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Inorganic/organic mesostructure directed synthesis of wire/ribbon-like polypyrrole nanostructures†

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We report here a simple strategy for the synthesis of wire/ribbon-like polypyrrole nanostructures using lamellar inorganic/organic mesostructures as templates which were formed during polymerization between surfactant cations and oxidising anions and which were degraded automatically after polymerization.

Electrically conducting polymers, including polyaniline (PAni), and polypyrrole (PPy), have been studied extensively owing to their great potential application in many fields.[1] Many of these applications require production of one dimensional (1D) nanostructures and thus synthesis of nanoscale conducting polymers, including nanotubes, nanowires and nanofibers, has attracted considerable attention.[2] Several kinds of template-directed synthesis of conducting polymers have been proposed including structurally well-defined "hard" templates[3] and a lyotropic liquid crystalline phase "soft" template.[4] More recently, surfactants[5] adsorbed on to flat surfaces have been employed as templates to control morphology during the synthesis of both PAni and PPy nanostructures.

We report here a simple strategy for the preparation of 1D nanostructural conducting polymers, which uses lamellar inorganic/organic mesostructures as templates. Such templates were formed *in-situ* during polymerization between surfactant cations and oxidising anions. When polymerization was complete, templates would automatically degrade due to the reduction of oxidising anions. By using this strategy, we were able to synthesize wire-like (nanowires) and ribbon-like (nanoribbons) polypyrrole in a controllable and reproducible fashion.

In a typical procedure, 0.3 mmol cetyltrimethylammonium (CTA) bromide was dissolved in 30 mL distilled water to form a homogeneous solution. 60 μL (for nanowires) or 30 μL (for nanoribbons) pyrrole monomer was then added to the above surfactant aqueous solution. The mixture was stirred vigorously for 10 minutes and then cooled to 0–5 °C. Precooled ammonium persulfate (APS) aqueous solution (0.90 mmol for nanowires and 0.45 mmol for nanoribbons dissolved in 6.5 mL distilled water) was added to the mixture dropwise with simultaneous vigorous stirring. A white flocculent precipitate appeared immediately, which gradually turned black in colour. The solution was allowed to stand at 0–5 °C for a further 24 hours, when the solid PPy was collected by filtration, washed with distilled water and absolute ethanol, and then dried *in vacuo* at 80 °C for 12 h.

TEM and SEM images of the PPy nanowires and nanoribbons synthesized by the above procedure are shown in Fig. 1. Both nanowires and nanoribbons were of uniform morphology. For nanowires, diameters were in the range 20 nm to 65 nm with lengths up to several micrometers. For nanoribbons, widths were in the range 25 nm to 85 nm, heights in the range of several nanometers and lengths up to several micrometers. Judging from X-ray powder diffraction (See Supporting Information†), both PPy nanowires and nanoribbons were amorphous.[6] The nanoribbons also showed a further feature in that their edges were not uniform with a series of rounded protrusions occurring at each edge along their full length (Inset in Fig. 1 bottom).

The FT-IR spectrum (See Supporting Information†) of the nanostructures showed characteristic PPy peaks at 1560 and 1480 cm^{-1}, which were due to the antisymmetric and symmetric ring-stretching modes, respectively.[7] Strong peaks near 1195 and 920 cm^{-1} indicated the doping state of polypyrrole, and a broad band at 3000–3500 cm^{-1} was attributed to N–H and C–H stretching vibrations. Peaks at 1050 cm^{-1} and 1315 cm^{-1} were attributed to C–H deformation vibrations and C–N stretching vibrations, respectively.[8] The two very weak peaks around 2924 cm^{-1} and 2854 cm^{-1} were attributed to the stretching vibration mode of methylene, indicating that surfactants had been almost completely eliminated from the final PPy nanostructures.

