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Novel crystalline supramolecular assemblies of amorphous polypyrrole nanoparticles through surfactant templating†

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A lamellar-structured crystalline polypyrrole (PPy) supramolecular assembly was prepared by surfactant templating, and the regularly linked amorphous PPy nanoparticles with tunable window sizes could play the role of crystalline lattices in the supramolecular assembly.

Currently, there is enormously widespread interest in nanostructured materials and their size-dependent properties. The synthetic methods used to fabricate metallic[1,2] and inorganic[3,4] nanoparticles with tunable nanostructures are well established, whereas the synthetic route for polymeric nanoparticles, especially with dimensions less than 10 nm, has scarcely been exploited.[5] Conducting polymer nanoparticles in this size domain are of particular interest in relation to understanding nucleation of polymer assembly, and the possible consequences of spatial confinement on their optical and electronic properties. Since 1987, various research groups have reported the preparation of surfactant-stabilized conducting polymer nanoparticles.[6–9] These particles were typically 100–200 nm diameter.

In this communication, we report on the facile fabrication of polypyrrole (PPy) nanoparticles with dimensions of several nanometers using low temperature microemulsion polymerization. The thermodynamically stable microemulsion micelles have been utilized as nanoreactors. Low temperature synthesis was appropriate for reducing the inner volume of a micelle due to the deactivated surfactant chain mobility.[10] In addition, this method allows the morphological transition of spherical nanoparticles into structured aggregates through surfactant templating. Intriguingly, amorphous ultrafine nanoparticles associate with one another to form crystalline lamellar structures over a critical surfactant concentration under our synthetic conditions. From the viewpoint of polymer crystalline formation, lamellar crystals are typical for linear polymers crystallized *via* 'chain folding'.[11] The basic reason behind the lamellar habit is the formation of a fold surface as an intermediate step towards a more stable crystalline state. Cross-linked macromolecules are not suitable for chain folding and are generally amorphous.[12] In this study, however, the regularly linked amorphous PPy nanoparticles could play the role of crystalline lattices in the supramolecular assembly, even though PPy has a cross-linked character through α–β coupling. This is the first experimental evidence for crystal formation of amorphous polymer nanoparticles through surfactant templating.

In a typical procedure, a variable amount of octyltrimethylammonium bromide (OTAB) was magnetically stirred in 40 ml of distilled water at 3 °C. 1.0 g (14.9 mmol) of pyrrole was added dropwise and 5.561 g (34.3 mmol) of ferric chloride was added into the solution. The polymerization of PPys in micelles proceeded with magnetic stirring for 3 h. The reaction product was moved to a separation funnel and methyl alcohol was added into the funnel in order to remove the surfactants and the residual ferric chloride. The upper solution containing surfactants and unreacted ferric chloride was discarded and the precipitates were dried in a vacuum oven at room temperature.

The FT-IR spectrum of the product showed characteristic PPy peaks at 1549, 1485, and 783 cm^{-1}, which were due to ring stretching, conjugated C–N stretching, and C–H wagging vibrations, respectively. Elemental analysis provided the composition, *i.e.* C (60.5), H (3.8), and N (17.3%). The ratio of H : N : C was 1.0 : 4.6 : 15.9, which is very similar to the composition of pure PPy. Energy dispersive X-ray (EDX) analysis showed the presence of C (57.7), N (16.8), Fe (8.4), and Cl (17.1%). The ratio of C/N was 3.5 and 3.4 for elemental analysis and EDX, respectively. Since a pyrrole has one N and four C, the C/N weight ratio of PPys is about 3.43. These results indicate that PPys were successfully synthesized and the surfactants were almost removed. It seems that the nanoparticles consist of the PPy doped with iron complex anion.

Fig. 1(a) shows a TEM image and the electron microdiffraction pattern of the PPy nanoparticles prepared using 0.44 M OTAB. The particle size was *ca.* 2 nm and fairly monodisperse. The PPy nanoparticles showed high BET surface area (1641 m^2 g^{-1}). The particle size (determined by counting 50 particles on the TEM image) was controllable from 2 to 8 nm

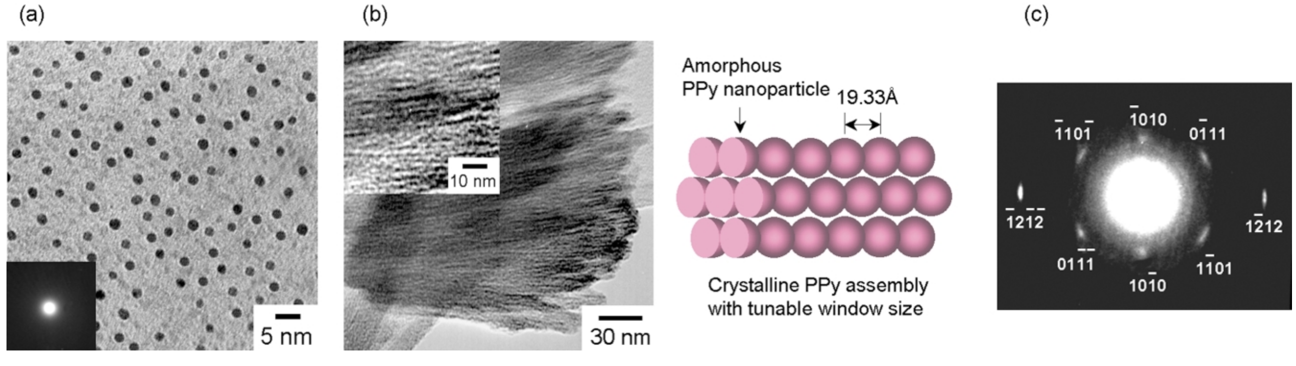

Fig. 1 Transmission electron micrographs and the electron diffraction patterns of spherical PPy nanoparticles prepared using 0.44 M OTAB at 3 °C (a) and the lamellar supramolecular assemblies fabricated using 0.76 M OTAB at 3 °C (b, c). The images were obtained with a JEOL JEM-2000FX analytical microscope.

