Iodide ions control galvanic replacement growth of uniform rhodium nanotubes at room temperature†

Yingpu Bi[ab] **and Gongxuan Lu***[a]

Received (in Cambridge, UK) 19th August 2008, Accepted 29th September 2008
First published as an Advance Article on the web 5th November 2008
DOI: 10.1039/b814335h

Hollow rhodium nanotubes with uniform and perfect structures have been successfully synthesized through the replacement reaction between Ag nanowires and $RhCl_3$ in saturated NaI solutions at room temperature, and the main effect of iodide ions is found to reduce the redox potential of Ag species and resolve the formed AgI precipitation.

Morphological control of metal nanocrystals is a fascinating objective in modern materials science, chemistry, and physics. The high interest lies in the fact that the unique properties such as catalytic,[1] electronic[2] and magnetic[3] properties derived from their size and shape. In view of the importance of these materials, diverse synthesis methods have been developed to control the morphology of metal nanoparticles, such as electrochemistry,[4] photochemistry,[5] templating,[6] seeding,[7] and electron beam irradiation,[8] *etc*. Recently, the galvanic replacement synthesis has proved to be an alternative approach for preparing shape-selective metal nanocrystals whereby a sufficiently oxidizing metal ion is reduced to its metallic state, and is accompanied by oxidation of another metal. For example, Xia and co-workers[9] and other groups[10] demonstrated that hollow metal nanostructures such as nanocages, nanospheres and nanotubes could be synthesized based on this replacement reaction between Ag nanostructures and Pt, Au or Pd compounds. Furthermore, their growth mechanisms, unique properties, and potential applications have been extensively investigated.[11] However, compared with the above noble metals, much less success has yet been achieved in the controlled growth of Rh hollow nanostructures because the standard reduction potential of the both Rh^{3+}/Rh pair (0.76 V *vs.* the standard hydrogen electrode, SHE) and Rh^{2+}/Rh (0.60 V) pair are lower than that of the Ag^+/Ag pair (0.80 V). In order to extend the controlled growth of hollow Rh nanocrystals and explore their unique properties and applications, it is highly desirable to develop new galvanic replacement methods.

Herein, we demonstrate, for the first time, that hollow Rh nanotubes with uniform and perfect structures could be synthesized in large quantities by directly mixing Ag nanowires and $RhCl_3$ in saturated NaI solutions at room temperature. In this replacement process, the iodide ions reduce the redox potential of Ag species markedly from +0.80 V (Ag^+/Ag *vs.* SHE) to −0.15 V (AgI/Ag), thereby a complete conversion from Ag nanocrystals into Rh hollow structures has been achieved. Moreover, their catalytic study for hydrogen production from formaldehyde solution indicates that the hollow Rh nanotubes exhibited higher catalytic activity than that of spherical Rh nanoparticles.

Fig. 1A and B show the SEM images of Ag nanoproducts, indicating that large quantity single crystal Ag nanowires with the length of 10 μm and an average diameter of ∼100 nm have been synthesized by 1,3-butylene glycol reduction. Fig. 1C and D and Fig. S1, ESI† show the typical SEM images of the Rh nanoproducts that were obtained by mixing the Ag nanowires and $RhCl_3$ in the saturated NaI aqueous solution at room temperature, in which Ag nanowire serves as both reducing agent and templates. It can be clearly seen from these SEM images that large quantities of uniform Rh nanotubes have been produced by this modified replacement reaction. Fig. 1D shows the enlarged images of such tubular structures, indicating that the Rh nanoproduct is composed of hollow nanotubes with smooth surface and uniform nanostructure. The FE-SEM images (Fig. S2, ESI† and Fig. 1D inset) indicates that the profiles of the tubes are constituted by uniform density of nanoshells with highly crystalline walls throughout the tubes. These images clearly exhibit that these Rh nanotubes are typically 10 μm in length, with an outer diameter of 110 to

