COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Controllable AuPt bimetallic hollow nanostructures

Han-Pu Liang,[ab] Yu-Guo Guo,[ab] Hui-Min Zhang,[a] Jin-Song Hu,[ab] Li-Jun Wan*[a] and Chun-Li Bai*[a]

[a] *Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China. E-mail: wanlijun@iccas.ac.cn; Fax: +86-10-62558934; Tel: +86-10-62558934*

[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100080, China*

Received (in Cambridge, UK) 23rd February 2004, Accepted 4th May 2004
First published as an Advance Article on the web 24th May 2004

We describe a facile procedure for one step, large-scale synthesis of AuPt bimetallic hollow tube-like 1-D nanomaterials and hollow nanospheres, which can be easily manipulated by merely changing the concentration of citric acid.

In recent years, nanostructured materials with specific morphologies have been intensively pursued because of their novel optical, electrical, catalytic and magnetic properties. Among the different morphologies of nanomaterials, hollow metallic nanostructures, in addition to advantages of high specific surface, low density, saving of material and reduction of cost, have particularly attracted considerable interest due to their intriguing surface plasmonic properties and catalytic activities different from their solid counterparts.[1,2] For example, Hyeon and co-workers have reported that hollow Pd spheres show good catalytic activities in Suzuki cross coupling reactions and can be reused many times without loss of catalytic activity.[2] Many metallic hollow spheres and nanotubes have already been reported.[3] Bimetallic nanostructured architectures represent a highly interesting class of materials exhibiting improved catalytic properties, surface plasmonic properties and magnetic properties, which are postulated to result from both electronic and structural effects of the bimetal.[4] For instance, AuPt bimetallic catalysts have received significant attention due to their special catalytic properties.[5] It is reported that the polymer-stablized AuPt bimetallic colloidal sol has exhibited more efficient catalytic activity than Pt colloid for both hydrogenations of olefins and visible light induced hydrogen generation from water.[6] As a result, it is essential to build AuPt bimetallic catalysts with hollow nanostructures for high catalytic activity and selectivity. Moreover, the catalytic and electronic properties are strongly dependent on the size and morphology of the nanomaterials, and therefore the synthesis of AuPt hollow nanostructures with well-controlled morphology and size could be critical for practical purposes in the construction of nanostructured catalysts.

We have reported a facile method based on replacement reactions for large-scale synthesis of Pt hollow nanospheres exploiting Co nanoparticles as sacrificial templates.[7] In this communication, we extended this method to prepare AuPt bimetallic hollow tube-like 1-D nanomaterials and nanospheres. The size and morphology of these hollow structures are well controlled by varying the concentration of citric acid. The feature of this technique is that it is facile, economical, and versatile.

Co nanoparticles play an important role as sacrificial templates in fabricating hollow nanostructures. In the present study, Co nanoparticles were fabricated according to the method by Kobayashi *et al*.[8] In brief, for the fabrication of hollow 1-D nanomaterials, Co nanoparticles were first fabricated by the addition of 0.1 mL of 0.4 M $CoCl_2$ solution to 100 mL of a deaerated aqueous solution containing 4 mM $NaBH_4$ and 4 μM citric acid under high-purity N_2 protection. H_2 was evolved during the reaction and continued for several minutes. When gas evolution ceased, 40 mL of the obtained solution were immediately added to 10 mL of mixed solution containing 0.4 mM H_2PtCl_6 and 0.6 mM $HAuCl_4$ stirred at room temperature. The concentration of citric acid was changed to 0.4 mM while keeping other experimental conditions constant for the fabrication of bimetallic hollow nanospheres.

The typical low-magnification TEM image in Fig. 1a shows as-synthesized nanostructures. It can be seen in the image that the center portions of these 1-D nanomaterials are lighter than their wall edge, indicating a hollow nanostructure. The high-magnification TEM image in Fig. 1b reveals the detailed structure. These 1-D nanomaterials (*ca.*100 nm in diameter) are in a hollow tube-like configuration formed by distorted hollow nanospheres. The low- and high-magnification SEM images in Fig. 2 indicate large-scale tube-like 1-D nanomaterials several microns in length have been fabricated. The results also suggest that these 1-D nanomaterials are robust enough to survive centrifugation and ultrasonic treatment. Fig. 1c gives the energy dispersed X-ray (EDX) analysis taken from

