

## Facile fabrication of polypyrrole nanotubes using reverse microemulsion polymerization†

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**Polypyrrole (PPy) nanotubes have been fabricated by reverse microemulsion polymerization in an apolar solvent, and factors affecting the formation of PPy nanotubes have also been investigated.**

Recently considerable attention has been directed towards hollow tubular structures. Hollow nanotubes have novel properties and possess different contact areas that can be functionalized in various ways. They also have potential applications in the fields of electronics, optics, catalysis, energy storage, and biological systems. Beginning with the discovery of carbon nanotubes, many inorganic nanotubes<sup>1</sup> composed of silicon, titanium oxide, vanadium oxide, silica, *etc.* have been fabricated and many approaches to fabricating organic nanotubes have also been presented.<sup>2</sup> Conducting polymer nanotubes have been synthesized due to their potential applications<sup>3</sup> such as nano-sized transistors, displays, and sensors. In addition, nanotubes and nanofibers of conducting polymers are excellent candidates to be used as molecular wire materials because of their one-dimensional structures and metal-like conductivity. Martin *et al.*<sup>4</sup> fabricated conducting polymer nanotubes and nanofibers by filling the nanopores of anodic aluminium oxide (AAO) or organic polymer filters. They reported that tubular and fibrillar nanostructures of conducting polymers have the potential to display a much higher conductivity than the bulk forms. Thus, polypyrrole, polythiophene and poly(*p*-phenylene vinylene) nanotubes<sup>5</sup> have been synthesized. Most of these researches have been focused on synthetic methods using organic/inorganic templates like alumina and polycarbonate membranes. Wan *et al.*<sup>6</sup> have reported the preparation of polyaniline tubular nanostructures through self-assembly in the presence of a dopant, which acted as a template. Especially, PPy tubular structures<sup>7</sup> prepared by the self-assembly method have only been achieved with micrometer-sized diameters and low aspect ratios.

In reverse microemulsion systems, water promotes the aggregation of surfactant molecules in apolar solvents through solvation of polar groups and hydrogen bonding. Hence, various reactants can be introduced into the nanometer-sized aqueous domains confined within the reversed micelles. These micelles act as 'nano-reactors'.<sup>8</sup> In the past few years, many studies<sup>9</sup> have been conducted on reverse microemulsion-mediated synthesis of polymeric nanoparticles, metallic nanoparticles, and ultrafine ceramic particles. However, polymeric nanotubes have not yet been successfully fabricated using a reverse microemulsion system.

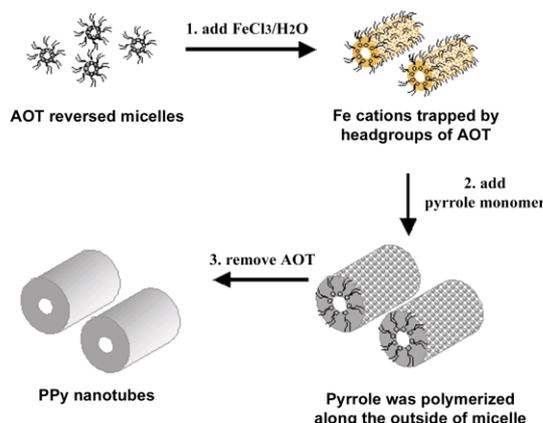
Here, we report the fabrication of PPy nanotubes using reverse microemulsion polymerization for the first time. The overall synthetic procedure of PPy nanotubes is presented in Scheme 1. To fabricate PPy nanotubes, 9 g (20.3 mmol) of sodium bis(2-ethylhexyl) sulfosuccinate, commercially known as AOT, was added to 40 mL of hexane at room temperature. AOT formed reversed micelles due to its double-tailed structure with a relatively small hydrophilic head group.<sup>10</sup> Then, 1 mL of

