Nanocoating of natural cellulose fibers with conjugated polymer: hierarchical polypyrrole composite materials†

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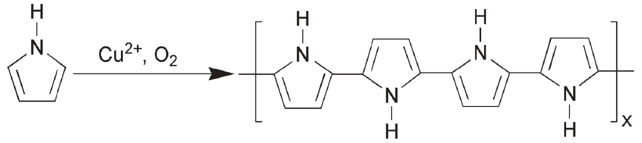
Astonishingly uniform polypyrrole nanocoating on morphologically complex cellulosic substances was achieved without disrupting the hierarchical network structures of individual cellulose fibers by means of polymerization-induced adsorption.

Natural fibrous substances have held a key role in worldwide chemical and textile industries. For example, cellulose fibers have been blended with synthetic polymers to be their reinforcements.[1] The unique morphologies of the natural substances afforded by the hierarchical self-assembly of the polymer chains give superior properties which are not seen in synthetic fibers. Recently, coating of individual cellulose fibers with metal oxide gel layers became possible.[2] Surface coating by polymers, such as layer-by-layer assembly of polyelectrolytes,[3] provided a way to control overall properties (*e.g.*, wettability, chemical resistance, biocompatibility, *etc.*) of the resultant composite materials. Chemical and electrochemical coatings of fibrous substrates with conjugated polymers have long been investigated to produce conductive textiles.[4] However, nanoprecise coating of the substances with hierarchical network structures has remained a challenge, because it is not easy to control the agglomeration of conjugated polymers, and the polymer chains are prone to deposit as irregular nanoparticles or sediments. The fine structures of fibrous substrates often disappear by being covered with insoluble conjugated polymers. We report herein the first successful example of the nanocoating of polypyrrole (PPy) on a natural cellulosic substance with complex nanostructures. Nanocomposites with morphological hierarchies down to nanometre scales were synthesized by means of a polymerization-induced adsorption process.

Thin films of conjugated polymers can be obtained *via in situ* deposition methods.[5] We developed the polymerization-induced adsorption process for the preparation of ultrathin films of insoluble polymers on solid substrates.[6] In the present study, we modified the deposition process to fit the nanocoating of cellulose fibers. Commercial filter paper was employed as the cellulose substrate.



Scheme 1

Oxidative polymerization of pyrrole monomer was started by copper chloride in 2-propanol (Scheme 1). In a typical procedure to prepare a PPy–cellulose bi-hybrid composite, a 2.0 mL $CuCl_2 \cdot 2H_2O$ solution (10 mg mL^{-1} in 2-propanol) was added dropwise into a 40.0 mL pyrrole solution (5 vol% in 2-propanol) with stirring. The reaction mixture turned black within a few minutes and a black PPy precipitate gradually formed. The polymerization was allowed to proceed for 30 min, and then the reaction mixture was filtered to remove the bulk PPy. The clear filtrate, a very dilute polymerization solution, was used for the PPy coating of cellulose fibers. Twenty millilitres of the filtered solution were added into a glass funnel, in which a piece of commercial quantitative ashless filter paper (Advantec Toyo, Japan) was placed, and the first 10 mL of the solution were slowly suction-filtered through the filter paper, and the solution was left to stand for 2 hours. PPy was slowly formed and continuously deposited on the surface of the cellulose fibers. The filter paper was observed to turn deep grey slowly due to the deposition of PPy, while the solution remained transparent. The remaining 10 mL of the solution were thereafter filtered off, and the filter paper was thoroughly washed with 2-propanol and water, followed by drying with an air flow.

The inset in Fig. 1a shows a photograph of the obtained PPy-coated cellulose sheet, which possesses the shape and flexibility of the cellulose filter paper, but should be mentioned as a new

