ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 6299–6301

www.rsc.org/chemcomm

COMMUNICATION

Facile synthesis of noble metal nanotubes by using ZnO nanowires as sacrificial scaffolds and their electrocatalytic properties†

Young Wook Lee,‡[a] Mi Ae Lim,‡[b] Shin Wook Kang,[a] Inkyu Park*[b] and Sang Woo Han*[a]

Received 21st December 2010, Accepted 30th March 2011
DOI: 10.1039/c0cc05701k

Pt and Pd nanotubes could be prepared rapidly with high yields and good uniformity through the reduction of metal precursors in the presence of ZnO nanowires as inexpensive sacrificial templates. The prepared nanotubes showed efficient electrocatalytic properties toward alcohol oxidation.

Pt- and Pd-based nanostructures have attracted a great deal of attention as catalytic materials due to their prominent activities in a wide range of heterogeneous chemical reactions and electrocatalytic oxidation/reduction reactions in polymer electrolyte membrane fuel cells (PEMFCs).[1] In this regard, large efforts have been focused on the controlled synthesis of Pt- and Pd-based nanostructures with specific morphologies because their catalytic properties can be tuned by tailoring their shapes and sizes.[2] In particular, the synthesis of one-dimensional (1D) nanostructures including nanotubes and nanowires is currently attracting considerable interest because of their unique structural and catalytic properties. Accordingly, various synthetic routes have been developed to prepare these types of nanomaterials.[3]

The controlled synthesis of 1D nanostructures has been usually achieved by template-based methods, wherein the inorganic templates such as anodized aluminium oxide (AAO) serve as structure-directing scaffolds.[4] Most of the previous template-assisted strategies have required extra template-removal steps. Recently, the galvanic replacement reaction of metal nanowires has been used as an alternative method to prepare the 1D nanostructures. For instance, Pt, Pd, and Pt–Pd nanotubes were synthesized by using Ag, Se, and Te nanowires as sacrificial templates,[5–9] and their electrocatalytic activities toward methanol oxidation[7,9] and oxygen reduction reaction[6] were investigated. However, a long reaction time was required for the complete replacement of nanowire templates and additional etching steps for the remaining template were necessary in some cases. Moreover, these methods are not cost-effective because rather expensive materials are used as sacrificial templates. On the basis of this fact, the development of simple, fast, low-cost, and versatile techniques for the production of 1D nanostructures is still highly required and challenging for their broader applications.

In this work, we demonstrate a facile chemical process for the controlled synthesis of uniform 1D noble metal nanotubes by using ZnO nanowires as inexpensive sacrificial templates. Pt and Pd nanotubes could be prepared rapidly with high yields and good uniformity through the reduction of metal precursors with sodium citrate in the presence of ZnO nanowires. The formation of tubular structures could be attributed to the *in situ* dissolution of ZnO during the reaction. Since such nanotube structures have commonly exhibited relatively large surface areas, it can be expected that the prepared nanotubes may show enhanced catalytic efficiencies. In this regard, we have also investigated the electrocatalytic activities of the synthesized nanotubes for methanol or ethanol oxidation.

In a typical synthesis of metal nanotubes, an aqueous solution of the metal precursor was added to an aqueous solution of sodium citrate, and then the ZnO nanowire array grown on a Si wafer was immersed into this growth solution. The average length and diameter of ZnO nanowires are about 1.5 μm and 55 nm, respectively (Fig. S1, ESI†). The reaction mixture was then heated at ~90 °C for about 1 h in a drying oven.

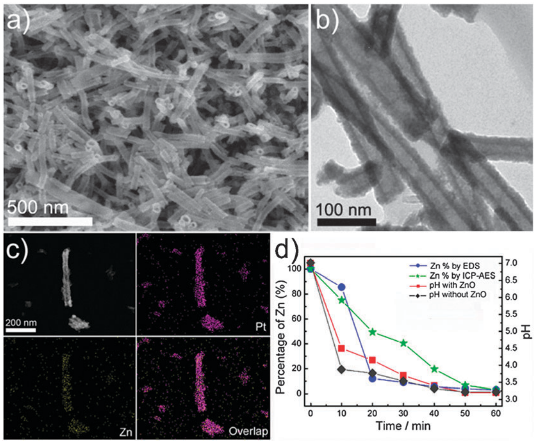

Fig. 1 (a) SEM and (b) TEM images of the Pt nanotubes. (c) HAADF-STEM image and the corresponding EDS mapping images of a Pt nanotube. (d) Changes in the pH of the reaction mixture and the mole% of Zn of the nanotubes during the reaction.

