doi:10.1246/cl.2012.982

One-step Synthesis of Conducting Polymer–Palladium Nanocomposite Fibers by Aqueous Chemical Oxidative Polymerization

Hiroyuki Hamasaki,[1] Hodaka Kanadani,[1] Yoshinobu Nakamura,[1,2] and Syuji Fujii*[1]
[1]*Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology,*
5-16-1 Ohmiya, Asahi-ku, Osaka 535-8585
[2]*Nanomaterials Microdevices Research Center, 5-16-1 Ohmiya, Asahi-ku, Osaka 535-8585*

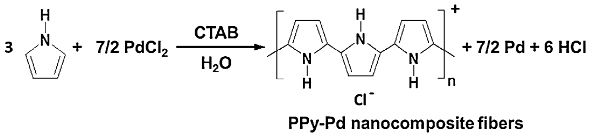
(Received July 4, 2012; CL-120715; E-mail: s.fujii@chem.oit.ac.jp)

Aqueous chemical oxidative polymerization of pyrrole using $PdCl_2$ oxidant was conducted in the presence of cetyltrimethylammonium bromide in order to synthesize polypyrrole–palladium (PPy–Pd) nanocomposite in one step. Interestingly, the PPy–Pd nanocomposite was synthesized with fibrous morphology. Transmission electron microscopy studies confirmed that Pd and PPy components formed composite in nanometer dimensions.

Conducting polymer–metal nanocomposites provide exciting opportunities to design advanced functional devices and catalysts.[1] There are many studies on synthesis, characterization, and application of the nanocomposites with diverse combinations of conducting polymers [e.g., polypyrrole (PPy), polyaniline, and poly(3,4-ethylenedioxythiophene)] and metallic nanoparticles. In the synthesis of conducting polymer–metal nanocomposites, metal ions are often reduced in the presence of preformed conducting polymers, and metal nanoparticles deposited on the surface of the polymers.[2] Chemical oxidative polymerization in the presence of preformed metal nanoparticles also leads to the formation of conducting polymer–metal nanocomposites.[3] Recently, it was reported that conducting polymer–metal nanocomposites can be synthesized by a one-step chemical oxidative polymerization using metal salts as an oxidant.[4,5] Selvan and co-workers polymerized pyrrole (Py) with tetrachloroauric acid as an oxidant, which led to the fabrication of PPy–gold nanocomposites.[4a] Some of the present authors reported successful syntheses of PPy–Ag[5a] and PPy–palladium (PPy–Pd)[5b-5e] nanocomposites by aqueous chemical oxidative polymerization using metal salts.

Synthesis of conducting polymers with fibrous morphology has attracted great attention mainly due to their potential applications in electronic circuits, chemical and electrochemical sensors, photovoltaic cells, electrochromic devices, and field emission applications.[7] PPy having the fibrous morphology has been chemically synthesized using insoluble (hard) templates,[8] seeds,[6] soluble (soft) templates, and conventional surfactants.[9] Synthesis of PPy nanofibers has been reported; however, there is no instance in which PPy–metal nanocomposite fibers were synthesized in one step by chemical oxidative polymerization.

In this communication, we report a novel one-step and one-pot synthesis of PPy–Pd nanocomposites with fibrous morphology by aqueous chemical oxidative polymerization of Py with $PdCl_2$ as an oxidant, for the first time (Scheme 1). This discovery substantially broadens and extends the scope of such nanocomposite material syntheses.



Scheme 1. Synthesis of polypyrrole–palladium (PPy–Pd) nanocomposite fibers by aqueous chemical oxidative polymerization of pyrrole using $PdCl_2$ in the presence of cetyltrimethylammonium bromide (CTAB).

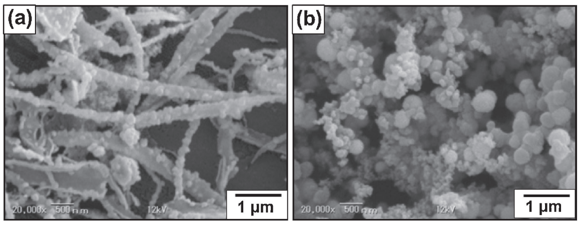


Figure 1. SEM images of PPy–Pd nanocomposites synthesized by aqueous chemical oxidative polymerization in the (a) presence and (b) absence of CTAB.

