

Starch-assisted synthesis of polypyrrole nanowires by a simple electrochemical approach†

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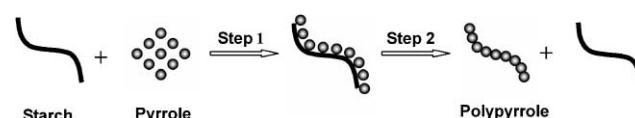
Starch, one of the most commonly used polysaccharides, has been adopted for the first time as morphology-directing agent to the electrochemical synthesis of polypyrrole (PPy) nanowires on various electrodes.

One-dimensional (1D) nanostructures of conducting polymers have attracted much attention in nanotechnology due to their widespread promising applications in various fields.¹ Up to now, nanowires or nanotubes of conducting polymers have been generally prepared using hard² or soft templates.³ Moreover, other methods, such as nanofiber seeding approach,⁴ interfacial polymerization,⁵ electrospinning,⁶ and mechanical stretching,⁷ have been developed to fabricate conducting polymer nanowires. Using biomolecules as morphology-directing agents is a new route to obtain 1D nanostructures of conducting polymers.⁸ Within the past few years, biomolecules have rapidly become promising templates for the synthesis of 1D nanostructures. By selecting suitable biomolecules, novel nanostructures of certain inorganic materials have been produced, such as DNA-assisted synthesis of Au,⁹ Ag¹⁰ particle nanowires, amino-acid controlled growth of tellurium nanotubes and nanowires,¹¹ protein-templated synthesis of bismuth nanowires,¹² polypeptide based synthesis of snowflake-like structures of bismuth sulfide nanorods,¹³ and virus-guided synthesis of magnetic and semiconductor nanowires.¹⁴ Very recently, organic conducting polymer 1D nanostructures including polypyrrole (PPy) nanowires and polyaniline nanofibers have been prepared in the presence of biomolecules, heparin and sodium alginate, respectively.⁸

Important requirements for the template applications of biomolecules are that they should possess the ability to guide the oriented growth of organic or inorganic substances, and should be thermally and chemically stable, easy to obtain, cheap, and, if possible, environmentally friendly. Starch, one of the most abundant polysaccharides stored in plants, meets all of these requirements. It has also been confirmed that the structure of starch is chain-shaped with many hydroxyl groups (–OH) on the surface¹⁵ and this chain-shaped structure has been used for the controlled growth of Te nanowires.¹⁶ However, it has not so far found application in the synthesis of 1D organic conducting

polymer nanomaterials. In this communication, we propose a convenient starch-assisted approach for the synthesis of PPy nanowires through electrochemical polymerization of pyrrole at room temperature. It is a simple, cheap, rapid, mild and environmentally benign method to produce uniform PPy nanowires with controllable average diameters as free-standing films on various electrodes. Interestingly, unlike the previously reported soft template synthesis of conducting polymer nanostructures, in which the template molecules such as anionic surfactants were assembled into spherical or tubular structures acting as both templates and dopants, the template molecule used here, starch, serves only as the structure-directing agent because it is a neutral molecule and thus can not be incorporated into PPy as dopants upon oxidation. This property is of particular interest especially in the case where template molecules are undesired in the final products. Moreover, it was found that PPy nanowires could be electrochemically generated on various electrodes including tin-doped indium oxide (ITO) film, stainless steel, titanium, gold and graphite through the present starch-assisted approach. Although 1D PPy nanostructures on the surfaces of inorganic materials have been electrochemically fabricated by other processes,¹⁷ to our knowledge, this is the first synthesis of PPy nanowires directly on so many different types of unmodified inorganic electrodes by a single electrochemical method. In addition, all these electrode materials are extensively used biomaterials in biomedical fields. For example, titanium and its alloys are widely used load-bearing implant materials in the orthopaedic field.¹⁸ The deposition of PPy nanowires directly onto these materials may lead to new types of organic/inorganic nanocomposites with both unique properties of conducting polymer nanostructures and inherent properties of these biomaterials.

The overall synthetic strategy of PPy nanowires in the presence of starch may involve two steps (Scheme 1). When dissolved in water, pyrrole monomers were first spontaneously adsorbed onto starch molecules through hydrogen bonds formed between pyrrole molecules and –OH groups of starch. Then the adsorbed pyrrole monomers were polymerized preferentially along the chain of the starch to form PPy nanowires as the electrochemical reaction was initiated. Here, the chain-shaped structure of starch plays a template-like role in the formation of PPy nanowires. The first step



Scheme 1 Simplified schematic representation of the synthetic strategy for the formation of PPy nanowires.