---

[a] *Department of Chemistry and KI for the NanoCentury, KAIST, Daejeon 305-701, South Korea. E-mail: sangwoohan@kaist.ac.kr*
[b] *Department of Mechanical Engineering and KI for the NanoCentury, KAIST, Daejeon 305-701, South Korea. E-mail: inkyu@kaist.ac.kr*

† Electronic supplementary information (ESI) available: Details for synthesis and characterization, and additional experimental data. See DOI: 10.1039/c0cc05701k

‡ These authors contributed equally to this work.

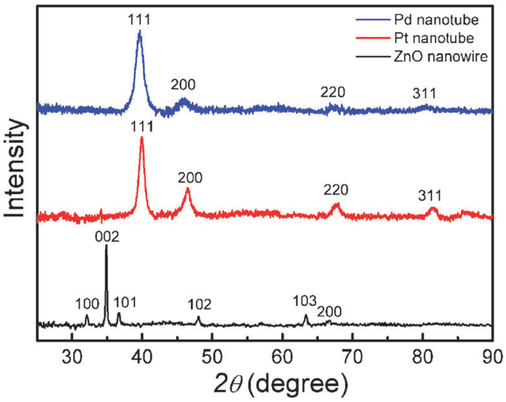

Fig. 2 XRD patterns of the Pt and Pd nanotubes and the pristine ZnO nanowires.

Fig. 1a shows a representative scanning electron microscopy (SEM) image of the samples prepared by using K_2PtCl_4 as a metal precursor, which clearly demonstrates the formation of nanotubes with open tips. The mean length of nanotubes is ~1.5 μm and their outer diameter is ranging from 40 to 60 nm. The transmission electron microscopy (TEM) image shown in Fig. 1b also confirms the successful preparation of the nanotubes; each nanotube has a well-defined hollow interior and a uniform wall with an average thickness of 13 ± 4 nm. Elemental mapping of Pt and Zn (Fig. 1c) and the compositional line profiles on a single nanotube (Fig. S2, ESI†) obtained by the high-angle annular dark-field scanning TEM energy-dispersive X-ray spectroscopy (HAADF-STEM-EDS) reveal that the prepared nanostructure is definitely a Pt nanotube, though there remains a trace amount of Zn. The Pt/Zn ratio was estimated to be 97 : 3 by using an inductively-coupled plasma-atomic emission spectrometer (ICP-AES).

Fig. 2 shows X-ray diffraction (XRD) patterns of the prepared Pt nanotubes as well as the pristine ZnO nanowire templates. Pt nanotubes exhibit four diffraction peaks which can be indexed to the (111), (200), (220), and (311) reflections of the face-centered cubic (fcc) structure of metallic Pt while the ZnO peaks completely disappeared, showing that the Pt nanotubes are well-crystallized along with the consumption of the ZnO template. High-resolution TEM (HRTEM) measurements of the Pt nanotubes identified the lattice planes forming the nanotubes (Fig. S3a, ESI†). A *d*-spacing of 2.30 Å for adjacent lattice planes corresponds to the (111) planes of fcc Pt,[10] indicating that most of the exposed facets of the Pt nanotubes are {111}.

