ag⁺ ions to come into the interior of the hollow nanosphere. The pH of the dispersion is maintained at 6.4, at which the PPy-CS shell shows the best permeability for ions (See Chapter 5). The second step involves the removal of the unwanted Ag⁺ ions outside the hollow spheres by dialysis using a membrane bag (Mw cut off: 3,500). The pH of the dispersion is lowered to 2.2 before dialysis. At this pH, the PPy-CS shell shows the least permeability. The last
The step is the formation of Ag nanoparticle inside the PPy-CS hollow nanosphere by ultraviolet irradiation using a low pressure mercury lamp ($\lambda = 365$ nm). Ag$^+$ ions are reduced to metallic Ag by the hydroxymethyl radicals generated by the photolysis of chitosan [249-250]. In this work, AgBr is used as a template to prepare PPy-CS hollow spheres. In fact, I have tried to produce Ag nanoparticles directly from the reduction of AgBr by NaBH$_4$ but it was unsuccessful as most of the Ag nanoparticles formed outside the hollow spheres. Moreover, direct conversion of AgBr nanoparticles to Ag nanoparticles by UV irradiation was attempted but it did not work.

![Figure 6.1](image)

**Figure 6.1** Schematic procedure for the preparation of PPy-CS hollow nanospheres containing movable Ag cores (Ag@PPy-CS).

Figure 6.2 shows the TEM images of PPy-CS hollow spheres and Ag@PPy-CS core-
shell nanoparticles. Figure 6.2a is a typical TEM image of PPy-CS hollow nanospheres. The image shows strong contrast between the dark ring and the pale center of the spherical particles, which indicates the formation of hollow structures. Most of the hollow nanospheres present the spherical shape while some have the irregular hollow shape. The difference between the shapes of hollow nanospheres does not affect the photoreduction process. The outer diameter of the hollow nanosphere is $100 \pm 15 \text{ nm}$ while the inner diameter is about $62 \pm 8 \text{ nm}$. Figure 6.2b is a TEM image of Ag@PPy-CS core-shell nanoparticles synthesized using the above approach ($\text{AgNO}_3$ concentration: $3.8 \times 10^{-3} \text{ M}$). It can be seen that each Ag nanoparticle is located in the interior of each PPy-CS hollow sphere. Only a very small amount of Ag nanoparticles are observed outside the PPy-CS hollow nanospheres (less than 5 %). The size of the Ag nanoparticles is about $20 \pm 4 \text{ nm}$. The spherical shape of the hollow nanosphere is maintained after the incorporation of Ag nanoparticle. It is observed that most of the Ag nanoparticles are not located in the center of these hollow nanospheres. The Ag core tends to stick to the wall as a result of the attractive force between their surfaces. Similar phenomena have been reported by other groups [154b,154c].
Figure 6.2 TEM images of (a) PPy-CS hollow nanospheres; (b) Ag@PPy-CS core-shell nanoparticles (size of Ag: 20 ± 4 nm); (c) Ag@PPy-CS core-shell nanoparticles (size of Ag: 36 ± 4 nm); (d) Ag@PPy-CS core-shell nanoparticles (size of Ag: 50 ± 6 nm); and (e) Ag@PPy-CS core-shell nanoparticles (size of Ag: 60 ± 7 nm). From (b) to (e), the concentration of AgNO$_3$ solutions are 3.8×10$^{-3}$ M, 5.7×10$^{-3}$ M, 7.6×10$^{-3}$ M, and 9.5×10$^{-3}$ M, respectively.
One advantage of the method presented in this chapter is that the size of the core nanoparticles could be easily controlled. By increasing the concentration of AgNO₃, the size of Ag nanoparticles is increased accordingly (Figure 6.2b - Figure 6.2e). Figure 6.2c shows the TEM image of Ag@PPy-CS core-shell nanoparticles with Ag size about 36 ± 4 nm. For Figure 2d, the size of Ag nanoparticle has increased to 50 ± 6 nm. Nearly half of the interior of the hollow nanosphere is occupied by Ag nanoparticle. Further increasing the size of Ag nanoparticle (60 ± 7 nm) caused filling of nearly 90 % of the interior of the hollow nanosphere. The effect of the concentration of AgNO₃ on the size of Ag nanoparticles formed in the interior of PPy-CS hollow nanospheres is plotted in Figure 6.3. The size of Ag nanoparticles increased with increasing the amount of AgNO₃ in the reaction medium.
Figure 6.3 Effect of the concentration of AgNO$_3$ on the size of Ag nanoparticles formed in the interior of PPy-CS hollow nanospheres. (The outer diameter of the hollow nanosphere is 100 ± 15 nm while the inner diameter is about 62 ± 8 nm)