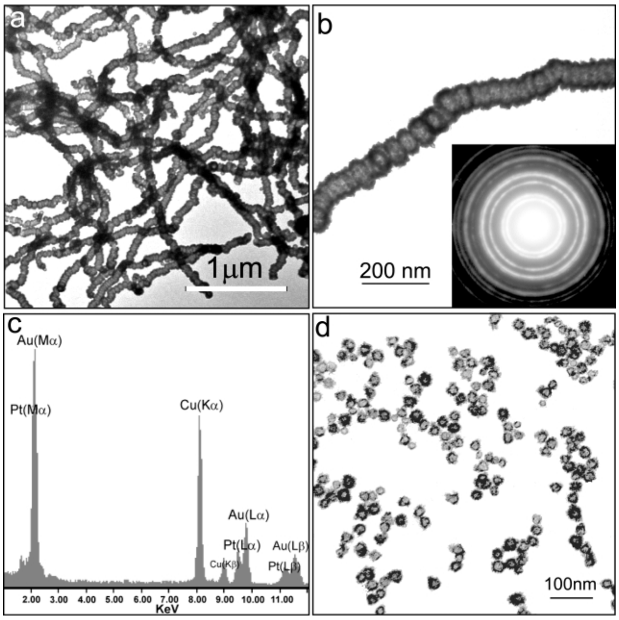

Fig. 1 (a) Low-, (b) high-magnification TEM images and (c) EDX of AuPt 1-D hollow nanomaterials. (d) TEM images of bimetallic hollow spheres. The inset in (b) shows an electron diffraction pattern taken from bimetallic hollow nanostructures.

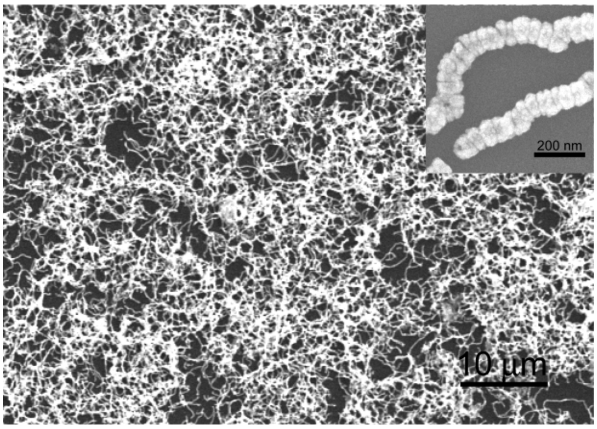

Fig. 2 SEM image of AuPt bimetallic hollow tube-like 1-D nanomaterials. The inset is a high-magnification SEM image.

DOI: 10.1039/b402745k

a random assembly of bimetallic hollow 1-D materials. The results demonstrate the coexistence of Au and Pt. The electron diffraction pattern of bimetallic nanomaterials shows regular rings in the inset of Fig. 1b, indicating that the 1-D material is in an fcc polycrystalline structure. The concentric rings in the diffraction pattern from the center-most ring can be assigned as diffraction from fcc polycrystals in the sequence of {111}, {200}, {220} and so on.

The mechanism for the formation of 1-D nanomaterials is proposed in Fig. 3. Co nanoparticles are considerably smaller than the theoretical critical single domain diameter (*ca.* 55 nm), such that single domain behavior is possible.[9] All the atomic magnetic spins of the nanoparticles are coupled in the same direction, and the nanoparticle behaves as a single magnetic dipole. These nanoparticles are ferromagnetic at room temperature as indicated in the literature,[8] thus magnetic interactions among them play a crucial role. The role that citrate acids play as capping agents is related to the adsorption of citric ions on the Co nanoparticle surface, preventing the growth of Co nanoparticles through double layer repulsion between negatively charged cobalt nanoparticles. When there is not enough citric acid, the dipole–dipole interactions are stronger than the repulsive steric interactions caused by citric acid. These ferromagnetic nanoparticles are prone to aggregate to form chain-like 1-D nanomaterials to minimize the magnetostatic energy. The magnetic dipoles should be in an alternating up and down arrangement in this assembly, as shown in Fig. 3. The formation of chains of magnetic nanoparticles have already been reported by other groups.[10] Since the standard reduction potential of the $PtCl_6^{2-}$/Pt redox pair (0.735 V *vs.* the standard hydrogen electrode (SHE)) and $AuCl_4^-$/Au redox pair (0.994 V *vs.* SHE) are much higher than that of the Co^{2+}/Co redox pair (−0.277 V *vs.* SHE), $PtCl_6^{2-}$ and $AuCl_4^-$ will be reduced to Au and Pt atoms as soon as Co nanoparticles are added to the solution. The color of the mixed solution turns from pale to dark yellow simultaneously, indicating the formation of hollow nanostructures. These bimetallic particles will nucleate and grow into very small aggregates, eventually evolving into a thin shell around Co nanoparticles to form hollow nanostructures. These materials should have an incomplete shell in the early stage of the replacement reaction because $PtCl_6^{2-}$, $AuCl_4^-$ and Co^{2+} can diffuse across this shell. At this stage, the remaining Co cores are still ferromagnetic and also tend to form 1-D nanostructures due to strong dipole–dipole interactions, resulting in the distortion of hollow sphere chains. The distortion process will continue until a balance between magnetic interactions and repulsive steric interactions of the bimetallic shell is reached or the remaining Co nanoparticles become superparamagnetic as their sizes decrease. Hence, hollow bimetallic tube-like 1-D nanomaterials comprising distorted hollow nanospheres were formed after Co templates had been completely exhausted.

