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A Highly Efficient Palladium Nanocatalyst Anchored on a Magnetically Functionalized Polymer-Nanotube Support**

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Heterogeneous catalysts have been extensively employed in various fields because they have fewer of the drawbacks of homogeneous catalysts, such as the difficulties in recovery and regeneration.[1] Nanometer-sized catalyst supports have recently attracted a great deal of interest because of their high surface area and outstanding stability and activity in the liquid phase.[2,3] In particular, nanotube-supported catalysts have been selected for highly efficient catalysis because they provide different contact areas that can be functionalized in various ways.[3a] Even though several significant studies regarding nanotube supports have been reported, their complicated functionalization and a lack of surface-functionality control remain major obstacles to practical applications. Magnetic supports have been used as an effective tool for convenient catalyst recycling by applying an external magnetic field.[2a,b] However, most of these examples suffer from the need for a sophisticated synthetic procedure for surface deposition and the aggregation of magnetic particles in the infiltration approach.[3b] Therefore, it is still important to develop a reliable synthetic route to highly efficient reusable catalysts.

Herein, we report a novel approach for the facile fabrication of magnetic polypyrrole nanotubes and subsequent controlled deposition of Pd nanocatalysts on the nanotube surface. Carboxylated pyrrole monomers are chemically polymerized in the presence of iron(III) chloride as an oxidizing agent, and magnetic phases are readily introduced into the nanotubes by precipitation of residual iron salt complexes during the template removal process. These magnetic carboxylated polypyrrole nanotubes (MCPPy NTs) provide the anchoring sites for metal salts, thus making it possible to generate Pd nanocatalyts quantitatively at room temperature without tedious surface functionalization. This is the first demonstration of the fabrication of a magnetically separable polymer nanotube support containing intrinsically functionalized repeating units.

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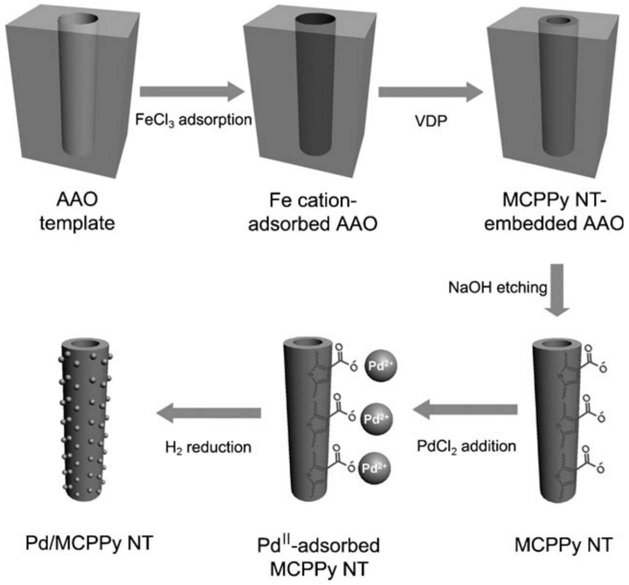
Scheme 1 describes the synthetic route to Pd nanocatalysts supported on magnetically functionalized nanotubes (Pd/MCPPy NTs). MCPPy NTs were first prepared by vapor-deposition polymerization (VDP).[4] Vaporized pyrrole-3-carboxylic acid monomers were chemically polymerized by Fe cations adsorbed on an anodic aluminum oxide (AAO) membrane at 150 °C and 10^{-2} Torr. The magnetic phases were introduced into the polymer during template removal by treatment with a base.[5] Typically, the conducting polymers exist in their oxidized forms owing to electron localization by the dopants (Fe salts).[6] These Fe salt complexes in the polymer backbone were reduced to magnetites by treatment with sodium hydroxide (0.1 M).



Scheme 1. Synthetic route to Pd/MCPPy NTs.

The MCPPy NTs provide a defined number of homogeneous surface carboxylate groups since the polymer nanotubes consist of pyrrole monomers with a carboxylic acid moiety. These surface functional groups were subsequently used as the nucleation sites for metal ions.[7] Thus, Pd cations were electrostatically bound to the carboxylate groups of the MCPPy NTs. The carboxylate groups induce electron transfer to Pd^{II} to form Pd^0 in the presence of H_2 as the reducing species.[8] The Pd nanoparticles were retained on the nanotubes because the carbonyl groups of MCPPy NTs coordinate strongly to the surface atoms of the nanoparticles.[9] Surface carboxylate groups therefore enhance the stability of Pd nanoparticles anchored by this salt reduction method.