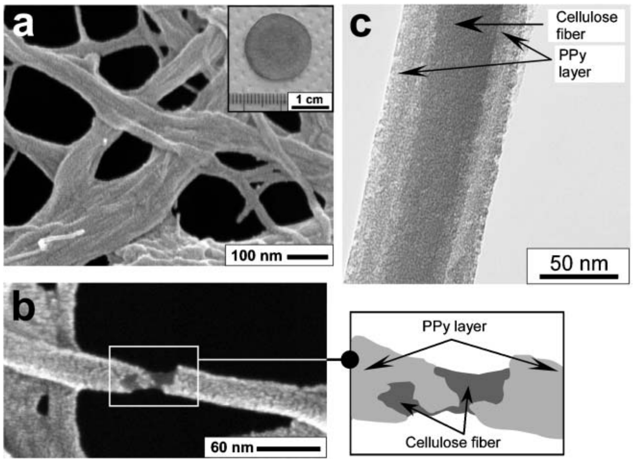


Fig. 1 (a) FE-SEM image of a PPy-coated cellulose sheet, displaying the fibrous assembly. The inset is a photograph of the bulk sheet. (b) FE-SEM image of a PPy-coated cellulose fiber which was broken by extended exposure to the electron beam. Morphology of the broken part is schematically illustrated in the right inset. (c) TEM image of a PPy-coated cellulose fiber.

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† Electronic supplementary information (ESI) available: experimental details, Figs. S1 and S2. See http://www.rsc.org/suppdata/cc/b4/b415339a/
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polymer textile. A field emission scanning electron microscopy (FE-SEM) image reveals that the sheet is composed of continuous interconnected nanofiber networks (Fig. 1a), which remains the original nanomorphology of filter paper. The nanofibers remarkably extended along the long axis when being focused by the electron beam during electron microscopy observation and occasionally resulted in the rupture of the PPy layer, showing a cable-like core-shell structure (Fig. 1b). Fig. 1c presents a transmission electron microscopy (TEM) image of an individual composite fiber, indicating that a flat and homogeneous PPy layer is seamlessly adhered onto the cellulose fiber. The thickness of the PPy layer is 20–25 nm, which can be precisely controlled by changing the adsorption time.[6]

Subsequently, we examined polymer nanocoating of modified cellulose fibers. We have reported that cellulose fibers (Fig. 2a) could be nanoprecisely coated with ultrathin titania layers[2] (Fig. 2b; calcination of the titania-coated cellulose fiber yields an anatase nanotube, as shown in inset 2). Here the titania-coated cellulose fibers were further coated with a thin PPy layer under the same experimental conditions as mentioned above. A photograph of the obtained titania–PPy bi-coated cellulose sheet is shown in the inset of Fig. 2d. The sheet is composed of fibrillar assemblies on the nanometre scale (Fig. 2d). Each cellulose fiber is coated with ultrathin layers of titania and PPy, as demonstrated by the TEM image shown in Fig. 2c. The PPy layer is homogeneous with a flat surface in spite of the roughness of the titania surface. Its thickness is 10–15 nm (Fig. 2e), thinner than that of the PPy layer which is directly deposited on the cellulose surface. This difference is probably caused by the different surface properties of cellulose and the titania gel layer.

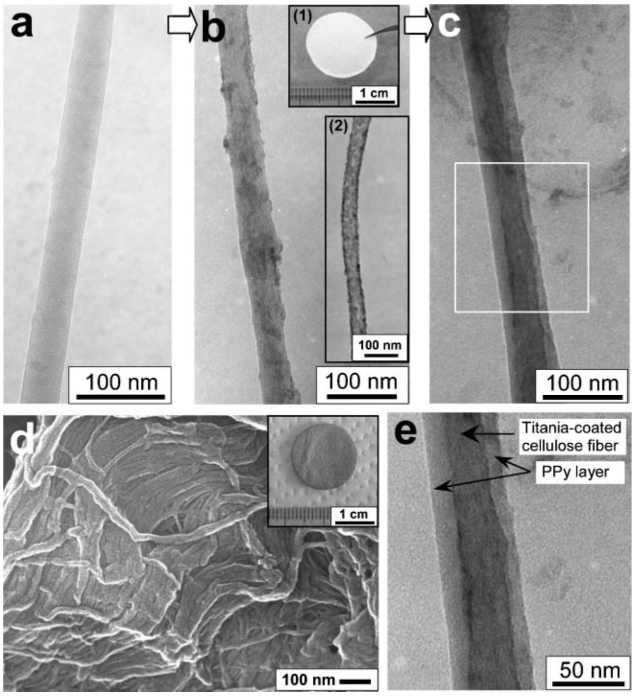

Fig. 2 (a) TEM image of a virgin cellulose fiber of filter paper. (b) TEM image of a titania-coated cellulose fiber. Inset 1 is a photograph of the as-prepared titania-coated cellulose sheet; inset 2 is a TEM image of a titania nanotube that was obtained by calcination of the above coated fiber. (c) TEM image of a PPy–titania bi-coated cellulose fiber. (d) FE-SEM image of the PPy–titania bi-coated cellulose sheet, demonstrating the fibrous assembly. The inset shows a photograph of the bulk sheet. (e) TEM image of the morphological details of the boxed area in (c).