The structural evolution of the Pt nanotubes could be monitored by TEM measurements on different reaction stages (Fig. S4, ESI†). Initially, Pt deposited onto the surface of ZnO nanowires which served as a seeding template. Interestingly, we found that the void spaces in the nanotubes appeared by increasing the reaction time to 20 min. As the reaction proceeded, the Pt deposited more densely and the hollow feature in each nanotube became more distinct. Beyond 50 min, no significant change in the structure was observed. This was also reflected in the change of mole% of Zn during the reaction measured from EDS and ICP-AES analyses (Fig. 1d). The observed growth of nanotubes could be attributed to the selective dissolution of ZnO templates during the reduction of Pt precursors. As shown in Fig. 1d, the pH of the reaction mixture was decreased rapidly with increasing reaction time. This might be due to the consumption of OH^- ions during the reduction of $PtCl_4^{2-}$ by citrate (Fig. S5, ESI†).[11] It has been known that ZnO can be dissolved in acidic solution by the reaction with H^+ ions ($ZnO(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2O(l)$).[12] Therefore, the hollow interiors of the nanotubes are formed by this *in situ* dissolution of ZnO nanowires by H^+ ions that is enhanced by the decrease of pH in the solution *via* the reduction of metal precursors. In fact, dissolved Zn has been identified by the ICP-AES measurements on the growth solution after the reaction. On the other hand, the pH of solution decreased more rapidly in the absence of the ZnO template under otherwise identical synthetic conditions (Fig. 1d). This is another experimental evidence for the consumption of H^+ by the ZnO nanowires.

By using the same synthesis protocol, the Pd nanotubes could also be prepared with K_2PdCl_4 as a metal precursor. Representative SEM and TEM images of the Pd nanotubes are shown in Fig. 3a and b, respectively. The average outer diameter and wall thickness of the Pd nanotubes are 130 ± 30 and 55 ± 12 nm, respectively. The compositional line profiles on a single nanotube (Fig. 3c) and elemental mapping of Pd and Zn (Fig. 3d) obtained by the HAADF-STEM-EDS clearly indicate that the synthesized nanostructure is a Pd nanotube. The XRD pattern of the prepared Pd nanotubes exhibits characteristic diffraction peaks which can be indexed to the fcc Pd (Fig. 2). A *d*-spacing of 2.24 Å for adjacent lattice planes shown in the HRTEM image of the Pd nanotubes reveals the predominance of {111} planes on the surface of the Pd nanotubes (Fig. S3b, ESI†).[2d]

To investigate the catalytic performance of the prepared nanotubes, their electrocatalytic activities toward alcohol oxidation were tested. For electrochemical experiments, Pt and Pd nanotubes were prepared by using ZnO nanowire arrays grown on indium tin oxide (ITO) glass as templates (Fig. S6, ESI†). Fig. 4a shows the cyclic voltammogram (CV) of methanol oxidation at the Pt nanotube in 0.1 M KOH solution containing 0.1 M methanol. Pt has been known to have a good electrocatalytic activity for methanol oxidation in alkaline media.[7,9,13] For comparison, the CV of methanol oxidation at the Pt nanoparticles (Experimental details and Fig. S7a, ESI†) is also shown in Fig. 4a. The current values were normalized with respect to the electrochemically active

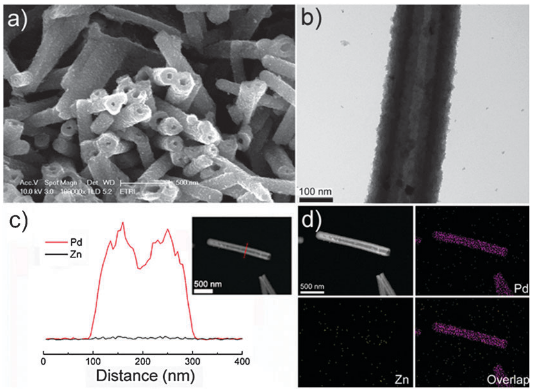

Fig. 3 (a) SEM and (b) TEM images of the Pd nanotubes. (c) HAADF-STEM image and cross-sectional compositional line profiles of a Pd nanotube. (d) HAADF-STEM-EDS mapping images of the Pd nanotube.