The successful polymerization to form MCPPy NTs was confirmed by Raman spectroscopy (Supporting Information). The characteristic bands of polypyrrole at 930, 1332, and 1580 cm^{-1} were attributed to the C–H, C–N, and C=C stretching modes, respectively. The peaks of the symmetrical C–H in-plane bending between 930 and 981 cm^{-1} were assigned to the dications (bipolaron) and radical cations (polaron). The relatively high intensity of the bipolaron peak at 930 cm^{-1} indicates a high charge-carrier density, as corroborated by the high electrical conductivity of $3\times 10^{-2}\,S\,cm^{-1}$.

Figure 1 shows TEM images of MCPPy NTs and Pd/MCPPy NTs. The MCPPy NTs (Figure 1A) have a tailored nanotube morphology, with a diameter of around 100 nm, a uniform wall thickness of 10–20 nm, and an inner vacant volume. The selected area electron diffraction (SAED) pattern confirmed the presence of magnetites. Figures 1B–D show TEM images of Pd/MCPPy NTs prepared using different $PdCl_2$ solutions. As the $PdCl_2$ concentration increases from 1×10^{-4} to 5×10^{-3} M (not shown), the size of the deposited Pd nanoparticles increases from a lower limit of 3.6 to an upper limit of 9.8 nm. Fast nucleation relative to growth produces a small particle size at low concentrations of Pd salt.[10] Figures 1B and 1C show that relatively uniform Pd nanoparticles are formed on the surface of the MCPPy NTs. The SAED pattern (inset in Figure 1B) of the Pd/MCPPy NTs also shows the presence of Pd on the nanotube. These Pd nanoparticles have a narrow size distribution (the inset histogram of Figure 1C). However, the nanoparticle size distribution becomes large as the concentration of Pd precursor increases (Figure 1D).

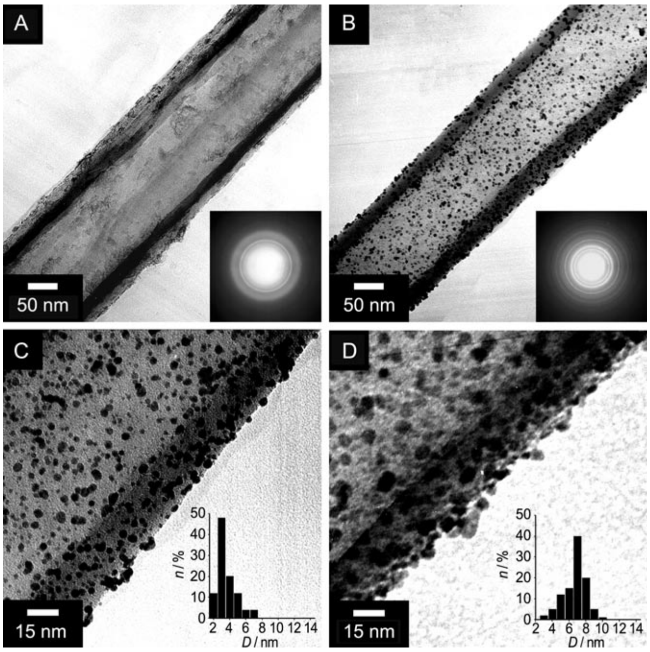


Figure 1. TEM images of A) a MCPPy NT and B) a Pd/MCPPy NT prepared with a dilute $PdCl_2$ solution (1×10^{-4} M). The inset images are the SAED patterns; C) and D) magnified TEM images of Pd/MCPPy NTs obtained using different $PdCl_2$ concentrations (1×10^{-4} and 1×10^{-3} M, respectively). The Pd nanoparticle size was determined by counting 100 Pd nanoparticles by TEM and is illustrated in the inset histogram (C: (3.6 ± 1.3) nm; D: (6.7 ± 3.1) nm).

The fraction of Pd deposited from solution onto the nanotubes was calculated by thermogravimetric analysis. Almost 99 % of the Pd ions in solution were deposited from a 10^{-4} M $PdCl_2$ solution, whereas only 69 % of the Pd in solution were deposited with a 5×10^{-3} M $PdCl_2$ solution, a consequence of the excess of Pd ions. This novel synthetic route to Pd/MCPPy NTs may provide a facile means of synthesizing other metal nanoparticles on MCPPy NTs.