9.0 M aqueous FeCl<sub>3</sub> solution was added to the AOT/hexane mixture. FeCl<sub>3</sub> aids the formation of rod-shaped micelles by decreasing the 'second critical micelle concentration (CMC II)' value and increasing the solvent's ionic strength.<sup>11</sup> The anionic polar head group of AOT extracts metal cations from the aqueous solution to the reverse micellar phase.<sup>12</sup> In other words, Fe<sup>3+</sup> ions concentrated in the reversed micelles were capped by the anionic polar headgroups of AOT so that they would maintain the rod-shape of AOT. Then, 0.5 g (7.5 mmol) of pyrrole monomers were added into the solvent, and pyrrole monomers were polymerized by Fe<sup>3+</sup> ions along the outside of the rod-shaped micelles. The polymerization of PPy proceeded for 3 h. The resultant product was moved to a separation funnel and an excess of ethanol was added to remove the surfactants. PPy nanotubes were precipitated after 2 h, and the upper solution containing surfactants was discarded.

The FT-IR spectrum (see ESI) of PPy nanotubes showed characteristic peaks at 3400, 1550, 1470, and 1290–1030 cm<sup>-1</sup>, which are considered to be the result of N–H stretching vibrations, pyrrole ring stretch, conjugated C–N stretching, and =C–H in plane vibrations, respectively. An elemental analysis was performed to confirm that AOT was removed from the PPy nanotubes. The result showed the presence of carbon (42.3%), hydrogen (3.6%), nitrogen (13.5%). Sulfur was not detected. Considering these facts, it is obvious that PPy nanotubes were successfully prepared and AOT was completely removed.

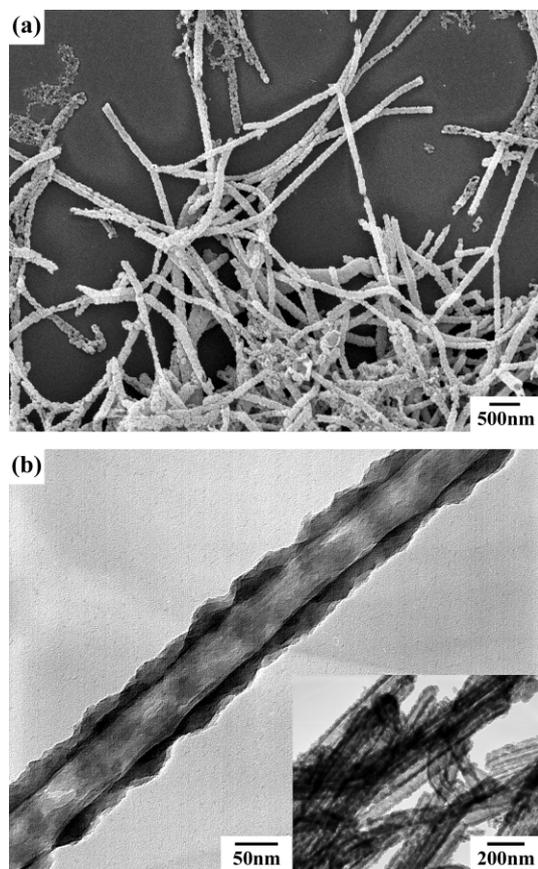
The morphology of PPy nanotubes was observed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Fig. 1a presents an FE-SEM image of the PPy nanotubes. The diameter of the PPy nanotubes was *ca.* 95 nm and the length was more than 5 μm. These data indicate that the diameter was smaller and the aspect ratio was higher than those of PPy tubes made by the self-assembly method.<sup>7</sup> The TEM image showed hollow structures as nanotubes, see Fig. 1b, and the wall thickness of the PPy tubes was *ca.* 22 nm.