Aqueous solution of Ag$^+$ ions in chitosan has been found to generate silver nanoparticles in the presence of UV-irradiation. It was seen that when the mixture was kept in the dark, chitosan solution failed to produce any silver particle even after a couple of days. Again, in water and PPy media, Ag$^+$ ion did not exhibit any color after 2 h of UV-irradiation. Based on these observations, the proposed formation mechanism of Ag nanoparticles within the hollow nanospheres can be best explained in term of a photoreduction process [251-252]. The Ag$^+$ ion is reduced to metallic Ag by the hydroxymethyl radicals generated from the photolysis of chitosan [249-250]. Here chitosan acts as the reducing agent. The primary hydroxyl group of chitosan is oxidized to the carboxylate group. Primarily, the nuclei are formed with a
homogeneous distribution throughout the solution. They tend to aggregate to form bigger particles and/or the remaining ions in the bulk get absorbed onto the surface of already formed particles where successive reduction takes place.

It is well-known that nanosized metal nanoparticles usually exhibit strong surface plasmon resonances [253-254], which is due to the interactions with the external electromagnetic field induced by light. For Ag nanoparticles, there is a surface plasmon absorption at about 400 - 450 nm, the position of which is dependent on factors such as particle size, shape, as well as dielectric properties of the surrounding media [254]. Figure 6.4 shows the UV-vis absorption spectra of PPy-CS hollow nanosphere and Ag@PPy-CS core-shell nanoparticles with different sizes of Ag. Figure 6.4a is the UV-vis absorption spectrum of PPy-CS nanosphere. A broad band centered at 440 nm together with a high intensity broad band in the range of 600 - 1100 nm confirms the presence of PPy, which is in agreement with the previous report [234]. The spectra from Figure 6.4b to Figure 6.4e show the UV-vis absorption spectra of Ag@PPy-CS core-shell nanoparticles with increased size of Ag. A strong surface plasmon absorption located at in range of 400 to 460 nm appears at all of the spectra. As the size of Ag nanoparticle increases, the position of the plasmon absorption of Ag shifts from 399.5 nm to 455 nm (Figure 6.3b - Figure 6.3e). This observation is consistent with the predictions based on the Mie scattering theory [5b,236,253]. Due to the strong plasmon absorption of Ag nanoparticles, the absorption peaks arising from the PPy-CS polymer shell are not observed in the
absorption spectra of Ag@PPy-CS core-shell nanoparticles.

Figure 6.4 UV-vis absorption spectra of (a) PPy-CS hollow nanospheres; (b) Ag@PPy-CS core-shell nanoparticles (size of Ag: 20 ± 4 nm); (c) Ag@PPy-CS core-shell nanoparticles (size of Ag: 36 ± 4 nm; (d) Ag@PPy-CS core-shell nanoparticles (size of Ag: 50 ± 6 nm); (e) Ag@PPy-CS core-shell nanoparticles (size of Ag: 60 ± 7 nm).

The crystalline structures of the PPy-CS hollow nanosphere and Ag@PPy-CS core-shell nanosphere are analyzed using X-ray diffraction (Figure 6.5). The XRD pattern of the PPy-CS hollow nanosphere (spectrum a) shows that there is a broad band centered at $2\theta = 26.5^\circ$, which is consistent with the amorphous structure of PPy-CS [234]. The XRD spectrum of Ag@PPy-CS core-shell nanoparticle (size of Ag: 20 ± 4 nm) (spectrum b) shows several sharp diffraction peaks in addition to the broad peak related to PPy-CS. The sharp peaks located at $2\theta = 38.2^\circ, 44.3^\circ, 64.5^\circ$ and $77.4^\circ$
are assigned to (111), (200), (220) and (311) planes of the cubic structure of metallic Ag. These data are in excellent agreement with the JPCDS data (File No.: PDF# 00-001-1164). No diffraction peaks that correspond to silver halide or silver oxide are observed, which confirms that component of the core is metallic Ag.