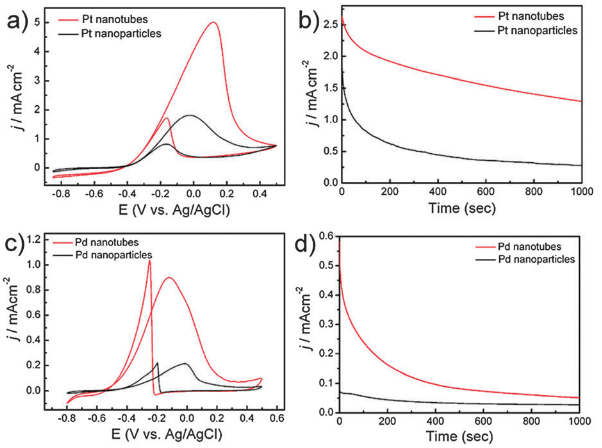

Fig. 4 (a) CVs in 0.1 M KOH + 0.1 M methanol of the Pt nanotubes and Pt nanoparticles on ITO electrodes. Scan rate: 50 mV s^{-1}. (b) CA curves for the Pt nanotubes and Pt nanoparticles at 0.0 V *vs.* Ag/AgCl. (c) CVs in 0.1 M KOH + 0.1 M ethanol of the Pd nanotubes and Pd nanoparticles on ITO electrodes. Scan rate: 50 mV s^{-1}. (d) CA curves for the Pd nanotubes and Pd nanoparticles at −0.2 V *vs.* Ag/AgCl.

surface area (ECSA), which were calculated by measuring the coulombic charge for oxygen desorption (Fig. S8, ESI†). As shown in Fig. 4a, characteristic well-separated anodic peaks in the forward and reverse sweeps associated with methanol oxidation were observed. It is noticeable that the current density of the Pt nanotubes is much higher than that of the Pt nanoparticles; the peak current densities are 5.01 and 1.81 mA cm^{-2} on the Pt nanotubes and Pt nanoparticles, respectively. Furthermore, the onset potential of the nanotubes has a more negative value than that of the nanoparticles; −0.415 and −0.342 V *vs.* Ag/AgCl for the nanotubes and nanoparticles, respectively. The enhanced electrocatalytic activity of the Pt nanotubes cannot be due to the presence of trace amounts of ZnO because the catalytic activity of the nanotubes slightly increased when the residual ZnO was completely removed by treating the nanotubes with an acidic solution (pH = 3.5) for about 1 h (Fig. S9, ESI†). The chronoamperometric (CA) experiments also reveal that the electrochemical stability of the Pt nanotubes for methanol electro-oxidation is superior to that of the Pt nanoparticles (Fig. 4b). On the other hand, Pd nanostructures have been reported to have efficient electrocatalytic activities toward ethanol oxidation in alkaline media.[14] On the basis of this fact, electrocatalytic activity and stability of the Pd nanotubes toward ethanol oxidation were tested and the results were compared with those of the Pd nanoparticles (Experimental details and Fig. S7b, ESI†). The CVs of ethanol oxidation at the Pd nanotube and Pd nanoparticles in 0.1 M KOH solution containing 0.1 M ethanol shown in Fig. 4c demonstrate the enhanced electrocatalytic activity of the Pd nanotubes toward ethanol oxidation. The peak current densities are 0.904 and 0.220 mA cm^{-2} on the Pd nanotubes and Pd nanoparticles, respectively, and the onset potential values of the nanotubes and nanoparticles are −0.501 and −0.440 V *vs.* Ag/AgCl, respectively. The CA data further show the higher electrochemical stability of the Pd nanotubes for ethanol electro-oxidation than that of the Pd nanoparticles (Fig. 4d). The improved catalytic activities and stabilities of the Pt and Pd nanotubes might be attributed to their high surface area and the presence of active sites on their surfaces.[6,15] Moreover, the enhanced mass transport and utilization of catalyst could be expected for the nanotube catalysts because of their anisotropic tubular morphologies.[7,16] Taken together, the present work might provide a promising strategy for developing efficient fuel cell catalysts.

In summary, we have presented a facile and cost-effective aqueous synthesis method for the preparation of Pt and Pd nanotubes by the reaction between ZnO nanowires and aqueous solution of a metal precursor under moderate temperature and mild chemical conditions. The successful synthesis of nanotubes could be achieved *via* the selective dissolution of ZnO templates during the reduction of metal precursors. The prepared nanotubes showed enhanced electrocatalytic properties toward alcohol oxidation. It is expected that our strategy can be extended to the fabrication of other single- or multi-component metal nanotubes for the improvement of catalytic performance in diverse chemical reactions.