The PPy–Pd nanocomposite fibers were prepared as follows: 0.15 g of $PdCl_2$ and 0.20 g of NaCl were added to an aqueous solution of cetyltrimethylammonium bromide (CTAB; 0.62 g) (total solvent volume = 10 mL; $PdCl_2$/CTAB molar ratio, 1/2) at 25 °C, which produced orange-colored precipitates. These precipitates seemed to be water-insoluble Pd ion–cetyltrimethylammonium ion (CTA) complex.[11] Py (0.05 g) was then injected via syringe into this solution containing precipitates, and chemical oxidative polymerization was started by heating in an oil bath at 60 °C without stirring. The solution turned black gradually, which indicated that the Py was oxidized by Pd ion, yielding PPy and elementary Pd simultaneously. CTAB was used because it has been reported that chemical oxidative polymerization of Py in the presence of CTAB using ammonium persulfate (APS) led to fibrous PPy.[9c] The polymerization was allowed to proceed for 24 h. This reaction mixture was then centrifuged at 3000 rpm for 10 min, and the resulting black sediment was redispersed in methanol/deionized water using an ultrasonic bath. This centrifugation/redispersion cycle was repeated six times (three times methanol and three times deionized water) in order to remove free CTAB, any water-soluble PPy oligomers, and chlorine and sodium ions. The final product was dried under vacuum overnight.

Scanning electron microscope (SEM) studies after the centrifugal washing indicated the production of nanofibers (Figure 1a). Number-average diameter of the nanofibers was measured to be 190 nm, and a length was over a few micro-

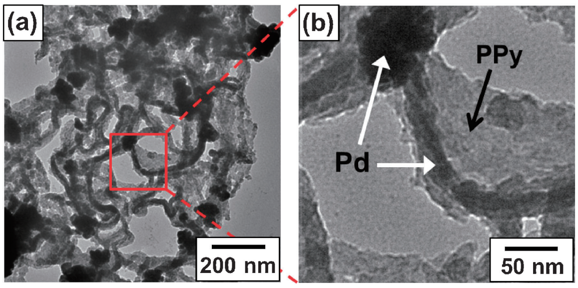


Figure 2. TEM images of PPy–Pd nanocomposite fibers. Figure 2b is a magnified image of Figure 2a.

meters. In addition to nanofibers, some ribbon-shaped nanocomposites were also observed, which had number-average width and thickness of 530 and 112 nm, respectively. On the surfaces of the nanofibers and nanoribbons, dots with sizes between a few tens nanometer and submicrometer were observed. Control experiment indicated that fused nano-/submicrometer-sized pseudospherical or globular nanocomposites were obtained by chemical oxidative precipitation polymerization of Py using $PdCl_2$ in the absence of CTAB, as observed in our previous studies (Figure 1b).[5b–5e] These results confirmed that CTAB played a crucial role for PPy–Pd nanocomposite formation with nanofibrous morphology.

In order to confirm the formation of a Pd component in the nanofibers, X-ray diffraction (XRD) studies were carried out.[11] In an XRD pattern of the PPy–Pd nanofibers, two peaks at around 39.9 and 46.5° (2θ), which correspond to the (111) and (200) lattice plane diffractions of Pd crystals, are clearly observed. These peaks are in agreement with those reported for Pd nanoparticles,[10] which provides unambiguous evidence that the reduction of Pd(II) to Pd(0) has taken place.

Typical transmission electron micrographs (TEM) of the dried nanocomposite fibers are shown in Figure 2. This TEM study indicates that the nanocomposite fibers should possess a "core–sheath" morphology. Taking stronger contrast in the core region into account, Pd which scatters electron more than organic polymer seems to form core, and PPy seems to form sheath. Number-average diameter of the Pd wire was measured to be 26 nm. In addition to the core–sheath structure, the heterogeneous character was also observed, which was composed of more transparent PPy nanofibers, with incorporated Pd nanoparticles (dark elements dispersed in/on the PPy matrix). Diameters of the Pd nanoparticles were measured to be between 20 and 145 nm.[11] In order to make the nanomorphologies clearer, further detailed characterizations should be conducted.

Zhang et al.[9c] synthesized PPy homopolymer nanofibers using APS as an oxidant in the presence of CTAB. They claimed that an insoluble lamellar precipitate of $(CTA)_2S_2O_8$ is first formed which acts as a template for subsequent oxidative polymerization of the Py present in the lamellar core. A lamellar structure was formed between the cations of the CTAB and the anions of the oxidizing agent in the aqueous solution and was attributed to leading the growth of fibrous PPy. A similar mechanism may occur in our system of Py/$PdCl_2$/CTAB. The mesostructures would be formed by self-assembly between the cations of cationic surfactant (CTAB) and anions of the oxidizing agent of $PdCl_4^{2-}$. These mesostructures may act as templates for the formation of nanocomposite fibers. Although precise mechanism of growth of the PPy–Pd nanocomposite fibers has not been fully understood, it is almost certainly related to the mesostructure of $(CTA)_2PdCl_4$ and supramolecular assemblies.