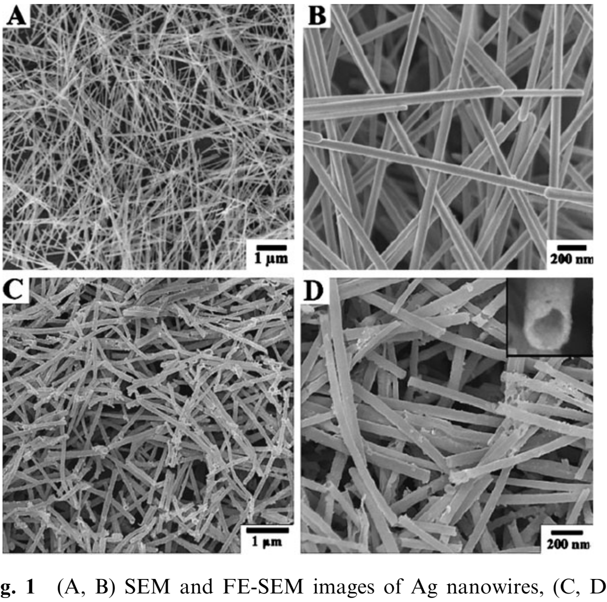


Fig. 1 (A, B) SEM and FE-SEM images of Ag nanowires, (C, D) SEM and FE-SEM images of as-prepared hollow Rh nanotubes.

---

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics Institution, Chinese Academy of Sciences Lanzhou, China. E-mail: gxlu@lzb.ac.cn; Fax: +86 931-4968178; Tel: +86 931-4968178*

[b] *Graduate School of the Chinese Academy of Sciences, Beijing, China*

† Electronic supplementary information (ESI) available: Experimental procedure, XRD pattern, EDS spectra and additional SEM images of the rhodium nanotubes. Detailed experimental procedures. See DOI: 10.1039/b814335h

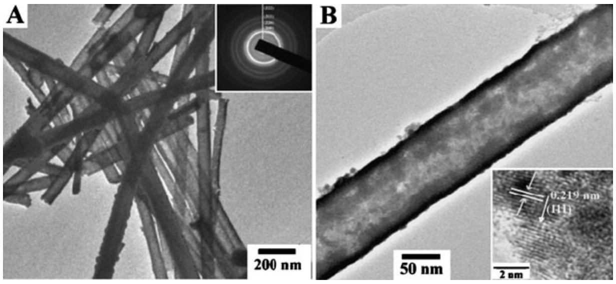
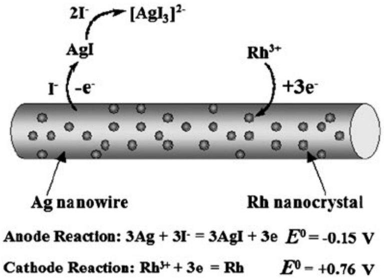


Fig. 2 (A) TEM images of rhodium nanotubes and their SAED pattern; (B) a single rhodium nanotubes and its high-resolution TEM images.

120 nm, an inner diameter of 100 nm, and a wall thickness between 10 to 15 nm. Moreover, these Rh nanotubes have been characterized in detail by TEM and the results have been shown in Fig. 2. The electron diffraction pattern (Fig. 2A inset) clearly indicates that these nanotubes are polycrystalline. High-resolution TEM micrograph (Fig. 2B inset) shows randomly oriented nanocrystals in the shell, which further confirms that the walls of the nanotubes are constructed by small rhodium particles. The X-ray diffraction (XRD) pattern of Rh nanotubes shown in Fig. S3, ESI† suggests that all peaks of nanotube should be assigned to diffraction from the (111), (200), (220), (311) and (222) planes of fcc Rh (PCPDF No. 05-0685), which is consistent with the experimental results of the ED patterns. The inset of Fig. S3, ESI† shows the EDS result of hollow Rh nanoproducts and indicates that except for the elements of Cu and Zn from the support, only Rh element has been observed in this EDS pattern.

