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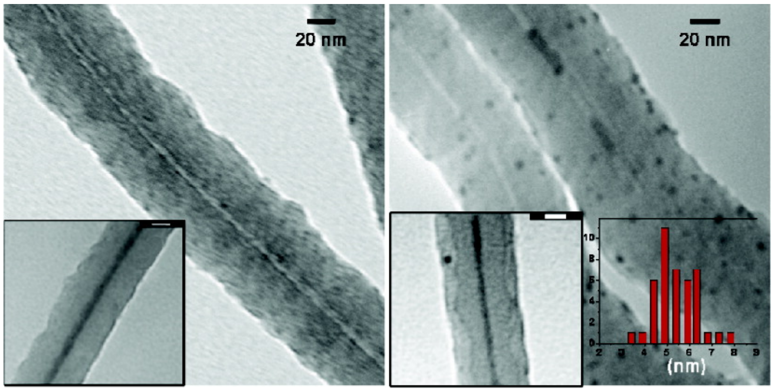

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Narrow Pore-Diameter Polypyrrole Nanotubes

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We describe the bulk synthesis of microns long electrically conducting polypyrrole nanotubes having 6 nm average pore diameter by chemical oxidative polymerization of pyrrole using $FeCl_3$ oxidant and V_2O_5 nanofibers as the sacrificial template. These nanotubes undergo a spontaneous redox reaction with noble metal ions under mild aqueous conditions, resulting in deposition of 3−8 nm size particles of Ag, Au, Pd, etc., on the tube surface. Metal nanoparticles rapidly migrate from the nanotube surface to the pore and, in the case of Ag, coalesce in the core, yielding 4−8 nm diameter coaxial cables of Ag surrounded by a 20−30 nm thick polypyrrole fiber sheath, affording a facile entry into this technologically important class of metal−polymer nanocomposites.

In contrast to the myriad of synthetic approaches to nanofibers of conducting polymers,[1] there are fewer reports on the synthesis of conducting polymer nanotubes.[2] Soft (organic) template approaches include the use of large organic dopant anions and surfactant-based reverse microemulsion systems,[3] while hard (inorganic) template approaches involve solution or vapor phase polymerization along the pore walls of anodic aluminum oxide,[4] track-etched membranes,[5] etc. Pore diameters in the 20−100 nm range have been synthesized using hard templates.[3,4] To the best of our knowledge, there has not been a report of conducting polymer nanotubes having inner (pore) diameter less than 10 nm. In this study, we report a simple and rapid method to chemically synthesize bulk quantities of 60−80 nm diameter (outer diameter) nanotubes of doped polypyrrole having pore diameter in the range of 4−8 nm using a variation of our recently reported "nanofiber seeding" method to synthesize nanofibers of polypyrrole (V_2O_5-seeding).[6] When used in larger amounts, V_2O_5 nanofibers do not act as seeds but as polymerization templates (V_2O_5-templating), yielding nanotubes composed of a solid V_2O_5 pore surrounded by a polypyrrole sheath. The V_2O_5 in the pore dissolves readily in dilute aqueous acids during the product purification step, yielding hollow polypyrrole nanotubes.

Polypyrrole nanotubes were synthesized by V_2O_5-templating as follows. A mixture of ethanol (50 mL) and 10−15 nm diameter nanofibers of V_2O_5 sol−gel (2.0 mL)[6] was magnetically stirred for 12 h, and pyrrole monomer (14.9 mmol) was added, followed by anhydrous $FeCl_3$ oxidant (10 mmol) to initiate the polymerization. The solution immediately turned dark brown, and after 1 h, the black precipitate of polypyrrole nanotubes having 10−15 nm diameter V_2O_5 cores was suction filtered and suspended in aq. 1.0 M HCl (100 mL) for 2 h to leach out the V_2O_5 from the pore. Suction filtration followed by drying under dynamic vacuum at 80 °C for 12 h yielded ~50 mg of polypyrrole nanotubes having conductivity of $\sigma_{RT} \sim 2$ S/cm (pressed pellet). The bulk precipitate is composed entirely of a nonwoven mesh of 2−4 μm long nanotubes of doped polypyrrole having 4−8 nm pore diameter and 60−80 nm outer diameter (Figure 1). The control experiment carried out in the absence of V_2O_5 yielded only granular polypyrrole•Cl, as shown in Supporting Information.