The electrical conductivity of PPy nanotubes was measured using the standard four-probe method.<sup>13</sup> The conductivity of



**Scheme 1** Schematic diagram of PPy nanotube fabrication using reverse microemulsion polymerization.

† Electronic supplementary information (ESI) available: FTIR spectrum and TEM images of PPy nanotubes. See <http://www.rsc.org/suppdata/cc/b2/b211716a/>



**Fig. 1** (a) FE-SEM image and (b) TEM image of PPy nanotubes. PPy nanotubes were prepared with 9 g of AOT, 1 mL of aqueous  $\text{FeCl}_3$  solution, and 0.5 g of pyrrole monomer in 40 mL of hexane at room temperature.

PPy nanotubes was  $30.4 \text{ S cm}^{-1}$ . In general, polymer conductivity is a function of the monomer and oxidant concentrations, solvent, reaction time and temperature. Thus the molar ratio of  $\text{FeCl}_3$ /pyrrole for the polymerization of pyrrole by  $\text{FeCl}_3$  has been suggested to be approximately 2.4.<sup>14</sup> Under these experimental conditions, the conductivity of PPy nanotubes was high although the molar ratio of  $\text{FeCl}_3$ /pyrrole was as small as 0.83. It was found that charge transfer rates in tubular PPy were significantly higher than those of granular PPy<sup>15</sup> and that the narrowest tubes showed the highest conductivity because such tubes had a higher proportion of ordered chain material.<sup>16</sup> In other words, PPy nanotubes have been found to have longer conjugation length than ordinary PPy, facilitating charge transport in the material which in turn results in enhanced conductivity.

Table 1 presents the influence of the amount of AOT and aqueous  $\text{FeCl}_3$  solution on the formation of PPy nanotubes. When the amount of aqueous  $\text{FeCl}_3$  solution was reduced to 0.5 mL, the diameter and conductivity of PPy nanotubes (see ESI) were retained, but irregular structures were observed as well as

**Table 1** Diameter and conductivity of PPy nanotubes according to the amount of AOT and aqueous  $\text{FeCl}_3$  solution (conditions: hexane 40 mL, pyrrole 0.5 g)

AOT/g	$\text{FeCl}_3$ solution <sup>a</sup> /mL	Diameter <sup>b</sup> /nm	Conductivity/ $\text{S cm}^{-1}$
9	1	95	30.4
9	0.5	90	26.5
7	1	135	17.8

<sup>a</sup> Molar concentration of aqueous  $\text{FeCl}_3$  solution was 9.0 M. <sup>b</sup> Average diameter was determined by TEM (50 nanotubes counted).

nanotubes. When the amount of AOT was reduced to 7 g, the diameter of PPy nanotubes (see ESI) increased and their conductivity decreased slightly. Therefore, the mechanism of PPy nanotube formation was found to be significantly dependent on the amount of AOT and aqueous  $\text{FeCl}_3$  solution.

In conclusion, PPy nanotubes were successfully prepared by reverse microemulsion polymerization, and they exhibited smaller diameters and higher aspect ratios than PPy tubes prepared by the self-assembly method.<sup>7</sup> The conductivity of the PPy nanotubes was also enhanced.

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## Notes and references

‡ Characterization of materials: Transmission electron micrographs were taken with a JEOL EM-2000 EX II microscope. The polypyrrole nanotubes were diluted in ethanol and the diluted solution was cast onto copper mesh grids. After drying, the images were examined at a voltage of 200 kV. Scanning electron micrographs were recorded on a JEOL JSM-6700 F microscope. Polypyrrole nanotubes were diluted in ethanol and the diluted solution was cast onto carbon tape. After drying, the specimens were coated with a thin layer of gold to eliminate charging effects and the morphology was examined at a voltage of 5.0 kV. A Bomem MB 100 FT-IR spectrometer was used to confirm the fact of polypyrrole polymerization. IR spectra were obtained by the transmission technique. 32 scans were collected with a spectral resolution of  $4 \text{ cm}^{-1}$ . The measurement of conductivity was performed by the standard four-probe method where a constant current was passed through a sample of known length, thickness and width.

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