The Pd/MCPPy NTs were also characterized by powder X-ray diffraction (XRD) analysis (Supporting Information) and X-ray photoelectron spectroscopy (XPS). The sharp O peak in Figure 2 demonstrates the presence of carbonyl groups in the Pd/MCPPy NTs and the two peaks at 335 and 341 eV for Pd 3d show that Pd is present as Pd^0. The XPS spectrum of the Fe 2p region (Figure 2, inset) clearly indicates that the magnetic phases are magnetites.

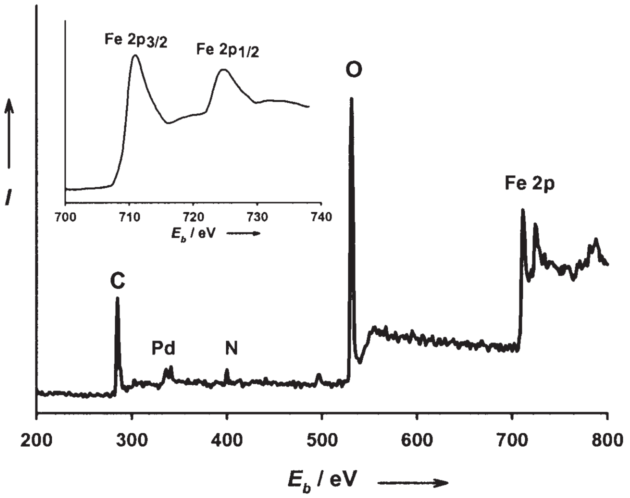


Figure 2. XP spectra of Pd/MCPPy NTs. The inset shows the spectrum in the Fe 2p region.

The magnetic properties of the MCPPy NTs were investigated with a SQUID magnetometer. The magnetization curve exhibits typical ferromagnetic behavior (Figure 3), and saturation of the magnetization ($6.7\,emu\,g^{-1}$) was found above 1.5 kOe. The coercivity (Hc) of the MCPPy NTs was observed at a field of 23 Oe. A significant enhancement of coercivity was observed relative to the value for bulk iron (Hc = 1 Oe) owing to the anisotropy of the magnetite embedded in the MCPPy NTs.[11] The photographs in Figure 3 demonstrate that the Pd/MCPPy NTs in aqueous solution can be harvested and separated by a magnetic field; this process takes about ten seconds.

To investigate the catalytic activity of Pd/MCPPy NTs three types of olefination of aryl iodides were investigated (Table 1). 4-Iodoanisole and 2-iodotoluene (entries 1 and 2) were chosen as activated aryl halides with an electron-withdrawing group and a methyl group, respectively, and butyl acrylate was used as a model aliphatic olefin as it a precursor of cinnamic ester derivatives. Cinnamic esters are used as UV absorbers in industry.[12] Iodobenzene and styrene were selected (Table 1; entry 3) as a non-activated aryl iodide and aromatic olefin, respectively. It has been reported that non-activated aryl halides are converted with only a low conversion yield.[13] The reaction was carried out in *N*,*N*-dimethylacetamide (DMA) in the presence of tributylamine and 3.6-nm Pd/MCPPy NTs.

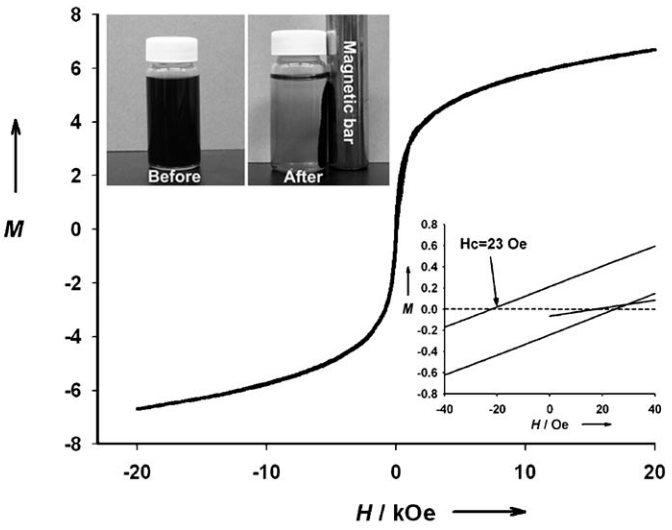
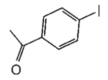
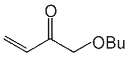
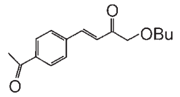
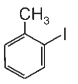
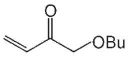
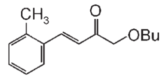
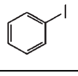
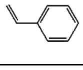
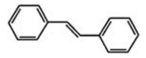