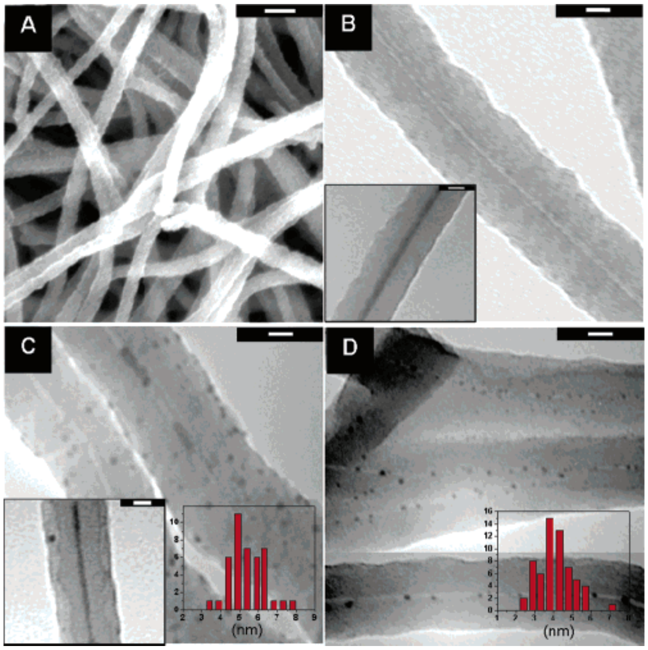

Figure 1. Polypyrrole•Cl nanotubes: (A) SEM, as-synthesized. (B) TEM, as-synthesized showing hollow tube. Inset: TEM showing pore filled with V_2O_5. (C) TEM, Ag nanocomposite. Insets: coaxial cable of Ag and particle size distribution (D) TEM, Au nanocomposite. Inset: particle size distribution. Scale: (A) 100 nm; (B, C, D) 20 nm.

The elemental composition of the nanofibers by EDX is as follows: C, 62.38; N, 18.83; Cl, 15.39; O, 3.40; consistent with the structure $(PPy)(Cl)_{0.32}(H_2O)_{0.16}$ and similar to polypyrrole•Cl nanofibers obtained in the V_2O_5-seeded polymerization of pyrrole in aq. 1.0 M HCl.[6] Vibrational spectra (KBr pellet) and aqueous electrochemistry are also consistent with polypyrrole•Cl nanofibers synthesized by V_2O_5-seeding. There are, however, significant differences in the synthetic method between the templating and seeding systems apart from the lower conductivity of nanotubes (2 S/cm) compared to that of nanofibers (50 S/cm). While fibrillar polymer growth is favored under aqueous acidic conditions having seed quantities of V_2O_5 nanofibers, tubular polymer growth is favored under nonaqueous neutral conditions containing larger amounts of V_2O_5 nanofibers; for example, 2−3 times the amount of V_2O_5 nanofibers is used in V_2O_5-templating versus V_2O_5-seeding systems. The reaction yield is also significantly lower (e.g., 18% for nanotubes versus 95% for nanofibers). The combination of low reaction yield and high V_2O_5 amounts in the reaction mixture is consistent with V_2O_5 nanofibers acting as templates rather than seeds during the polymerization; that is, there are sufficient V_2O_5 nanofibers to constitute the core of the polypyrrole nanotubes that are formed. We believe that nanotube formation proceeds as follows: (i) adsorption and oxidative polymerization of pyrrole on the surface of the V_2O_5 nanofiber template, which constitutes the

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pores of the tube, and (ii) removal of the V_2O_5 template by aq. 1.0 M HCl during the purification step. We have previously shown in the V_2O_5-seeded system that V_2O_5 nanofibers act as sacrificial seeds and dissolve readily in aq. 1.0 M HCl during the synthesis of polypyrrole nanofibers.[6] Under neutral and largely nonaqueous conditions, however, the V_2O_5 nanofibers would remain in suspension and act as templates for polymerization, yielding, as the initial product, coaxial cables composed of 10−15 nm diameter V_2O_5 core encased in 60−80 nm diameter polypyrrole sheath (Figure 1B inset). Both TEM images and elemental analysis of this initial product (C, 56.06; N, 16.38; Cl, 11.96; O, 4.92; V, 4.51; Fe, 6.17) are consistent with this rationale. Upon "washing" with aq. 1.0 M HCl, there is complete removal of both V and Fe ($FeCl_4^-$ dopant replaced by Cl^-), resulting in tubes with a pore diameter in the 4−8 nm range. It is important to note that, although the pore diameter gets smaller upon removal of V_2O_5, the tube does not collapse to yield a fiber, opening opportunities to "back-fill" the core with oxides, metals, etc.