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† Electronic supplementary information (ESI) available: FT-IR spectrum and the peak assignment of PPy nanoparticles. See http://www.rsc.org/suppdata/cc/b2/b207744m/

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with changing the surfactant amount. As the surfactant amount increased, the PPy nanoparticle size decreased. Micelle aggregation number (*n*), which is the number of surfactant molecules required to form a micelle, is independent of the surfactant concentration to fairly high surfactant concentration.[13] Therefore, the number of micelles increases with increasing surfactant concentration, resulting in the size reduction of nanoparticles at a fixed monomer amount. The spherical PPy nanoparticles are amorphous according to the diffraction pattern (Fig. 1(a)). The structure of PPys doped with any of the common anion species is invariably reported to be amorphous, even though the PPy chain is expected to have a planar configuration.[14]

The morphological transition of the PPy nanoparticles into lamellar aggregates occurred over a critical concentration (*ca.* 0.68 M OTAB). This originates from a consequence of the force balance between interfacial and stretching energies in the microdomains. The critical concentration of the morphological transition was lower than critical micelle concentration II (CMC II) of OTAB.[15] It is known that small amounts of solubilized oil inside micelles can have a significant effect on the equilibrium microstructure of a dilute micellar system, producing dramatic one-dimensional growth of the micelles.[16] In this experiment, pyrrole monomer acts as an oil before polymerization. Pyrrole added to the solution is preferentially adsorbed into the hydrophobic interior of the micelles. This reduces the local tail concentration in the oily core of the micelle, and thus increases the effective cross-sectional area of the tails. The packing factor is then increased and the surfactant preferentially interfaces with lower overall curvature. Consequently, the micelles can grow in one dimension below CMC II of normal oil–water phase.

Fig. 1(b) and (c) show TEM images and the selected area electron diffraction (SAED) pattern of the lamellar supramolecular assemblies fabricated using 0.76 M OTAB. The magnified image shows 2 nm nodes. The SAED pattern shows a well-defined crystalline pattern. The regularly linked nanoparticles could play the role of crystalline lattice in the supramolecular assemblies. Even though the surfactants were removed, the regular assembly was still maintained. The particles were interconnected by a small size of window. As the monomer/surfactant mass ratio increased from 0.17 to 0.33, the window size was reduced from 1.3 nm to 0.4 nm and the product looked like a noded structure.

Ying and co-workers have reported a morphological transition in P123-templated mesoporous silica by adding TMB.[17] The morphological change from cylindrical micelles back to spherical micelles was driven by the requirement to cover an increasing volume of oil with a fixed amount of surfactant. The mesophase change of micelles can also be explained by the need to decrease micelle surface-to-volume ratio as more oil was added to the solution with a fixed amount of surfactant. However, the transition resulted in a negligible change in the mean curvature of the surfactant-stabilized oil–water interface. In our study, as the pyrrole amount increased, lamellar arrays were susceptible to being a noded structure in order to minimize micelle surface-to-volume ratio. The mean curvature of the node was very similar to that of spherical micelles right before the morphological transition, *i.e.* the curvature was similar to that of 2 nm spherical nanoparticles.

The powder X-ray diffraction (XRD) pattern of the PPy supramolecular assembly is presented in Fig. 2. The XRD pattern shows a lamellar structure with a cell parameter of 19.33 Å, which is similar to a single nanoparticle size (Fig. 1(b)). The XRD pattern strongly supports the fact that the amorphous PPy nanoparticles act as crystalline lattices. The electrical conductivity was measured using the four-point probe method. The conductivity of the spherical PPy nanoparticles was 2.1 S cm^{-1}. On the other hand, the conductivity value of the lamellar-structured assembly showed 5.4 S cm^{-1}. The slightly higher conductivity of the lamellar-structured assembly is thought to originate from the linked noded structure.

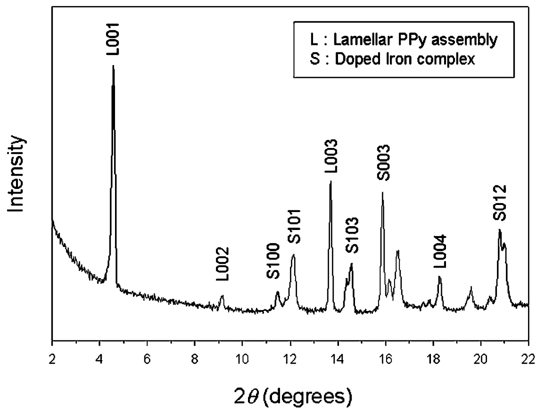

Fig. 2 Powder X-ray diffraction pattern for the PPy supramolecular structure prepared using 0.76 M OTAB at 3 °C. The diffraction pattern shows a lamellar structure with a cell parameter of 19.33 Å. The analysis was performed with a Scintag PADX diffractometer.

In conclusion, microemulsion micelles at low temperature have been successfully utilized as nanoreactors to fabricate PPy nanoparticles with dimensions of several nanometers. The PPy nanoparticles were amorphous and fairly monodisperse. The morphological transition of the PPy nanoparticles into lamellar aggregates occurred over a critical concentration. The regularly connected amorphous PPy nanoparticles could play the role of crystalline lattices in the lamellar-structured supramolecular assemblies. This is the first experimental evidence for the formation of crystalline supramolecular assembly from amorphous polymer nanoparticles without a chain folding mechanism.

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