

Facile fabrication of polymer and carbon nanocapsules using polypyrrole core/shell nanomaterials†

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Core/shell nanomaterials composed of only polypyrroles (PPys) were fabricated by microemulsion polymerization using two oxidants with different chemical oxidation potentials, and used as a precursor for the fabrication of PPy and carbon nanocapsules.

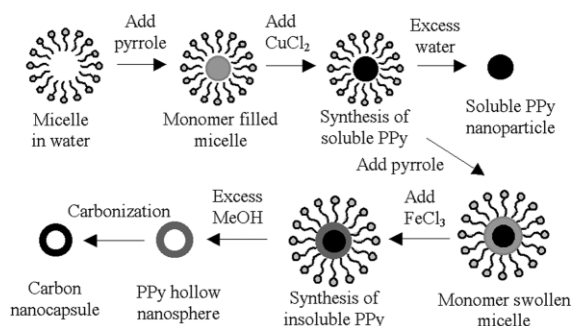
Hollow nanospheres have been attracting intense interest because of their diverse potential applications such as in drug delivery,¹ heterogeneous catalysis,² nanostructured composites,³ dye encapsulation,⁴ contaminated waste removal,⁵ and the protection of enzymes and proteins.⁶ Polymer hollow nanospheres are of particular interest in relation to their feasibility to encapsulate a wide range of guest molecules and modify the surface functionalities of nanoparticles. Therefore, these polymeric nanocapsules have been fabricated with various methods including colloidal templating,⁷ layer-by-layer adsorption,⁸ encapsulation of a non-solvent,⁹ crosslinking of micellar coronas,¹⁰ vesicles,¹¹ and self-assembling approach utilizing covalent bonds and hydrogen bonds.¹² However, most synthetic approaches have employed different materials as core and shell parts, for example, inorganic-organic, metallic-organic, and disparate organic-organic materials. The methods have also required multi-step etching processes to remove the core and the surfactants. Herein, we report a novel fabrication of polymer hollow nanospheres using core/shell nanomaterials composed of an identical polymer.

The overall experimental procedure is illustrated in Scheme 1. Cationic surfactants such as octyltrimethylammonium bromide (OTAB), decyltrimethylammonium bromide (DeTAB), and cetyltrimethylammonium bromide (CTAB) were used to form micelles as nanoreactors. In the synthesis of PPy core/shell nanomaterials, pyrrole monomers and different oxidants, *i.e.* copper(II) chloride and iron(III) chloride, were added stepwise into the micellar solution. Coupled with the characteristics of the O/W microemulsion system, the hydrophilic oxidants with different chemical oxidation potentials produced PPys with different solubility in alcohol. Copper(II) chloride, with lower oxidation potential ($E^\circ = +0.16$ V), produced a linear PPy core, which was soluble in alcohol. On the other hand, iron(III) chloride, with higher oxidation potential

($E^\circ = +0.77$ V), created a crosslinked PPy shell, which was insoluble in alcohol. When excess methyl alcohol was added into the reaction solution, the linear PPy core was etched out along with the surfactants and the residual oxidants, and the crosslinked PPy nanocapsules were obtained. In addition, the PPy hollow nanospheres could be transformed into carbon nanocapsules by carbonization. To our knowledge, this novel methodology describes the first demonstration of the fabrication of polymer hollow nanospheres using an identical polymer as the core/shell nanomaterials.

Fig. 1a shows a TEM image of soluble PPy nanoparticles used as the templating core. The soluble PPy was prepared using pyrrole (7.5 mmol) and copper(II) chloride (3.8 mmol) in 0.45 M DeTAB. The average diameter of soluble PPy nanoparticles was 23 ± 1 nm. After loading pyrrole (14.9 mmol) and ferric chloride (7.4 mmol) subsequently, linear PPy/crosslinked PPy core/shell nanomaterials composed entirely of spherical particles with a mean diameter of 33 nm were synthesized (Fig. 1b). Fig. 1c exhibits a TEM image of PPy hollow nanocapsules obtained by etching the soluble PPy core with methyl alcohol. The pore size of PPy nanocapsules was similar to the diameter of the soluble PPy core. This means that the soluble PPy core acted successfully as the template. The average wall thickness of PPy hollow nanospheres was 5 nm. According to elemental analysis (EA), PPy nanocapsules consisted of C (56.8%), N (16.4%), and H (3.6%), which was similar to the composition of pure PPy. Energy-dispersive X-ray (EDX) analysis indicated the presence of C (59.5%), N (17.4%), Fe (5.2%), and Cl (17.9%). The absence of copper supported that the linear PPy core doped with copper complex anion was etched out.

In the pyrrole-pyrrole coupling reaction, protons in the α position are more easily eliminated than those in the β position. The α - α coupling reaction leads to a linear PPy, whereas the α - β coupling reaction produces a crosslinked PPy. In general, PPys synthesized either electrochemically or chemically are known to be



Scheme 1 Schematic diagram of the fabrication of PPy and carbon hollow nanospheres.

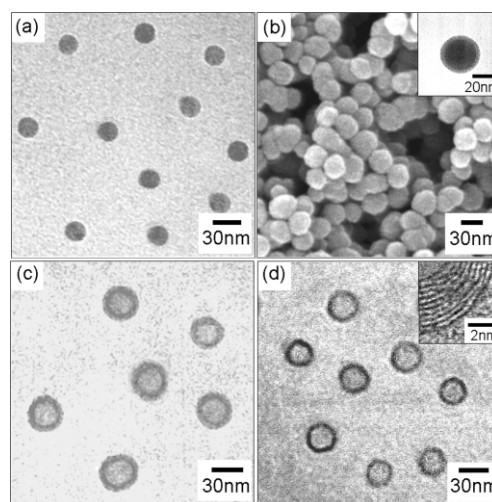


Fig. 1 TEM and SEM images of PPy nanoparticles and hollow nanospheres: (a) soluble PPy nanoparticles fabricated using 0.45 M DeTAB; (b) linear PPy/crosslinked PPy core/shell nanoparticles; (c) PPy nanocapsules; (d) carbon nanocapsules (inset: a HRTEM image of the wall).