As-synthesized doped polypyrrole nanotubes with hollow pores spontaneously reduce noble metal ions to the corresponding metal nanoparticles at room temperature without any capping or dispersing agents and are themselves oxidized in the process.[7] For example, 3−5 nm nanoparticles of Ag, Au, and Pd, etc., deposit readily on the surface of the tubes, which then migrate spontaneously to the pore. Metal ion reduction is extremely rapid in the Ag^+/Ag system and is complete in less than 5 min, while Au^{3+}/Au system takes ~1 h. Narrow particle-size distributions are observed for both Ag and Au nanocomposites, that is, 3−8 nm range with an average of 5.4 nm for Ag and 2−7 nm range with an average of 4.1 nm for Au (Figure 1C,D). Ag nanoparticles also readily agglomerate in the pore, yielding 4−8 nm diameter Ag nanocables encased in a polypyrrole sheath (Figure 1C inset), and these nanocables are present alongside Ag nanoparticles on the tube surface and in the interior of the polypyrrole sheath. In contrast, Au nanoparticles are observed in the pore region (Figure 1D).

While there are a few recent reports on the synthesis and applications of metal/polyaniline nanocomposites,[8] to our knowledge, the present study is the first use of doped conducting polypyrrole to chemically synthesize noble metal nanoparticles less than 5 nm in size under mild aqueous conditions. We believe significant opportunities exist at particle sizes below 10 nm when surface free energy contributions to the total free energy of the system become more important. In a recent study on the aqueous electrochemistry of 3−7 nm size monolayer-coated Ag nanoclusters,[9] a correlation was observed between particle size and separation between anodic and cathodic peaks ($E_{ox} - E_{red}$), although the high resistivity of the monolayer coating was responsible for small peak currents and considerable irreversibility in redox behavior. In contrast, Ag/polypyrrole composites display high currents and excellent reversibility that is most likely facilitated by the electrically conducting and redox active polypyrrole matrix (Figure 2). Compared to Ag wire (control), the redox peaks for the Ag/polypyrrole composite are more symmetric with a significantly smaller $E_{ox} - E_{red}$ value consistent with small Ag particle size (400 versus 600 mV).[9] Redox equilibrium is established quickly in the composite with very little drift in the redox peak positions from the initial scan. The magnitude of $E_{ox} - E_{red}$ as a function of scan rate is also similar for the two systems, indicating rapid electron transfer despite a semiconducting polypyrrole matrix (Figure 2 inset). In this regard, it is to be noted that the conductivity of the Ag/polypyrrole composite (10^{-2} S/cm) is lower than that of as-synthesized polypyrrole nanotubes (2 S/cm), presumably as a result of oxidation of the polypyrrole backbone (over-oxidation) during redox reaction with noble metal ions (see Supporting Information).

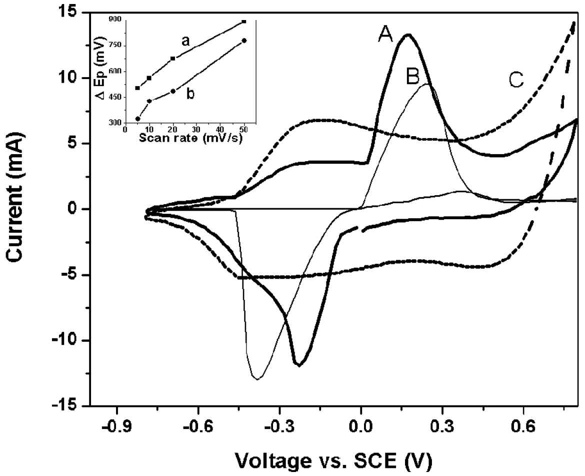

Figure 2. Cyclic voltammetry of (A) Ag/polypyrrole nanotube composite; (B) Ag wire. (C) As-synthesized polypyrrole nanotubes (aq. 1.0 M NaCl electrolyte, 20 mV/s, SCE reference). Inset: Scan rate dependence of (a) Ag wire; (b) Ag/polypyrrole nanotube composite.

In summary, the rapid, one-step reaction of the as-synthesized polypyrrole nanotubes with metal ions to yield highly electroactive nanoparticles coupled with the equally facile synthesis of small pore diameter polypyrrole nanotubes could open new opportunities in a myriad of applications, such as energy storage systems, catalysis, fuel cell membranes, nanoelectronics devices, and antibacterial coatings. The method is general and can be extended to other conducting polymers, such as polythiophene and PEDOT nanotubes.

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Supporting Information Available: SEM, TEM, FTIR of polypyrrole and composites. This material is available free of charge via the Internet at http://pubs.acs.org.

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