![XRD patterns](image)

**Figure 6.5** XRD patterns of (a) PPy-CS hollow nanospheres; and (b) Ag@PPy-CS core-shell nanoparticles (size of Ag: 20 ± 4 nm).

### 6.4 Conclusions

In this chapter a simple but efficient photoreduction method is presented for the synthesis of a novel nanostructure: Ag@PPy-CS core-shell nanoparticle with movable Ag core. This method has the following two characteristics: (i) core nanoparticles are formed only after the formation of the hollow spheres and (ii) formation of Ag
nanoparticles is a simple one-step photoreduction process. No additional reduction reagent is needed. Although only silver is demonstrated in this work, other inorganic materials (*e.g.* Au, CdS, or TiO$_2$) can also be incorporated into the interior of the hollow nanospheres. The surface plasmon absorption of Ag@PPy-CS core-shell nanoparticle could be tuned in the range of 399.5 - 455 nm by simply changing the size of Ag nanoparticles. This novel core-shell nanostructure may find application as a new drug delivery system.
Chapter 7

Conclusions and Outlook
7.1 Conclusions

The purpose of this work is to develop new methods to prepare hybrid nanostructured materials and to explore their properties related to the structures. This work focuses on three nanostructures, functionalized nanoparticles, polymeric hollow nanoparticles and core-shell nanoparticles.

In the first part of this thesis (Chapter 2 & 3), two surface-functionalized conducting nanocomposites, PANI-CS and PPy-CS nanoparticles were prepared using the dispersion polymerization technique, respectively. Chitosan, a natural biocompatible material, was developed as the steric stabilizer to prevent the aggregation of PANI and PPy. Both PANI-CS and PPy-CS nanoparticles can be dispersed readily in acidic aqueous media (pH < 6), which is due to the solubility of chitosan. XPS study shows that amine groups of chitosan are present on the surface of both PANI-CS and PPy-CS nanoparticles, which is confirmed by XPS study. Zeta potential studies show that both PANI-CS and PPy-CS nanoparticles carry positive charges, which is attributable to the presence of chitosan on their surfaces. PPy-CS nanoparticles prepared in this work have a regular spherical shape while PANI-CS nanoparticles have a non-spherical shape, which may be due to the different formation rate of these two nanoparticles. The chemical structure of PANI-CS and PPy-CS are extensively characterized by FT-IR and UV-vis. TG studies show that there existed certain interaction between PANI and the chitosan. This interaction increases the decomposition temperature of the PANI main chain in PANI-CS nanocomposite substantially by 200 degrees as compared with that of PANI.
In the second part of this thesis (Chapter 4 & 5), a facile template-assisted method was developed for the preparation of silver halide@PPy-CS core shell nanoparticles and subsequently PPy-CS hollow nanostructures. AgCl and AgBr were developed for the first time as templates for the nucleation and growth of the PPy. Control over particle dimensions (e.g. core shape, core diameter and shell thickness) can be achieved easily. Polymeric hollow nanospheres, hollow nanocubes and hollow plate were prepared using AgBr template with the corresponding shapes. This template-assisted method is easy to manipulate and all materials used are easily available and inexpensive. These advantages make the large scale production of these hollow structures feasible. These hollow nanostructures were extensively characterized. FT-IR studies confirm that the PPy-CS shell is composed of chitosan and PPy. UV-vis spectra show that both AgCl@PPy-CS and AgBr@PPy-CS core-shell particles have absorption peaks in the range of 250 – 350nm, which indicate the presence of nanometer-sized particles. XRD studies confirm that AgCl or AgBr particles were present and served as templates during the preparation of the hollow structures. In addition, the permeability of the PPy-CS shell was also studied by UV-vis absorption method. The results show that the permeability of polymeric shell can be controlled by the pH of the medium. The fastest transport rates of the ions through PPy-CS shell was observed at weak acidic conditions (pH = 6.4).