Nanocoating of PPy was free from the macroscopic morphological change of substrates. However, interesting surface behaviors were observed for the above cellulose-derived composite sheets. Pure cellulose filter paper is extremely hydrophilic, and the PPy-coated cellulose sheet (Fig. 1a, inset) behaves in the same way. In contrast, the titania-coated cellulose sheet (Fig. 2b, inset 1) shows remarkable hydrophobicity with a contact angle of $\sim 120^\circ$ for water. However, after subsequent PPy coating, the resulted hybrid sheet (Fig. 2d, inset) shows decreased hydrophobicity with a contact angle of $\sim 50^\circ$ (Fig. S1, see ESI†). It is noteworthy that our current nanocoating approach provides a way to control the surface physical properties of cellulosic substances.

In previous reports, coating of nanoparticles with PPy was performed by template polymerization using surfactant bilayers that adsorbed on the nanoparticle surface.[7] Pyrrole monomers were firstly condensed onto the bilayers, followed by oxidative polymerization to form PPy shells. Yang *et al.* developed an interfacial polymerization technique to coat copper sulfide nanorods with thin PPy layers, which was based on the adsorption of pyrrole monomers on a Cu_2S surface.[8] Unfortunately, neither of the above approaches is applicable to cellulose fibers, because pyrrole monomers cannot be adsorbed (or immobilized) onto a cellulose surface. The current achievement of PPy nanocoating is due to the advantage of the polymerization-induced adsorption, which is based on the adsorption of growing polymer chains from solution, and on the subsequent immobilization to give thin films.[6] Conformation of PPy chains is fixed parallel to the surface of cellulose fibers, since the oligomers are flatly adsorbed on the surface and further polymerized in the lateral direction while the polymer chain has the mobility. By using a very dilute polymerization solution, an ultrathin PPy layer can be deposited on various substrates with different nanomorphologies. For example, the titania (anatase) nanotubes (Fig. 2, inset 2) were coated with a PPy layer with a thickness of less than 10 nm, providing a novel composite material (Fig. S2, see ESI†).

The potential applications of conjugated polymers are often hampered by their inherent intractability. Although nanostructured conjugated polymers have been synthesized by various approaches to overcome the drawbacks and to obtain enhanced physical and mechanical properties,[9] hierarchical deposition and morphology control of the conjugated polymers remains to be a very stimulating challenge. Our current approach provides an efficient methodology for designing conjugated polymeric materials with unique morphological features. The achievement of nanoprecise polymer coating on natural cellulose substances offers ideal materials with good processability for real applications such as novel types of conductive textiles. Moreover, the resultant polymer-contained composite sheets possess high mechanical strength due to the existence of the cellulose network, as well as a large surface area of polymer due to the fibrillar morphology. In addition, conjugated polymer–metal oxide composites are attracting a great deal of interest because of the combination of the unique photonic, electronic, and chemical properties of both components.[10] The current fiber nanoengineering provides a pathway to various practical hybrid materials with desired functions thanks to the rich varieties of natural fibers, metal oxides, and conjugated polymers.

In conclusion, a facile chemical approach was developed to enable nanoprecise coating of conjugated polymers on natural cellulose fibers without disrupting their morphological hierarchies. The technique is of sufficient generality for various polymers and substrates, and opens up new doors for nanostructured materials of insoluble conjugated polymers.

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Notes and references

1 Y. Li, Y.-W. Mai and L. Ye, *Compos. Sci. Technol.*, 2000, **60**, 2037; B. Singh, M. Gupta, A. Verma and O. S. Tyagi, *Polym. Int.*, 2000, **49**, 1444; A. Carlmark and E. Malmström, *J. Am. Chem. Soc.*, 2002, **124**, 900; A. Carlmark and E. Malmström, *Biomacromolecules*, 2003, **4**, 1740.