As reported in previous studies,[12–14] the Ag-engaged replacement reaction can be only applied to the metals whose redox potential is higher than that of the Ag^+/Ag pair (0.80 V *vs.* SHE), such as the Au^{3+}/Au pair (1.50 V), the Pt^{2+}/Pt pair (1.2 V), and the Pd^{2+}/Pd pair (0.95 V). However, in our reaction system, the replacement reaction occurs between Rh^{3+} (Rh^{3+}/Rh = 0.76 V) and Ag nanowires quite readily at room temperature and hollow Rh nanotubes with uniform shells and smooth surfaces can be synthesized in high yields. Herein, we identified a potential mechanism explaining the synthesis of Rh nanotubes under these conditions and a schematic illustration is shown in Scheme 1. In the presence of the saturated NaI solution, the redox potential of Ag species is decreased markedly from +0.80 V (Ag^+/Ag pair) to −0.15 V (AgI/Ag pair), which is much lower than that of the Rh^{3+}/Rh couple, thereby many electrons generated in the oxidation process migrate rapidly to the surface of the Ag nanowires, where they reduce Rh^{3+} to Rh atoms. At the same time, the AgI precipitation produced from the replacement process can be easily dissolved by the saturated I^- ions to form the complex of $[AgI_3]^{2-}$.

To further confirm this hypothesis about the changes of standard potential for Ag species, the morphology evolutions of Rh products in the presence of other saturated sodium halide solutions have also been investigated. As shown in Fig. 3A and B, when NaI was replaced by NaBr in this process, the obtained Rh nanoproducts were in the form of tubular nanostructures and the surfaces of these structures are composed of spherical nanoparticles. When this replacement process has been performed in the saturated NaCl solution, the Ag nanowires were transformed into curved structures with rough surfaces and many large particles (Fig. 3C and D). These demonstrations suggest that the galvanic replacement reaction in the presence of both NaCl and NaBr solution only produces Rh nanostructures with poor crystallinity and irregular shapes. Furthermore, the standard potential of the AgI/Ag pair (−0.15 V *vs.* SHE) is lower than that of AgBr/Ag pair (0.007 V) and AgCl/Ag pair (0.223 V), which greatly enhances the replacement rate between Ag and Rh and results in a product with homogeneous rather than a heterogeneous structure.



Scheme 1 Schematic illustration of the typical replacement process between Ag nanowires and Rh^{3+} ions.

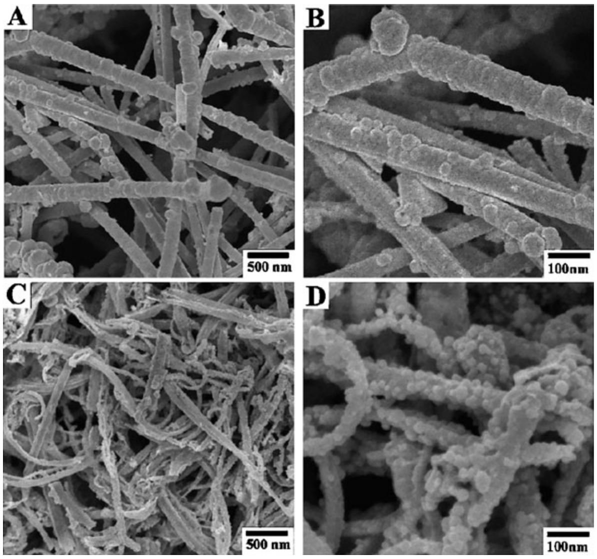


Fig. 3 (A, B) SEM and FE-SEM images of the Rh nanoproducts prepared in saturated NaBr solution; (C, D) SEM and FE-SEM images of the Rh nanoproducts prepared in saturated NaCl solution.

