

Fabrication of Conducting Polymer Nanomaterials Using Soft Template Method

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Introduction

Today, the so-called "nanotechnology" has brought about a significant paradigm shift in fabricating various kinds of materials: from bulk features with micron size to ultrafine features with nanometer size. The precise size control of materials in nanoscale allows the generation of superior chemical and physical properties that are quite different from those of their bulky counterparts. Accordingly, numerous researches on diverse nanomaterials consisting of metals, semiconductors, polymers, biomaterials have been extensively carried out all over the world. In particular, there has been noteworthy progress in the preparation of metallic and inorganic nanomaterials. A rich variety of chemical and physical methods have been developed for the size- and shape-control of metallic and inorganic nanomaterials. However, in contrast, the advance in preparation of polymeric nanomaterials has been relatively slow until now.

In general, polymeric nanomaterials with well-defined structure can provide a number of advantages over other materials because they have tunable surface functionality, mild synthetic condition, flexibility and so forth. Of the synthetic polymers, conducting polymers have been attracting considerable attention from both scientific and industrial perspectives by virtue of the beneficial electrical and optical properties originating from their unique π -conjugated system (Table 1). Many efforts have been devoted toward generating conducting polymer nanomaterials, leading the development of synthetic routes to conducting polymer nanospheres, nanocapsules, nanofibers, nanotubes, and mesocellular foams.¹ Among the various synthetic strategies, template method is a very powerful tool to fabricate conducting polymer nanomaterials. The template method involves the inclusion of an appropriate precursor such as monomer and polymer melt/solution inside the void spaces of a host material, followed by the conversion of the precursor to the desired materials. This approach is classified into hard and soft template methods by kinds of templates used. While mesoporous silica, zeolite, and porous alumina and polymer membranes can be utilized as hard templates, soft templates include surfactant, liquid crystal, and organogel. The hard template method is of advantage in tailoring the dimensions of nanomaterials. However, owing to complicated synthetic process and comparatively high cost, the use of hard templates has the significant drawback that scale-up for industrial applications is highly difficult. Therefore, soft template method has appeared as an alternative strategy against hard template method.

For last a few years, our research group has intensively studied the fabrication and application of conducting polymer nanomaterials. In this talk, the recent achievement in the synthetic methodology based on the use of soft templates will be discussed.

Table 1. Typical conducting polymer structures (undoped form)

Name	Structure
Polypyrrole	
Polyaniline	
Polythiophene	
Poly(3,4-ethylenedioxythiophene)	

Soft Template Method

Soft template method has been employed for the fabrication of various morphologies of conducting polymer nanomaterials. Several kinds of soft templates including surfactants, soluble polymers, and cyclodextrin have been employed for fabricating nanospheres, hollow nanoparticles, nanofibers/nanotubes, mesoporous materials.

Nanospheres. Spherical conducting polymer nanoparticles have been mostly by chemical oxidation polymerization with the aid of surfactants in an aqueous solution. Surfactant molecules form spontaneously spherical micelles above critical micelle concentration (CMC), and thus they can be acted as the "nanoreactor" (Figure 1). As a typical example, polypyrrole (PPy) nanoparticles (a few nanometers in diameter) were prepared via low temperature polymerization.^{2,4} The micellar growth could be retarded by deactivating the chain mobility of the surfactant molecules at low temperature, which resulted in the generation of PPy nanoparticles as small as 2 nm in diameter.

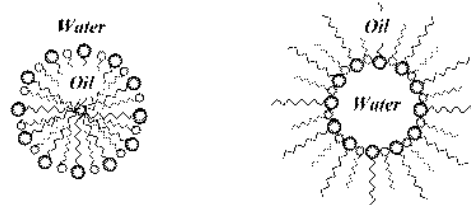


Figure 1. Schematic illustration of oil-in-water (left) and water-in-oil (right) micelles.

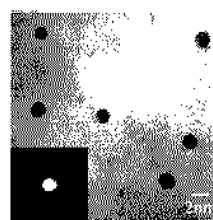


Figure 2. Transmission electron microscopy (TEM) image and nanobeam electron diffraction pattern (inset) of the PPy nanoparticles prepared with cationic surfactant (dodecyltrimethylammonium bromide, DTAB) at 3 °C.

Recently, the multigram-scale production of monodisperse PPy nanoparticles could be achieved in the DTAB/decyl alcohol micelle system.^{5,6} The amount of PPy nanoparticles obtained in a single polymerization reaction was approximately 12 g, a very large quantity in a laboratory-scale synthesis (Figure 3).



Figure 3. Photograph showing a Petri dish containing 12 g of PPy nanoparticles.