† Electronic Supplementary Information (ESI) available: Experimental details for the synthesis and carbonization of PPy nanocapsules, instrumentation, XRD pattern and Raman spectrum. See <http://www.rsc.org/suppdata/cc/b3/b316881f/>

insoluble and infusible due to the crosslinking and the strong inter- and intra-molecular interactions.¹³ Under our experimental conditions, highly soluble PPy was successfully synthesized by microemulsion polymerization using an oxidant with weak oxidation potential. The O/W microemulsion system prohibited the water-soluble oxidant from penetrating into the hydrophobic interior of micelles. In addition, the microemulsion system optimizes the arrangement of reactive monomer rings and increases the extent of the π -conjugation length.¹⁴ It could be considered that the relatively weak chemical oxidation potential of the oxidant and the characteristic of microemulsion system significantly suppressed the α - β coupling reaction of PPy.

Fig. 1d shows a TEM image of the PPy nanocapsules carbonized at 1000 °C. The average diameter was 30 ± 1 nm. EDX analysis provided the composition of the carbonized PPy nanocapsules, *i.e.* C (72.3%), N (1.2%), and Fe (3.8%). The shrinkage (*ca.* 9%) in diameter is thought to result from the formation of more compact structures accompanied by denitrogenation, dehydrogenation, and aromatization in the carbonization process. XRD and Raman spectroscopy analyses indicated that the carbon nanocapsule consists of semicrystalline graphitic carbon. The HRTEM image of the carbon nanocapsule wall shows the partially ordered graphene layers. The doped transition metal is considered to promote the graphitization.¹⁵ The pore size distribution of the carbon nanocapsules was derived from the N₂ adsorption branches at 350 K by the Barrett–Joyner–Halenda (BJH) method, and found to exhibit pore sizes that were uniformly distributed about a center of 21 nm. In addition, the Brunauer–Emmett–Teller (BET) surface area of carbon nanocapsules was *ca.* 361 m² g⁻¹.

Fig. 2a demonstrates the size variation of PPy hollow nanospheres as a function of surfactant concentration at room temperature. The average diameter of PPy nanocapsules increased with increasing surfactant chain length. The enhanced flexibility of longer spacers provides more free volume inside the micelles as nanoreactors, which results in the production of larger particles. The micelle aggregation number (*n*), which is the number of

surfactant molecules required to form a micelle, becomes smaller with shorter chain length.¹⁶ This means that the number of micelles increases with shorter spacer length at the same surfactant concentration, which causes the size reduction of the polymer nanoparticle synthesized at a fixed amount of monomer. The average size of polymer nanoparticles also decreased with increasing surfactant concentration because of the increment in the number of micelles.

The diameter change of the soluble PPy core as a function of pyrrole concentration is illustrated in Fig. 2b. When the surfactant (DeTAB) concentration was fixed at 0.45 M, the average diameter of soluble PPy nanoparticles was tunable from 22 to 33 nm by changing the monomer amount from 0.19 to 0.57 M. In order to evaluate the shell thickness, the crosslinked PPy shell was synthesized onto the soluble PPy cores with diameter of *ca.* 22 nm. The shell thickness also increased gradually from 6 nm to 14 nm with increasing the feeding amount of monomer from 0.37 to 1.13 M. This is because the size of the micelle can be enlarged to some degree with increasing the amount of feeding monomer.

In conclusion, linear PPy/crosslinked PPy core/shell nanomaterials were fabricated stepwise by microemulsion polymerization using two oxidants with different chemical oxidation potentials. PPy hollow nanospheres could be obtained by one-step solvent etching of the linear core and surfactants, and transformed into carbon nanocapsules through carbonization. Our novel approach demonstrates the first experimental evidence for the fabrication of polymer nanocapsules using an identical polymer as the core/shell nanomaterial.

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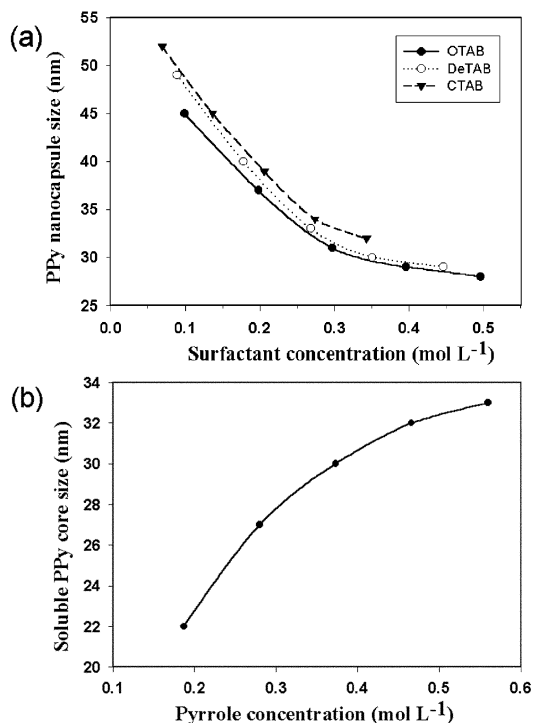


Fig. 2 (a) The size change of PPy hollow nanospheres as a function of surfactant concentration. (b) The diameter variation of the linear PPy core with increasing monomer amount at a fixed surfactant (DeTAB) concentration of 0.45 M. The average size was determined by TEM (50 particles counted).