Figure 3. Magnetic behavior of Pd/MCPPy NTs at 300 K between −20 and +20 kOe (*M* in $emu\,g^{-1}$). The inset shows the magnified area between −40 and +40 Oe. The photographs demonstrate that MCPPy NTs in aqueous solution can be attracted and arranged vertically by a magnetic bar (0.3 T). MCPPy NTs completely suspended in aqueous solution can be harvested within 10 s.

Table 1: Olefination of aryl iodides.[a]

Entry	Aryl iodide	Olefin	*t* [h]	Product	Yield[b] [%]
1			3		99
2			3		98
3			3		97

[a] The reaction was carried out in DMA (20 mL) at 120°C with tributylamine (3.0 mmol), aryl iodide (2.0 mmol), and olefin (2.6 mmol) in the presence of 3.6-nm Pd/MCPPy NTs (0.01 g, 21 wt% Pd). [b] The yield was calculated by GC analysis, as described elsewhere.[1f,3a]

When the activated aryl iodides and butyl acrylate were coupled, the yields were approximately 99 and 98 %, respectively. More importantly, the non-activated aryl iodide was also converted with a high yield of 97 % under the same experimental conditions. The reaction yield with a conventional carbon-supported Pd catalyst is approximately 53 %.[3a] This remarkable increase in yield is due to the higher available surface area of the Pd nanoparticles, where edge and vertex sites are abundant.[14] Importantly, there was no loss of catalytic activity for conversion of the non-activated aryl iodide and no morphological change of the Pd/MCPPy NTs after recycling and repeating the reaction five times. On the basis of these data, the Pd/MCPPy NTs are excellent potential candidates for reusable and recoverable catalysts.

In conclusion, Pd/MCPPy NTs have been successfully fabricated by the chemical reaction of iron and palladium salts immobilized on a polymer-nanotube support prepared by vapor-deposition polymerization. In particular, the template removal process endows the Pd/MCPPy NTs with enhanced magnetic performance without the need for a complicated attachment of magnetic particles. The Pd/MCPPy NTs show excellent catalytic activity (above 97%) for the Heck coupling of aryl iodides resulting from the narrow size distribution and high surface area of the Pd nanocatalyst. In addition, these Pd/MCPPy NTs show excellent behavior as reusable catalysts of the Heck coupling. This facile methodology could be expanded to allow the fabrication of organic and inorganic nanocarriers in fields such as chemical and biosensors, data storage, separation, and drug-delivery systems.

Experimental Section

MCPPy NTs: Fe cations were adsorbed onto an AAO membrane by immersing the membrane in an $FeCl_3$ solution (0.1 M) for 5 min and then drying it in a vacuum oven for 5 h. Residual Fe cations were removed by absorbing three times with disposable sorbents to reduce the possible closing and interconnecting of the nanotubular edges. The Fe-cation-adsorbed AAO membrane and pyrrole-3-carboxylic acid (0.14 mmol) were placed into a reactor which was evacuated at 10^{-2} Torr for 15 min. The monomer (Acros Organics) was purified by distillation. Vapor-deposition polymerization was performed at 150°C for 5 h. The AAO template was removed by treatment with NaOH solution (0.1 M) at room temperature for 3 h and the MCPPy NTs were collected by applying an external magnetic field. The detailed procedure is given in the Supporting Information.

Pd/MCPPy NTs: An MCPPy NTs solution (5 mL, 0.5 $\text{mg}\,\text{mL}^{-1}$) was added to a solution $PdCl_2$ (30 mL; 1×10^{-4} to 5×10^{-3} M). Pd salts conjugated to the carboxylate moieties on the nanotube surface were reduced in the presence of an excess of H_2 gas at room temperature. The H_2 gas was bubbled through the mixture for 2 min at a rate of 0.5 $\text{L}\,\text{min}^{-1}$. Residual $PdCl_2$ was removed by washing with distilled water. The detailed procedure is described in the Supporting Information.

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