This work was supported by Basic Science Research Programs (2008-0062042, 2010-0029149, 2010-0015290), Future-based Technology Development Program (Nano Fields) (2009-0082640), and Pioneer Research Center Program (2009-0082813) through the National Research Foundation (NRF) funded by the Korean government (MEST), and Open Innovation Research Program of Hewlett Packard (HP) Company, USA.

Notes and references

1 (*a*) N. P. Brandon, S. Skinner and B. C. H. Steele, *Annu. Rev. Mater. Res.*, 2003, **33**, 183; (*b*) M. Chen, D. Kumar, C.-W. Yi and D. W. Goodman, *Science*, 2005, **310**, 291; (*c*) J. Chen, B. Lim, E. P. Lee and Y. Xia, *Nano Today*, 2009, **4**, 81; (*d*) V. Mazumder, Y. Lee and S. Sun, *Adv. Funct. Mater.*, 2010, **20**, 1224.
2 (*a*) Y. Xiong and Y. Xia, *Adv. Mater.*, 2007, **19**, 3385; (*b*) S. E. Habas, H. Lee, V. Radmilovic, G. A. Somorjai and P. Yang, *Nat. Mater.*, 2007, **6**, 692; (*c*) Z. Peng and H. Yang, *Nano Today*, 2009, **4**, 143; (*d*) Y. W. Lee, M. Kim and S. W. Han, *Chem. Commun.*, 2010, **46**, 1535.
3 A. Roucoux, J. Schulz and H. Patin, *Chem. Rev.*, 2002, **102**, 3757.
4 (*a*) M. Steinhart, Z. Jia, A. K. Schaper, R. B. Wehrspohn, U. Gösele and J. H. Wendorff, *Adv. Mater.*, 2003, **15**, 706; (*b*) Y. Zhao, Y.-G. Guo, Y.-L. Zhang and K. Jiao, *Phys. Chem. Chem. Phys.*, 2004, **6**, 1766; (*c*) X. Zhang, D. Dong, D. Li, T. Williams, H. Wang and P. W. Webley, *Electrochem. Commun.*, 2009, **11**, 190.
5 B. Mayers, X. Jiang, D. Sunderland, B. Cattle and Y. Xia, *J. Am. Chem. Soc.*, 2003, **125**, 13364.
6 Z. Chen, M. Waje, W. Li and Y. Yan, *Angew. Chem., Int. Ed.*, 2007, **46**, 4060.
7 Y. Bi and G. Lu, *Chem. Mater.*, 2008, **20**, 1224.
8 H.-W. Liang, S. Liu, J.-Y. Gong, S.-B. Wang, L. Wang and S.-H. Yu, *Adv. Mater.*, 2009, **21**, 1850.
9 Y. Bi and G. Lu, *Electrochem. Commun.*, 2009, **11**, 45.
10 J. Xu, T. Zhao, Z. Liang and L. Zhu, *Chem. Mater.*, 2008, **20**, 1688.
11 I. O. Jiménez, F. M. Romero, N. G. Bastús and V. Puntes, *J. Phys. Chem. C*, 2010, **114**, 1800.
12 (*a*) G.-W. She, X.-H. Zhang, W.-S. Shi, X. Fan, J. C. Chang, C.-S. Lee, S.-T. Lee and C.-H. Liu, *Appl. Phys. Lett.*, 2008, **92**, 053111; (*b*) J. Liu, Y. Li, H. Fan, Z. Zhu, J. Jiang, R. Ding, Y. Hu and X. Huang, *Chem. Mater.*, 2010, **22**, 212.
13 C. Xu, L. Cheng, P. Shen and Y. Liu, *Electrochem. Commun.*, 2007, **9**, 997.
14 C. Bianchini and P. K. Shen, *Chem. Rev.*, 2009, **109**, 4183.
15 X. Zhang, W. Lu, J. Da, H. Wang, D. Zhao and P. W. Webley, *Chem. Commun.*, 2009, 195.
16 K. Lee, J. J. Zhang, H. J. Wang and D. P. Wilkinson, *J. Appl. Electrochem.*, 2006, **36**, 507.