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is a self-assembly process and thus the method we propose here is essentially a simple, one-step route to produce PPy nanowires.

The electrochemical synthesis of PPy nanowires was carried out at room temperature in a one-compartment cell with the use of a TD73000 Electrochemical System under computer control. The typical working electrode was a piece of tin-doped indium oxide (ITO) glass with active area of 0.5 cm² and the counter electrode was a platinum coil. All potentials were referred to a saturated calomel electrode (SCE). The typical electrolyte was an aqueous solution of 0.14 M pyrrole, 0.02 wt% soluble starch, 0.07 M lithium perchlorate and 0.20 M phosphate buffer solution (pH = 6.86). The solutions were deaerated by a nitrogen stream before polymerization. PPy nanowires were grown from the surface of the ITO electrode by electropolymerization at a constant applied potential of 0.85 V for 150 s. All samples were washed thoroughly with de-ionized water in order to remove the adsorbed soluble starch and dried at room temperature before characterization. PPy was also synthesized without soluble starch by the same process for comparison.

The morphologies of the resulting PPy products were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1(a) and (b) show typical SEM images of the PPy induced by soluble starch. Fig. 1(a) shows uniform wire-like PPy nanostructures with average diameter of *ca.* 100 nm and length of hundreds of nanometers to several microns. The high-magnification SEM image in Fig. 1(b) clearly shows these wires have fine structures with smooth surfaces. The TEM image (Fig. 1(c)) reveals that the nanostructures are solid, which corroborates the formation of PPy nanowires. These results meet our expectations, as PPy nanowires have been synthesized successfully in the presence of soluble starch. It is important to note that when PPy was prepared in the absence of soluble starch by the same process, only cauliflower-like morphology of PPy was observed (Fig. 1(d)), suggesting that soluble starch plays an important role in the formation of PPy nanowires.

The effects of the concentrations of pyrrole and soluble starch on the morphology of PPy nanostructure were investigated. As the concentration of pyrrole was varied from 0.06 to 0.22 M, the average diameter of PPy nanowires increased from 60 to 150 nm (Fig. S1, ESI[†]). Further increase of the pyrrole concentration

(more than 0.22 M) leads to PPy without wire-like morphology. On the other hand, as the concentration of soluble starch was increased from 0.004 to 0.020 wt%, the average diameter of PPy nanowires decreased from 100 to 70 nm (Fig. S2, ESI[†]). When the concentration of soluble starch is lower than 0.004 wt%, more nodular PPy are formed and coexist with the nanowires. These results are consistent with the synthetic strategy mentioned above and reveal that the average diameters of PPy nanowires can be controlled easily by changing the concentrations of pyrrole and soluble starch.

The reflectance FTIR spectra of soluble starch, PPy nanowires, and cauliflower-like PPy synthesized without soluble starch were measured over the range 4000–400 cm⁻¹ (Fig. S3, ESI[†]). The IR spectra of nanowires and cauliflower-like PPy are nearly identical and show the characteristic PPy peaks, such as the asymmetric and symmetric ring stretching at 1555 and 1469 cm⁻¹, the C–N stretching vibration at 1188 cm⁻¹, and C–H wagging vibrations at 782 cm⁻¹, *etc.* However, no characteristic peaks of soluble starch are observed in the IR spectrum of PPy nanowires. These results indicate that PPy nanowires have been successfully prepared and the soluble starch is not incorporated into the PPy nanowires as dopant. The elemental composition of the PPy nanowires was investigated by X-ray photoelectron spectroscopy (XPS) to confirm the absence of soluble starch in the final PPy nanowires (Fig. S4, ESI[†]). The result shows the presence of carbon (73.58%), nitrogen (18.48%), oxygen (6.76%), phosphorus (0.64%) and chlorine (0.54%). The mole ratio of C/N is 3.98 for XPS analysis, which is almost identical to the theoretical value of C/N mole ratio of PPy (4.00). Considering these facts, it is clear that no soluble starch remains in the final PPy nanowires. Consequently, the neutral starch serves only as the morphology-directing agent in the present work, which is different from the role of the biomolecules used in the previous studies,⁸ in which heparin and sodium alginate serve not only as structure-directing agents but also as polyanion dopants.