2 J. Huang and T. Kunitake, *J. Am. Chem. Soc.*, 2003, **125**, 11834; R. A. Caruso, *Angew. Chem., Int. Ed.*, 2004, **43**, 2746; J. Huang, T. Kunitake and S. Onoue, *Chem. Commun.*, 2004, 1008.

3 Y. Lvov, G. Decher and H. Möhwald, *Langmuir*, 1993, **9**, 481; Y. Lvov, H. Haas, G. Decher and H. Möhwald, *J. Phys. Chem.*, 1993, **97**, 12835; F. Caruso, R. Caruso and H. Möhwald, *Science*, 1998, **282**, 1111.

4 R. V. Gregory, W. C. Kimbrell and H. H. Kuhn, *Synth. Met.*, 1989, **28**, 823; H. H. Kuhn and W. C. Kimbrell, *US Patent 4975317*, 1990; K. W. Oh, K. H. Hong and S. H. Kim, *J. Appl. Polym. Sci.*, 1999, **74**, 2094; M. S. Kim, H. K. Kim, S. W. Byun, S. H. Jeong, Y. K. Hong, J. S. Joo, K. T. Song, J. K. Kim, C. J. Lee and J. Y. Lee, *Synth. Met.*, 2002, **126**, 233.

5 J. H. Cheng, A. F. Fou and M. F. Rubner, *Thin Solid Films*, 1994, **244**, 985; A. C. Fou and M. F. Rubner, *Macromolecules*, 1995, **28**, 7115; M. S. Paley, D. O. Frazier, H. Abdeldeyem, S. Armstrong and S. P. McManus, *J. Am. Chem. Soc.*, 1995, **117**, 4775.

6 I. Ichinose, H. Miyauchi, M. Tanaka and T. Kunitake, *Chem. Lett.*, 1998, 19; I. Ichinose and T. Kunitake, *Adv. Mater.*, 1999, **11**, 413.

7 G. Cho, D. T. Glatzhofer, B. M. Fung, W.-L. Yuan and E. A. O'Rear, *Langmuir*, 2000, **16**, 4424; G. Cho, B. M. Fung, D. T. Glatzhofer, J.-S. Lee and Y.-G. Shul, *Langmuir*, 2001, **17**, 456; H. J. Shin, I.-W. Hwang, Y.-N. Hwang, D. Kim, S. H. Han, J.-S. Lee and G. Cho, *J. Phys. Chem. B*, 2003, **107**, 4699.

8 W. Zhang, X. Wen and S. Yang, *Langmuir*, 2003, **19**, 4420.

9 C. R. Martin, *Science*, 1994, **266**, 1961; A. D. W. Carswell, E. A. O'Rear and B. P. Grady, *J. Am. Chem. Soc.*, 2003, **125**, 14793; Y. Ma, J. Zhang, G. Zhang and H. He, *J. Am. Chem. Soc.*, 2004, **126**, 7097; B. W. Maynor, S. F. Filocamo, M. W. Grinstaff and J. Liu, *J. Am. Chem. Soc.*, 2002, **124**, 522; J. Huang and R. B. Kaner, *J. Am. Chem. Soc.*, 2004, **126**, 851; W. Li and H.-L. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 2278; X. Zhang, W. J. Goux and S. K. Manohar, *J. Am. Chem. Soc.*, 2004, **126**, 4502; J. Jang and H. Yoon, *Chem. Commun.*, 2003, 720; J. Jang and J. H. Oh, *Chem. Commun.*, 2004, 882.

10 R. Gangopadhyay and A. De, *Chem. Mater.*, 2000, **12**, 608; H. Xia and Q. Wang, *Chem. Mater.*, 2002, **14**, 2158; D. C. Schnitzler, M. S. Meruvia, I. A. Hümmelgen and A. J. G. Zarbin, *Chem. Mater.*, 2003, **15**, 4658; S. Roux, G. J. A. A. Soler-Illia, S. Demoustier-Champagne, P. Audebert and C. Sanchez, *Adv. Mater.*, 2003, **15**, 217; R. Cervini, Y. Cheng and G. Simon, *J. Phys. D: Appl. Phys.*, 2004, **37**, 13.