

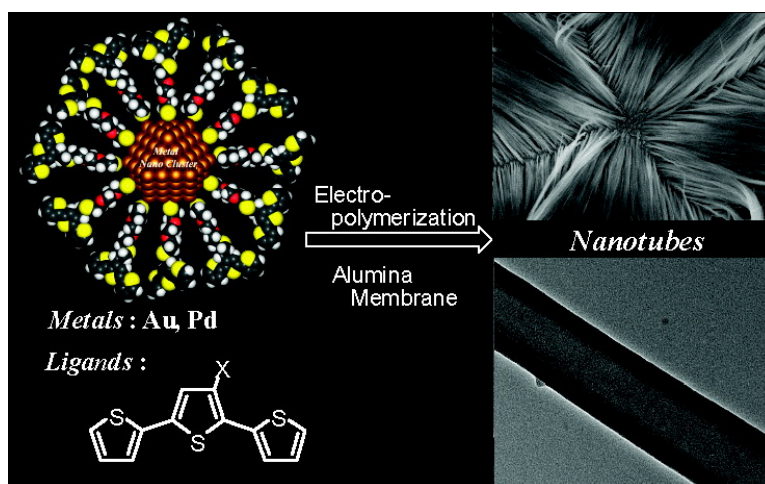
Communication

## Nanotube Composites Consisting of Metal Nanoparticles and Polythiophene from Electropolymerization of Terthiophene-Functionalized Metal (Au, Pd) Nanoparticles

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## Nanotube Composites Consisting of Metal Nanoparticles and Polythiophene from Electropolymerization of Terthiophene-Functionalized Metal (Au, Pd) Nanoparticles

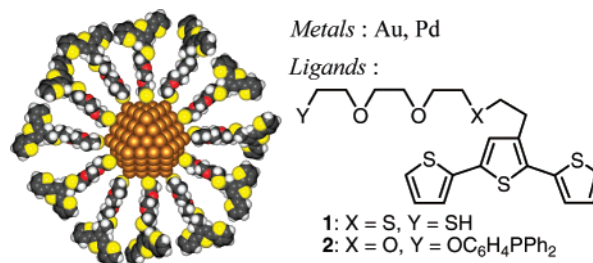
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In recent years, nanostructured materials such as carbon nanotubes, polymer nanotubes, metal nanotubes, and metal nanoparticles have received a great deal of attention due to their unique physical and chemical properties as well as their enormous potential applications such as catalysts, nanoelectronic devices, magnetic devices, sensors, and biomaterial separation membranes.<sup>1–5</sup> It is advantageous or required to modify their nanotubes by physical or chemical methods to optimize their use in many applications. Although several methods have been developed to functionalize carbon nanotubes with inorganic and organic materials,<sup>1</sup> related works on polymer nanotubes and metal nanotubes have been reported in only a few cases. Polymer nanotubes of thiophene, pyrrole, and aniline have been prepared by their electrochemical and chemical oxidations in a nanoporous alumina membrane as a template.<sup>2</sup> The functionalization of the polymer nanotubes with organic molecules or metal nanoparticles has received less attention.<sup>3</sup> Analogously, only a few examples on the synthesis of metal nanotubes have been reported,<sup>4</sup> which deal with the reduction of metallic complexes and immobilization of metal nanoparticles within the pores of a nanoporous alumina template. Metal nanoparticles have been the focus of much current research due to their potential uses in catalysis and nanotechnology.<sup>5–7</sup> In particular, the combination of conducting polymers and metal nanoparticles provides an exciting system to investigate with the possibility of designing nanotube functionality. There are fewer reports on the synthesis of functionalized polymer nanotubes with metal nanoparticles, in which metal nanoparticles were deposited into the cavities or onto the external walls of polymer nanotubes by a reduction of metal ions.<sup>3</sup> In contrast, the preparation of nanotube composites consisting of metal nanoparticles and polythiophene (PT) as a constituent of nanotubes (NTs) by electropolymerization of thiophene-modified metal nanoparticles has never been reported.