The electrochemical activity of the electrode made with PPy nanowires was evaluated by cyclic voltammetry in physiological saline solutions, along with the electrode composed of cauliflower-like PPy prepared in the absence of soluble starch for comparison. The cyclic voltammograms (Fig. S5, ESI[†]) show that both samples are electrochemically active, and for the nanowire electrode, the corresponding cathodic and anodic peaks are relatively stronger than that of the cauliflower-like PPy electrode, indicating PPy nanowires have a higher active specific surface area. The X-ray diffraction (XRD) pattern of PPy nanowires (Fig. S6, ESI[†]) shows a broad peak around $2\theta = 22.7^\circ$, which is attributable to the scattering of PPy chains at an interplanar spacing close to the van der Waals distance for aromatic groups,¹⁹ indicating that the resulting nanowires are amorphous.

Besides ITO film, other inorganic materials were also used as substrates for the electrochemical synthesis of PPy nanowires in the presence of starch. Fig. 2 shows the SEM images of the PPy samples formed on graphite (A), titanium (B), gold (C) and stainless steel (D) electrodes. It can be seen that all samples have wire-like morphology with average diameters of ~ 100 nm and lengths up to several microns. This indicates that electrode materials have no obvious influences on the morphology of PPy nanowires. Therefore, this simple biomolecule-assisted method can be extended to prepare PPy nanowires on the surfaces of various

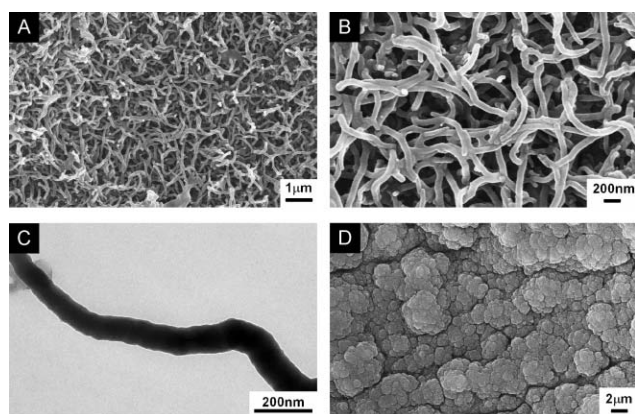


Fig. 1 (A, B) SEM images of PPy nanowires synthesized in the presence of soluble starch at different magnifications; (C) TEM image of PPy nanowires; (D) SEM image of cauliflower-like PPy prepared in the absence of soluble starch.

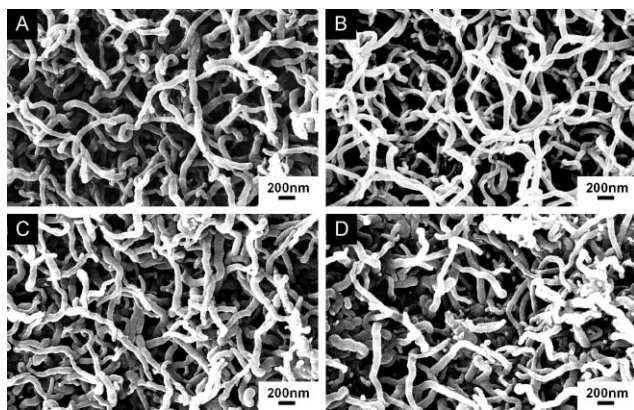


Fig. 2 PPy nanowires synthesized in the presence of soluble starch on different electrodes: (a) graphite, (b) titanium, (c) gold and (d) stainless steel.

inorganic materials and afford the resulting organic/inorganic nanocomposites with attractive properties due to its electrochemical activity and high active surface area, which will be of interest to chemists, materials scientists, as well as biologists.

In summary, we have developed an efficient method for the electrochemical fabrication of uniform PPy nanowires with controllable average diameters with the assistance of biomolecule starch, which serves only as the morphology-directing agent during the growth of nanowires and thus does not require removal from the final PPy nanowires. Since starch is cheap and environmentally friendly, and the process is simple, mild and rapid, it is expected that this approach will be of great use in the synthesis of conducting PPy nanowires. In addition, the method we described here also provided a versatile one-step route to obtain various novel conducting polymer-based organic/inorganic nanocomposites that may find further promising applications in the field of biomedical science.

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