Hollow Nanoparticles. A novel route to hollow polymer nanoparticles has been demonstrated using core-shell nanomaterials composed of an identical polymer.^{7,8} Soluble and intractable PPy nanoparticles were sequentially prepared by the microemulsion polymerization using two different oxidizing agents. Cupric chloride ($E^\circ = +0.16$ V) generated linear PPy cores (which were soluble in alcohol (Figure 4, left), and ferric chloride ($E^\circ = +0.77$ V) yielded crosslinked PPy shells. Subsequent removal of the soluble cores led the formation of hollow PPy nanoparticles (Figure 4, right).

Poly(3,4-ethylenedioxythiophene) (PEDOT) nanocapsules were also fabricated using surfactant-mediated interfacial polymerization (SMIP).⁹ Cationic surfactants were used to form micelles in an aqueous solution, and the micelles were able to capture the redox initiator (cerium ammonium nitrate, CAN) due to electrostatic interactions between the cerium complex and the surfactant molecules.

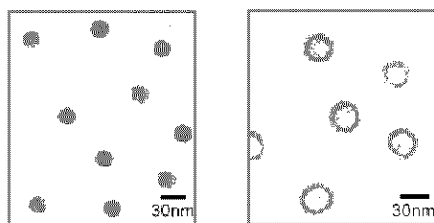


Figure 4. TEM images of soluble PPy cores (left) and hollow PPy nanoparticles (right).

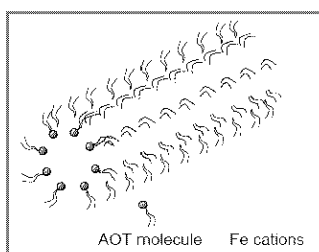


Figure 5. Schematic illustration of an AOT reverse cylindrical micelle.

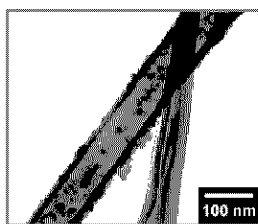


Figure 6. A typical TEM image of PPy nanotubes prepared using AOT reverse cylindrical micelle templating.

To generate hollow structure, cyclohexane (hydrophobe) was introduced into the core of micelles. Then, the addition of EDOT monomer resulted in the formation of PEDOT shells at the micellar surface.

Nanofibers/Nanotubes. Cylindrical micelles could be used as a useful tool for fabricating conducting polymer nanotubes. Sodium bis(2-ethylhexyl) sulfosuccinate (commercially known as "AOT") was employed in order to generate reverse cylindrical micelles in an apolar solvent.¹⁰⁻¹³ When an appropriate amount of ferric chloride was added into the AOT solution, spherical AOT micelles could be transformed into cylindrical micelles. It can be explained that the incorporation of metal salt into AOT emulsion strongly affects the micelle aggregation number as well as the second CMC. Importantly, ferric cations (oxidizing agent) were concentrated in the anionic headgroup of AOT due to electrostatic interactions. Therefore, when pyrrole and EDOT monomers were introduced into the AOT cylindrical micelle phase, they were chemically polymerized by ferric cations along the surface of the cylindrical micelles. This facile and effective approach allowed the formation of PPy nanotubes and several one-dimensional PEDOT nanomaterials.

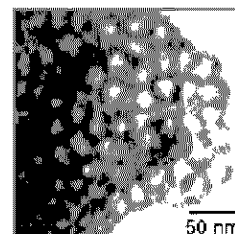


Figure 7. A typical TEM image of PEDOT mesocellular foam.

Mesocellular foams. PEDOT mesocellular foams were fabricated by chemical polymerization at the surface of micelle aggregates (Figure 7).⁹ Spherical micelles with vacant interiors are used as a kind of porogen and served as the polymerization sites. The morphology of the resulting product is strongly dependent on the concentration of surfactant. This methodology offers a convenient route to mesoporous materials and might be expanded to fabricate versatile polymer nanomaterials.

Conclusions

Nowadays, the fabrication of functional materials with tailored properties for specific applications is considered as a critical research topic in contemporary material science. Conducting polymer nanomaterials can be applied to chemical sensor and biosensor, transistor, data storage, supercapacitor, photovoltaic cell, electrochromic device, field emission display, actuator, surface coating, and so forth.¹ In this sense, there are increasing demands for reliable synthetic ways to versatile conducting polymer nanomaterials. The fabrication methodologies described here remove some of the obstacles to progress in the production of conducting polymer nanomaterials. However, it is still challenging to develop the general approach for fabricating large quantities of polymer nanomaterials with a well-defined morphology.

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