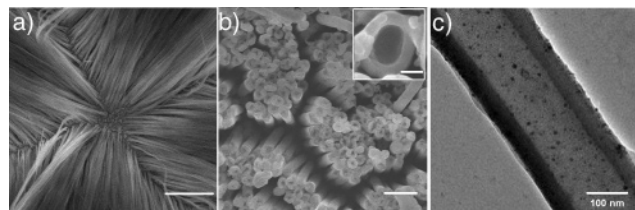
We have developed a new method for the fabrication of metal nanoparticle/polythiophene nanotube composites, i.e., the template-based electrochemical oxidative polymerization of terthiophene-linked oligoethyleneoxy-thiol (**1**) and -phosphine (**2**)-stabilized gold and palladium nanoparticles (**1**-Au, **1**-Pd, and **2**-Pd) in a nanoporous alumina membrane as a template gave the nanotube composites (**1**-Au-PT-NTs, **1**-Pd-PT-NTs, and **2**-Pd-PT-NTs) of polythiophene and the metal nanoparticles without aggregation of the metal nanoparticles.<sup>8</sup> This novel approach offers a new way for efficiently creating hybrid nanotubes. Moreover, we have found that the Pd nanoparticle/polythiophene nanotube composites can efficiently catalyze the carbon–carbon coupling reaction, in which the nanotubes can be recovered after the reaction and reused.<sup>9</sup> This communication presents a new method for the fabrication of metal nanoparticle/polythiophene nanotube composites and the preliminary test for the catalytic property of the Pd nanoparticle/polythiophene nanotube composites.



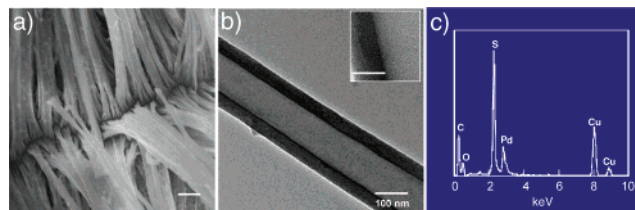
The nanotube composites (**1**-Au-PT-NTs and **1**-Pd-PT-NTs) from **1**-Au ( $2.3 \pm 0.7$  nm) and **1**-Pd ( $2.7 \pm 0.6$  nm) nanoparticles<sup>10</sup> were synthesized through an electrochemical polymerization method using a nanoporous alumina membrane (Whatman Anodisc; average pore diameter of about 200 nm, thickness of 60  $\mu$ m) as the template.<sup>11</sup> The electrochemical synthesis was performed by attaching the alumina membrane to a Pt electrode, another Pt electrode was used as the counter electrode, and Ag/0.1 M AgNO<sub>3</sub> was used as the reference electrode. The electrolysis solution contains **1**-Au or **1**-Pd nanoparticles (12 mg) in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>–CH<sub>2</sub>Cl<sub>2</sub> (3 mL). A voltage of 1.0 V was applied. After the electrochemical synthesis, the alumina membranes were dissolved in 1 M NaOH. The UV–vis spectrum of **1**-Pd-PT-NTs exhibits the absorption due to the polythiophene at 520 nm, while the absorption at 550 nm for **1**-Au-PT-NTs is ascribed to the polythiophene and the surface plasmon resonance of the Au nanoparticles.<sup>10</sup> The nanotube composites (**1**-Au-PT-NTs and **1**-Pd-PT-NTs) were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The SEM images of gold nanoparticle/polythiophene nanotube composites, **1**-Au-PT-NTs, show better morphology in Figure 1a,b. Figure 1b shows an SEM image of **1**-Au-PT-NTs, which were grown using the alumina template;<sup>11</sup> most of them have outer diameters of about 210–250 nm. The TEM image of **1**-Au-PT-NTs reveals that the outer diameter of the nanotubes is about 240 nm, with a wall thickness of around 50 nm (Figure 1c). The elemental composition of **1**-Au-PT-NTs was confirmed by the energy-dispersive X-ray (EDX) analysis of single nanotubes, which reveals the presence of Au and S.<sup>10</sup> The size range of the particles of **1**-Au-PT-NTs is about 2–9 nm from the TEM observations.

Similarly, the nanotube composites of palladium nanoparticles and polythiophene (**1**-Pd-PT-NTs) can be prepared from the electropolymerization of **1**-Pd nanoparticles as evidenced from the SEM and TEM images (Figure 2). The TEM image of **1**-Pd-PT-NTs shows the outer diameter of about 200 nm which corresponds to the pore diameter of the alumina membrane and the inner diameter of 110 nm (Figure 2b). Figure 2c gives the EDX spectrum taken from the sample shown in Figure 2b, evidencing that the nanotubes are composed of Pd and S. The TEM observations of **1**-Pd-PT-NTs show that the palladium nanoparticles did not



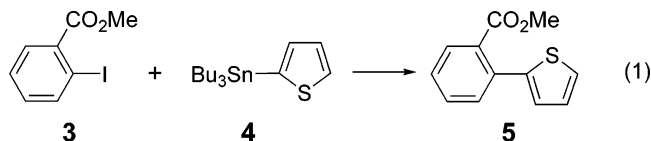
**Figure 1.** 1-Au-PT-NTs: (a) and (b) SEM image [scale bar: (a) 5  $\mu\text{m}$ ; (b) 1  $\mu\text{m}$ ]. Inset (scale bar = 100 nm): the high-magnification image. (c) TEM image.