Plasmon absorption spectroscopy is usually used to examine size- and shape-controlled nanoparticles because their optical properties in aqueous suspensions are related to these properties. Hence, UV-Vis absorption spectra of Ag nanowires and Rh nanotubes has been investigated in this work and shown in Fig. 4. In the case of Ag nanowires, it reveals a strong peak at 380 nm and a small shoulder peak at 350 nm, which could be attributed to the transverse plasmon mode of silver nanowires and the plasmon resonance of bulk silver, respectively. In the absorption spectra of the Rh nanotubes, it reveals a broad plasmon absorption peak at 500 nm. Generally, it is well documented that both thin films and spherical nanoparticles of Rh do not exhibit any extinction peaks in the visible region

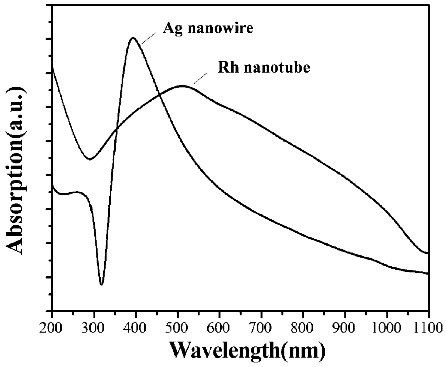


Fig. 4 UV-visible absorption spectra of silver nanowires and hollow rhodium nanotubes.

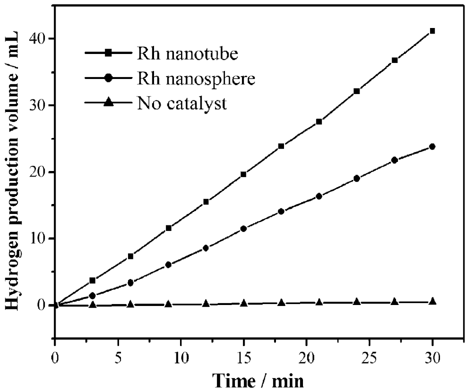


Fig. 5 Catalytic activities of colloidal rhodium nanocatalysts for the hydrogen generation reaction from 1.5 wt% HCHO + 4 wt% NaOH solution at room temperature.

as a result of the very small imaginary part of the dielectric constant. Recently, Xia and co-workers[15] reported that branched Rh nanocrystals displayed an attractive surface plasmon resonance (SPR) feature and exhibited a weak and broad peak around 380 nm. In this case, the plasmon absorption peak appearance should be related to the formation of hollow structures and uniform walls for the Rh nanotubes. This demonstration of optical tuning indicates that such hollow Rh nanostructures may find uses in optical sensing and SERS applications.

Finally, the catalytic behaviours of the hollow Rh nanostructures were explored for hydrogen generation from HCHO solution at room temperature.[16] To the best of our knowledge, these colloid rhodium nanotubes were used, for the first time, as catalysts for this reaction. For comparison, catalytic properties of Rh nanoparticles reduced by $NaBH_4$ reduction have also been investigated. The comparison in the reactivity for the various shaped Rh nanocrystals has been shown in Fig. 5. It can be seen that the catalytic activities were greatly dependent on the structural evolutions of Rh nanocatalysts. Furthermore, the Rh nanotubes showed higher activity than that of spherical nanoparticles. During 30 min reaction, the calculated average hydrogen generation rate was 275 and 159 mL $min^{-1}g^{-1}$ on Rh nanotubes and Rh nanospheres ($NaBH_4$ reduction), respectively, demonstrating the superior catalytic properties of the Rh nanotubes to spherical nanoparticles. The improved activity of the Rh nanotubes might be due to the higher surface area and mesoporous structure and potentially more active surface in comparison to smooth, crystalline structures.