To determine the mechanism by which the PPy nanowires and nanoribbons formed, we examined the role of specific reagents used in the above procedure. The surfactant was examined first by replacing the cationic surfactant CTA bromide with an anionic surfactant sodium dodecyl sulfate (SDS). In this case, no white precipitates were observed and no nanostructures were formed. The role of the oxidising anion was then examined by replacing APS with ferric chloride. Again no white precipitates occurred and no

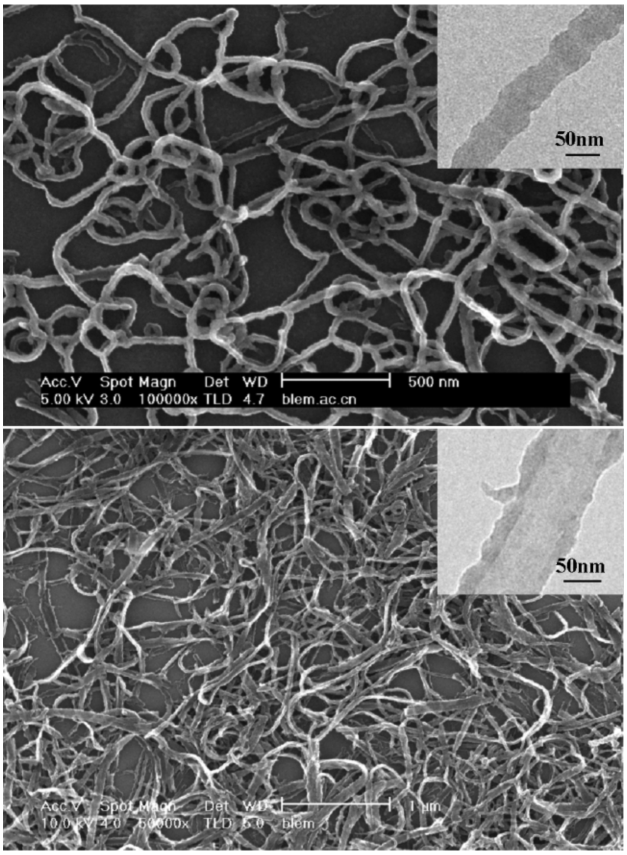

Fig. 1 SEM images of PPy nanowires (top) and nanoribbons (bottom). (Inset: high resolution TEM image of individual PPy nanostructures.)

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† Electronic supplementary information (ESI) available: FT-IR spectra, powder XRD pattern and conductivities of as-made PPy nanostructures. See http://www.rsc.org/suppdata/cc/b4/b405255b/

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nanostructures were formed. This indicated that the white precipitates played a key role in the synthesis of PPy 1D nanostructures.

Since precipitation was clearly a key step in nanostructure formation, the elemental composition of the initial white precipitate was determined. This revealed a composition (mass percent) of: [C] 59.74, [H] 10.70, [N] 3.47, [O] 17.44, [S] 8.75, total 100.10. Such a composition is consistent with $(CTA)_2S_2O_8$, *i.e.* the persulfate salt of CTA. This indicated that the white precipitate was formed between the quaternary ammonium cation of the CTA bromide and the persulfate anion of APS.

Low-angle X-ray powder diffraction (XRD) patterns of $(CTA)_2S_2O_8$ indicated that, when precipitated from a 1 : 3 mixture of water : ethanol, $(CTA)_2S_2O_8$ showed a typical lamellar mesostructure (Fig. 2 bottom). The precipitate structure from the aqueous solution was less clear. We concluded that two types of lamellar mesostructures were formed due to expansion of the layer spacing of $(CTA)_2S_2O_8$ by water molecules (Fig. 2 top).

Since sulfate is produced during polymerization and is an important doping component of the polymers, the effect of sulfate ions on precipitation was examined. Attempts were thus made to precipitate CTA bromide using ammonium sulfate. Again, no white precipitates were generated, which indicates no mesostructures form between the quaternary ammonium cations of the CTA bromide and the sulfate anions reduced form APS in aqueous solutions.