**Figure 2.** 1-Pd-PT-NTs: (a) SEM image (scale bar = 5  $\mu\text{m}$ ). (b) TEM image. Inset (scale bar = 50 nm): the high-magnification image. (c) EDX spectrum. Cu peaks are from the supporting copper grid.

aggregate after the electropolymerization of 1-Pd nanoparticles in the alumina membrane. These results clearly indicate that the electropolymerization of 1-Au or 1-Pd nanoparticles in a nanoporous alumina template led to the formation of the nanotube composites consisting of Au or Pd nanoparticles and polythiophene as constituents of nanotubes.

A great interest has been placed on the use of metallic nanoparticles for nanocatalysis.<sup>5,7</sup> To evaluate the catalytic capability of the nanotubes, we have studied the Stille coupling reaction which is a very important carbon–carbon bond-forming reaction (eq 1).<sup>7,12</sup> The Stille coupling reaction of methyl-2-iodobenzoate (**3**) with 2-(tributylstannyl)thiophene (**4**) in the presence of the nanotubes, 1-Pd-PT-NTs, in THF at 50 °C for 5 h gave the corresponding coupling product (**5**) in a low yield of 30%. In order to improve the catalytic activity of nanotubes, we have synthesized nanotube composites of polythiophene and palladium nanoparticles stabilized by the phosphine ligand instead of the thiol group in **1**, since generally alkyl thiols and thiolates are well-known as poisons that inhibit the catalysis of reactions by metal nanoparticles.<sup>13</sup> Terthiophene-linked oligoethyleneoxy-phosphine (**2**), the phosphine **2**-stabilized palladium nanoparticles (2-Pd), and the nanotubes (2-Pd-PT-NTs) have been prepared.<sup>10</sup> The catalytic property of 2-Pd nanoparticles was tested in the Stille coupling reaction (eq 1), i.e., the reaction of **3** with **4** in the presence of 2-Pd nanoparticles and KF in THF at 50 °C for 5 h afforded the product **5**, but Pd black due to aggregation was formed during the reaction.<sup>14,15</sup> In contrast, significantly, no precipitation of Pd nanoparticles after the reaction was observed when the nanotubes of 2-Pd-PT-NTs were used for the Stille reaction. Typically, the reaction of **3** (266 mg, 1 mmol) and **4** (372 mg, 1 mmol) in the presence of 2-Pd-PT-NTs (4 mg) and KF (174 mg, 3 mmol) in THF was carried out at 60 °C for 5 h under argon to give the coupling product **5** in a quantitative yield. The nanotubes as catalyst were reused under the same conditions with essentially no loss in activity. Importantly, this finding demonstrates that the surface atoms of the palladium in 2-Pd-PT-NTs possess catalytic activity.



In summary, the novel nanotube composites consisting of Au or Pd nanoparticles and polythiophene have been successfully fabricated by the electropolymerization of terthiophene-functionalized Au or Pd nanoparticles in a nanoporous alumina membrane. The Pd/polythiophene nanotube composites (2-Pd-PT-NTs) are recyclable highly effective catalysts for the carbon–carbon coupling reaction, although 2-Pd nanoparticles were aggregated during the reaction. This new method is currently being extended to other metal and metal oxide nanoparticles/polythiophene nanotube composites to realize a wide range of hybrid nanomaterials with controllable surface chemistry. We expect this work to yield a broad range of potential applications in catalysis, nanoelectrochemistry, chemical/biological separation, and sensor developments.

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**Supporting Information Available:** Synthesis of **1**, **2**, 1-Au, 1-Pd, 2-Pd, and the nanotubes, the spectral data, the SEM and TEM images, and the EDX spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Compounds (**1** and **2**) were designed for the following reasons: (i) Since metal nanoparticles are unstable with respect to aggregation and precipitation to the bulk metal, stabilizers such as thiols and phosphines are used in their preparation to prevent agglomeration.<sup>5</sup> (ii) The oxidation potential of terthiophene is lower than that of thiophene. (iii) The oligoethyleneoxy linkage is hydrophilic in nature since the pore walls of the porous alumina membrane possess hydrophilic sites.
- (9) Palladium nanoparticles have been of increasing scientific interest as a catalyst for the carbon–carbon coupling reaction.<sup>7</sup>
- (10) See the Supporting Information.
- (11) The diameter of the alumina membrane obtained from Whatman Inc. was found to be 220  $\pm$  15 nm, as revealed by SEM.
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- (14) Pd nanoparticles are known to aggregate easily and form Pd black.<sup>5,7</sup>
- (15) The catalytic properties of the Pd nanoparticles and their nanotube composites are discussed in the Supporting Information.

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