In the last part of this work (Chapter 6), a novel photoreduction method was developed for the fabrication of PPy-CS hollow nanospheres with movable Ag nanoparticles inside (Ag@PPy-CS). The novelty of this method is that, unlike other reported techniques, polymeric hollow nanosphere is prepared in advance before the formation of the core nanoparticles. This makes it easier to control the size of the core
nanoparticle and to introduce different materials into the interior of the hollow nanospheres. Ag nanoparticles were formed by ultraviolet irradiation of AgNO$_3$ in the interior of PPy-CS hollow nanospheres, which was a simple one-step photoreduction process. TEM images confirm the formation of core-shell nanostructure. XRD results show that the component of the core was metallic Ag, not AgBr or Ag$_2$O. UV-vis studies show that the surface plasmon absorption of Ag@PPy-CS core-shell nanoparticle could be tuned in the range of 399.5 - 455 nm by simply changing the size of Ag nanoparticles (from 20 to 60 nm).

7.2 Outlook

Chitosan, the steric stabilizer developed in this work can be used to stabilize other polymers such as polystyrene and poly(acrylic acid). Using the well-developed dispersion polymerization technique, it is possible to prepare other water-dispersible functional nanoparticles such as polystyrene-chitosan and poly(acrylic acid)-chitosan nanoparticles. The PANI-CS and PPy-CS nanoparticles developed in this work may find potential applications in biomedical science. They can be used as carriers in controlled drug delivery or be used as “marker” particles in immunodiagnostic assays. The PANI-CS and PPy-CS nanoparticles prepared in this work dispersed very well in acidic aqueous media. The functionality of the nanoparticles comes from the amino groups on their surfaces. They can be used to react with other materials or to interact with other molecules via the hydrogen bond. However, in some cases, after reacting or interacting with other materials, it was found that the nanoparticles lost their solubility in water. This may be due to change of the configuration of amine groups after the reaction. The solubility of these nanoparticles needs to be improved in future studies.
The synthetic method developed in the second part of this work can prepare PPy-CS hollow nanostructures with different sizes and shapes. It was found that if the size of the hollow nanostructure become very big (larger than 300 nm), the hollow structure would be compressed and thus the shell was destroyed. The shell cannot sustain its original structure. This may be caused by the vacuum condition (< $10^{-5}$ torr) used by the TEM observation or by the weak mechanical stability of the polymeric shell. To confirm it, other characterization tools which do not need vacuum (such as atomic force microscopy or dynamic light scattering) should provide more reliable results. The pH-responsive hollow nanostructures developed in this work may find applications in the protection, delivery, storage of chemicals with unstable properties or be used as nanoreactors. The next immediate step would be the incorporation of some chemicals into the hollow nanospheres and study their release behavior under external changes. The release properties of chemicals which response to the change in external stimulation (e.g. pH, ion strength, temperature) will be of high interest.

The Ag@PPy-CS core-shell nanospheres developed in Chapter 6 may find applications as novel drug delivery devices such as smart laser-responsive carrier systems. The presence of Ag nanoparticles provides an efficient light-absorption component for this purpose. It is well known that the surface plasmon resonance of Ag nanoparticles is very sensitive to the changes in environment media. The presence of Ag nanoparticles would provide a convenient probe for detecting the diffusion of chemicals in the hollow nanospheres. The photoreduction method developed in this work can be used to introduce other light-sensitive materials into the interior of the PPy-CS to construct novel core-shell nanostructures such as Au@PPy-CS and TiO$_2$@PPy-CS. It is also desirable to incorporate Ag particles with other shapes (e.g.
rod, triangulate and cube) into the interior of PPy-CS hollow nanospheres. Since the surface plasmon resonance of Ag nanorods, nanotriangulate and nanocube are different from those of Ag nanospheres, the incorporation of these particles may provide additional optical information in their application as probes.
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