From these investigations it was possible to put forward a mechanism for PPy 1D nanostructure formation (Fig. 3). It is well known that hydrophobic pyrrole molecules will locate themselves at the interior of micelles in aqueous solutions of the cationic surfactant CTA bromide. When a small quantity of APS was added to CTA solutions, lamellar mesostructural $(CTA)_2S_2O_8$ precipitated (white precipitate), containing pyrrole monomers (molar concentrations of APS and CTA were consistent throughout). Thereafter pyrrole was oxidatively polymerized by the persulfate anions in the lamellar $(CTA)_2S_2O_8$, simultaneously reducing persulfate to sulfate. After completion of polymerization and reduction of APS, mesostructual $(CTA)_2S_2O_8$ would then degrade leaving behind the PPy nanoribbons. With excess APS, there would be some persulfate anions left in the solution. This could diffuse into the vicinity of the degraded $(CTA)_2S_2O_8$ mesostructure reforming it and ensuring that any residual pyrrole monomer could be further oxypolymerized. According to the TEM results (inset in Fig. 1 bottom), PPy nanoribbons can be grown preferentially at their two edges along their long axes, so they are easily curved into wire-like morphologies,[9] and finally oxypolymerized into PPy nanowires.

In summary, conducting PPy nanowires and nanoribbons were synthesized using *in situ* formed lamellar inorganic/organic mesostructures. Morphologies of PPy nanostructures were easily changed between nanowires and nanoribbons by altering the concentrations of monomers and mesostructural precursors. This simple approach for synthesizing conducting polymer nanowires and nanoribbons will have great potential for nanosensors and other electronic and optical nanodevices.

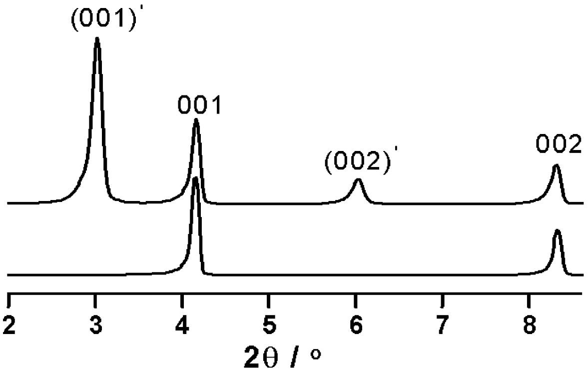

Fig. 2 Low-angle XRD pattern of $(CTA)_2S_2O_8$ precipitated from aqueous solution (top) and 1 : 3 mixed solution of water : ethanol (bottom).

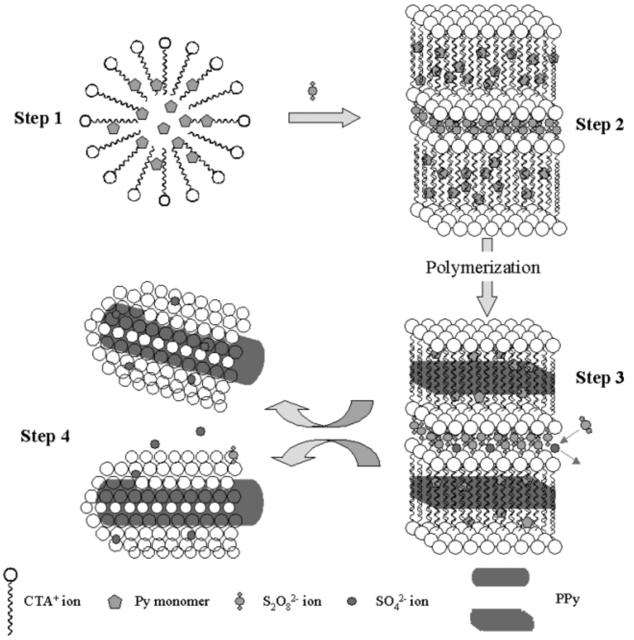

Fig. 3 Schematic depictions of different stages in a typical synthesis of PPy 1D nanostructures templated by and polymerized with inorganic/organic mesostructures. If pyrrole monomer was exhausted at Step 3, simultaneously all persulfate would be reduced to sulfate and the procedure would stop resulting in PPy nanoribbons. Otherwise PPy nanoribbons could grow further and curve into nanowires. Due to degradation of persulfate at Step 4, bonding of persulfates between lamellae would disappear. Two nanowires would then be produced from Step 3 as shown.

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