In summary, we have demonstrated an effective approach to produce hollow Rh nanotubes with uniform and perfect structures through the galvanic replacement reaction between Ag nanowires and aqueous $RhCl_3$ in the saturated NaI solution at room temperature. In this replacement process, the presence of saturated I^- ions greatly reduces the redox potential of the Ag species from +0.80 V (Ag^+/Ag pair) to −0.15 V (AgI/Ag pair), hence Rh^{3+} ions can be rapidly displaced by Ag nanowires and hollow Rh nanotubes formed. Furthermore, we believe that this rational room-temperature synthetic route should be adapted for the preparation of other metal nanocrystals with hollow structures and applied in many fields such as electronics, sensing, photonics and catalysis.

This work was supported by the National Basic Research Program of China (no. 2003CB214500, 2007CB613305 and 2009CB220003).

Notes and references

1 K. M. Bratlie, H. Lee, K. Komvopoulos, P. Yang and G. A. Somorjai, *Nano Lett.*, 2007, **7**, 3097.
2 V. Berry, S. Rangaswamy and R. F. Saraf, *Nano Lett.*, 2004, **4**, 939.
3 V. F. Puntes, K. M. Kroshnan and A. P. Alivisatos, *Science*, 2001, **191**, 2115.
4 K. Esumi, K. Matsuhisa and K. Torigoe, *Langmuir*, 1995, **11**, 3285.
5 F. Kim, J. H. Song and P. Yang, *J. Am. Chem. Soc.*, 2002, **124**, 14316.
6 B. M. Van der Zande, I. M. R. Bohmer, L. G. J. Fokkink and C. Schonenberger, *Langmuir*, 2000, **16**, 451.
7 T. K. Sau and C. J. Murphy, *J. Am. Chem. Soc.*, 2004, **126**, 8648.
8 Y. J. Kim and J. H. Song, *Nanotechnology*, 2007, **18**, 445603.
9 (*a*) X. Lu, H.-Y. Tuan, J. Chen, Z.-Y. Li, B. A. Korgel and Y. Xia, *J. Am. Chem. Soc.*, 2007, **129**, 1733; (*b*) J. Chen, J. M. McLellan, A. Siekkinen, Y. Xiong, Z.-Y. Li and Y. Xia, *J. Am. Chem. Soc.*, 2007, **128**, 14776; (*c*) Y. Sun and Y. Xia, *J. Am. Chem. Soc.*, 2007, **126**, 3892; (*d*) Y. Sun and Y. Xia, *Adv. Mater. (Weinheim, Ger.)*, 2004, **16**, 264.
10 (*a*) Y. Yin, C. Erdonmez, S. Aloni and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2006, **128**, 12671; (*b*) Z. Chen, M. Waje, W. Li and Y. Yan, *Angew. Chem., Int. Ed.*, 2007, **46**, 4060; (*c*) Y. Bi and G. Lu, *Nanotechnology*, 2008, **19**, 275306; (*d*) Y. Bi and G. Lu, *Chem. Mater.*, 2008, **20**, 1224.
11 M. H. Kim, X. Lu, B. Wiley, E. P. Lee and Y. Xia, *J. Phys. Chem. C*, 2008, **112**, 7872.
12 X. Lu, L. Au, J. McLellan, Z.-Y. Li, M. Marquez and Y. Xia, *Nano Lett.*, 2007, **7**, 1764.
13 J. Chen, B. Wiley, J. McLellan, Y. Xiong, Z.-Y. Li and Y. Xia, *Nano Lett.*, 2005, **5**, 2058.
14 Y. Sun, B. Wiley, Z. Y. Li and Y. Xia, *J. Am. Chem. Soc.*, 2004, **126**, 9399.
15 N. Zettsu, J. M. McLellan, B. Wiley, Y. Yin, Z. Li and Y. Xia, *Angew. Chem., Int. Ed.*, 2006, **45**, 1288.
16 Y. Bi and G. Lu, *Int. J. Hydrogen Energy*, 2008, **33**, 2225.