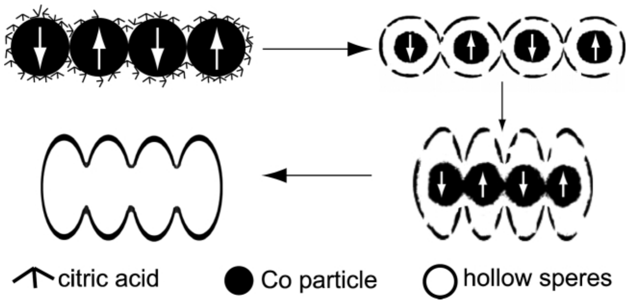

Fig. 3 Schematic illustration of hollow tube-like 1-D nanomaterial formation.

We deliberately increased the concentration of citric acid to 0.4 mM to enhance the repulsive steric interactions between magnetic particles while keeping other experimental conditions constant. As shown in Fig. 1d, large-scale AuPt bimetallic hollow spheres were obtained. The EDX experiment (not shown here) of an individual hollow nanosphere was also carried out, confirming the coexistence of Au and Pt. The average diameter of a sphere is reduced distinctively and calculated statistically to be 24 ± 2 nm. Tube-like 1-D hollow nanomaterials cannot be found on the whole sample. This result confirms that the mechanism we put forward is correct. The decrease of the diameter of hollow spheres can be attributed to the reduction of Co nanoparticle size.

In summary, we have demonstrated a facile procedure for one step, large-scale synthesis of AuPt bimetallic hollow tube-like 1-D nanomaterials and hollow nanospheres. The size and morphology of the hollow nanostructure can be easily manipulated by merely changing the concentration of citric acid. This observation of exclusive formation of hollow tube-like 1-D nanomaterials comprising distorted hollow spheres offers powerful evidence that magnetic nanoparticles tend to form chain-like 1-D materials in solution when magnetic dipole interactions are stronger than the repulsive steric interactions. The magnetic Co nanoparticles as sacrificial templates should be a promising candidate for facile synthesis of metallic and bimetallic hollow nanostructures. A study on the catalytic properties of as-synthesized nanostructures in various reactions is in progress.

This work was supported by National Natural Science Foundation of China (No. 20025308, 20177025, 10028408 and 20121301), National Key Project on Basic Research (Grant G2000077501) and the Chinese Academy of Sciences.

Notes and references

1 (*a*) J. B. Jackson and N. J. Halas, *J. Phys. Chem. B*, 2001, **105**, 2743; (*b*) Y. Sun and Y. Xia, *Anal. Chem.*, 2002, **74**, 5297.
2 S.-W. Kim, M. Kim, W. Y. Lee and T. Hyeon, *J. Am. Chem. Soc.*, 2002, **124**, 7642.
3 (*a*) M. Steinhart, Z. Jia, A. K. Schaper, R. B. Wehrspohn, U. Gösele and J. H. Wendorff, *Adv. Mater.*, 2003, **15**, 706; (*b*) J. Bao, C. Tie, Z. Xu, Q. Zhou, D. Shen and Q. Ma, *Adv. Mater.*, 2001, **13**, 1631; (*c*) D. Zhang, L. Qi, J. Ma and H. Cheng, *Adv. Mater.*, 2002, **14**, 1499.
4 (*a*) F. Maroun, F. Ozanam, O. M. Magnussen and R. J. Behm, *Science*, 2001, **293**, 1811; (*b*) M. Heemeier, A. F. Carlsson, M. Naschitzki, M. Schmal, M. Bäumer and H.-J. Freund, *Angew. Chem., Int. Ed.*, 2002, **41**, 4073; (*c*) O. S. Alexeev and B. C. Gates, *Ind. Eng. Chem. Res.*, 2003, **42**, 1571; (*d*) S. Link, Z. L. Wang and M. A. El-Sayed, *J. Phys. Chem. B*, 1999, **103**, 3529; (*e*) S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989.
5 (*a*) G. Schmid, A. Lehnert, J.-O. Malm and J.-O. Bovin, *Angew. Chem., Int. Ed.*, 1991, **30**, 874; (*b*) Y. Lou, M. M. Maye, L. Han, J. Luo and C.-J. Zhong, *Chem. Commun.*, 2001, 473.
6 (*a*) C. W. Chen and M. Akashi, *Polym. Adv. Technol.*, 1999, **10**, 127; (*b*) N. Toshima and T. Yonezawa, *Makromol. Chem., Macromol. Symp.*, 1992, **59**, 281.
7 H.-P. Liang, H.-M. Zhang, J.-S. Hu, Y.-G. Guo, L.-J. Wan and C.-L. Bai, *Angew. Chem., Int. Ed.*, 2004, **43**, 1540.
8 Y. Kobayashi, M. Horie, M. Konno, B. Rodríguez-González and L. M. Liz-Marzán, *J. Phys. Chem. B*, 2003, **107**, 7420.
9 T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen and T. P. Russell, *Science*, 2000, **290**, 2126.
10 (*a*) V. F. Puntes, K. M. Krishnan and A. P. Alivisatos, *Science*, 2001, **291**, 2115; (*b*) F. S. Diana, S.-H. Lee, P. M. Petroff and E. J. Kramer, *Nano Lett.*, 2003, **3**, 891.