In conclusion, we have demonstrated one-step facile and versatile synthetic route to the PPy–Pd nanocomposite fibers. This synthetic route is advantageous because the reaction takes place in aqueous media, and production on an industrial scale is much more likely compared to two-step synthetic route. Potential applications for these new nanocomposite materials include catalysts and novel electronic and optical devices.

This work was partially supported by Tanaka Kikinzoku Group Research Fund (MMS prize) and Japan Science and Technology Agency, Japan and Adaptable and Seamless Technology transfer Program (A-STEP), Japan (No. AS232Z01455D).

References and Notes

1 R. Gangopadhyay, A. De, *Chem. Mater.* **2000**, *12*, 608.

2 E. T. Kang, Y. P. Ting, K. G. Neoh, K. L. Tan, *Polymer* **1993**, *34*, 4994.

3 S. M. Marinakos, J. P. Novak, L. C. Brousseau, III, A. B. House, E. M. Edeki, J. C. Feldhaus, D. L. Feldheim, *J. Am. Chem. Soc.* **1999**, *121*, 8518.

4 a) T. Selvan, J. P. Spatz, H.-A. Klok, M. Möller, *Adv. Mater.* **1998**, *10*, 132. b) A. Chen, K. Kamata, M. Nakagawa, T. Iyoda, Wang, X. Li, *J. Phys. Chem. B* **2005**, *109*, 18283. c) M. C. Henry, C.-C. Hsueh, B. P. Timko, M. S. Freund, *J. Electrochem. Soc.* **2001**, *148*, D155. d) S. V. Vasilyeva, M. A. Vorotyntsev, I. Bezverkhyy, E. Lesniewska, O. Heintz, R. Chassagnon, *J. Phys. Chem. C* **2008**, *112*, 19878.

5 a) S. Fujii, A. Aichi, K. Akamatsu, H. Nawafune, Y. Nakamura, *J. Mater. Chem.* **2007**, *17*, 3777. b) S. Fujii, S. Matsuzawa, Y. Nakamura, A. Ohtaka, T. Teratani, K. Akamatsu, T. Tsuruoka, H. Nawafune, *Langmuir* **2010**, *26*, 6230. c) S. Fujii, M. Kodama, S. Matsuzawa, H. Hamasaki, A. Ohtaka, Y. Nakamura, in *Advances in Nanocomposite Technology*, ed. by A. Hashim, InTech, Rijeka, **2011**, Chap. 2, p. 47. doi:10.5772/16911. d) S. Fujii, S. Matsuzawa, H. Hamasaki, Y. Nakamura, A. Bouleghlimat, N. J. Buurma, *Langmuir* **2012**, *28*, 2436. e) H. Hamasaki, N. Fukui, S. Fujii, S.-i. Yusa, Y. Nakamura, *Colloid Polym. Sci.* **2012**, in press. doi:10.1007/s00396-012-2646-6.

6 L. Pan, H. Qiu, C. Dou, Y. Li, L. Pu, J. Xu, Y. Shi, *Int. J. Mol. Sci.* **2010**, *11*, 2636.

7 a) M. Ikegame, K. Tajima, T. Aida, *Angew. Chem., Int. Ed.* **2003**, *42*, 2154. b) C. R. Martin, *Science* **1994**, *266*, 1961.

8 X. Zhang, S. K. Manohar, *J. Am. Chem. Soc.* **2004**, *126*, 12714.

9 a) A. D. W. Carswell, E. A. O'Rear, B. P. Grady, *J. Am. Chem. Soc.* **2003**, *125*, 14793. b) M. Omastová, M. Trchová, J. Kovářová, J. Stejskal, *Synth. Met.* **2003**, *138*, 447. c) X. Zhang, J. Zhang, W. Song, Z. Liu, *J. Phys. Chem. B* **2006**, *110*, 1158.

10 a) M. Zhang, W. Zhang, *J. Phys. Chem. C* **2008**, *112*, 6245. b) F. Wen, W. Zhang, G. Wei, Y. Wang, J. Zhang, M. Zhang, L. Shi, *Chem. Mater.* **2008**, *20*, 2144.

11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.