Synthesis and magnetic properties of Co–Sn–O nanorings†

Cheng Peng, Lian Gao* and Songwang Yang

Received (in Cambridge, UK) 12th June 2007, Accepted 27th July 2007
First published as an Advance Article on the web 14th August 2007
DOI: 10.1039/b708803e

A novel Co–Sn–O nanoring structure was synthesized *via* a simple hydrothermal route; the difference in diffusion rates of ions was considered to be the main reason for the formation of such a ring structure.

The rapid arising of nanotechnology is deepening the synthesis chemistry of inorganic nanomaterials. Considerable methods have been developed for the synthesis of morphologically special nanoparticles such as nanowires, nanorods, nanocubes, nanobelts and nanorings so far. Meanwhile, the developments of the preparation methods for the nanoparticles also dig out many new fundamental chemical and physical phenomena, such as the oriented aggregation mechanism for crystal growth,[1–3] the Kirkendall effect for hollow nanostructure formation,[4–7] *etc.*

Nanostructured transition metal oxides have been widely studied due to their potential applications in new materials. For instance, SnO_2 and CoO, as technologically important semiconductor materials, both have important applications in gas sensing.[8,9] Meanwhile, ternary metal oxide nanostructure is another subject of research fields, such as titanates and ferrites,[10–13] *etc.* However, there were few reports on ternary metal oxide nanostructures of solid solutions, and only reports on the bulk Co–Sn–O system.[14,15] In this communication, we investigated the Co–Sn–O system *via* hydrothermal routes and successfully synthesized nanorings of ternary metal oxide solid solution, which remained with a tetragonal SnO_2 crystal nature. During the synthesis process, we noticed that the morphologies of the final products strongly depended on the cobalt concentration in the system and the difference in diffusion rates of the components in the solid solution resulted in the formation of a nanoring structure.

The Co–Sn–O nanostructures were prepared *via* a simple hydrothermal method with varied Co : Sn ratios. Fig. 1 shows the XRD patterns of all the prepared samples. When a small amount of cobalt ions are introduced, they can access the lattice of SnO_2 and the XRD patterns can be well indexed as tetragonal SnO_2 (JCPDS 77-0452). When the content of cobalt reaches 50 atom%, the samples show low crystallinity of SnO_2 and a minor impurity peak appears, which can be indexed as (420) of $Co(Sn(OH)_6)$ (JCPDS 74-0365). A possible reason for the $Co(Sn(OH)_6)$ impurity might be the reaction between $Co(OH)_2$ and $Sn(OH)_2$. When the content of cobalt is up to 80 atom%, the sample has $Co(OH)_2$ as the main phase, and SnO_2 and $Co(Sn(OH)_6)$ impurities since the amount of generated SnO_2 is too small to accommodate all the Co^{2+} ions and excess ions exist in the form of $Co(OH)_2$.

Fig. 2 shows the morphological properties of the prepared samples. The high morphological yield of nanorings in Fig. 2a–d were gained by using 70 atom% cobalt concentration *via* hydrothermal treatment for 22 h. The SEM image clearly indicates the nanoring structure of the product (Fig. 2a). The rings have outer diameters ranging from 75 to 220 nm and inner diameters from 35 to 150 nm. The dark "rodlike" morphologies in Fig. 2b are the profiles of nanorings, which come from the projection of the erect nanorings in the TEM grid, and we can thus determine the average thickness of the rings, 22.63 ± 5.66 nm. The high resolution TEM (HRTEM) image shows the dominant {101} lattice fringes of SnO_2 structure. The selected area electron diffraction (SAED) pattern reveals that the nanorings are single crystalline with the rutile SnO_2 structure (Fig. 2d). When the concentration of cobalt is reduced to 50 atom%, nanorings with spokewise rods are observed (Fig. 2e). Interestingly, the ratio of Co : Sn in the region of the rings is a little higher than that in the region of the rods (EDX results, see ESI†). In a control experiment, the concentration of cobalt was fixed at 70 atom% and, while the other conditions remained the same, only the reaction time was cut to 10 h and nanoplatelets were obtained. The

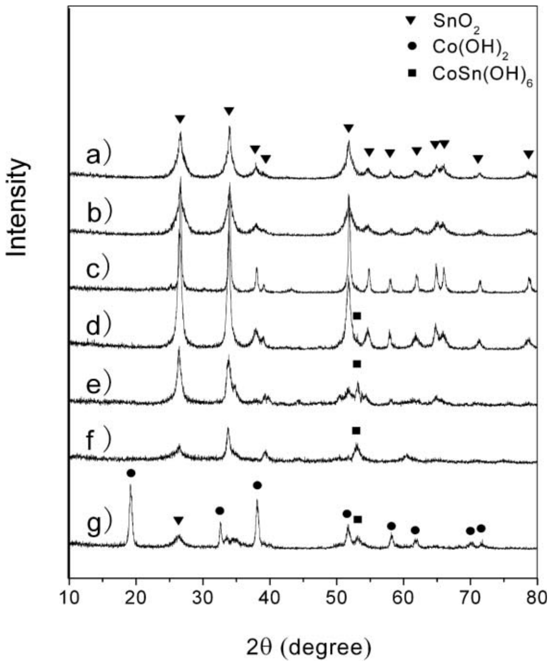


Fig. 1 XRD patterns of as-prepared samples with varied cobalt concentrations: (a) 0; (b) 5; (c) 10; (d) 20; (e) 50; (f) 70; (g) 80 atom%.

State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, P. R. China. E-mail: liangaoc@online.sh.cn; Fax: +86-21-52413122; Tel: +86-21-52412718

† Electronic supplementary information (ESI) available: Experimental details, TEM images, magnetic hysteresis loops of the samples with varied cobalt contents, EDX analysis of the rings with spokewise rods, and pore distribution of Co–Sn–O nanorings. See DOI: 10.1039/b708803e

platelets have thicker edges, on which some spherical particles can be found (Fig. 2f).

The experiments for varied concentrations of cobalt were also conducted and the detailed experimental results are listed in the ESI.† When no cobalt ions were introduced, SnO_2 nanoparticles were obtained without a tendency to form nanorings. The morphologies of the nanostructures changed from spherical particles to rings with the increase in the cobalt concentration in the system. It seems that the Co : Sn ratio plays an crucial role in the morphological evolution of the Co–Sn–O nanostructures. In fact, the Co : Sn ratio determines whether solid solution is formed in the reaction system. The radius of Co^{2+} ion is 0.72 Å, which is close to that of Sn^{4+} ion, 0.71 Å,[16] and so it is likely for Co^{2+} ions to access the SnO_2 crystal lattice and form solid solution. The chemical reactions under the hydrothermal conditions can be formulated as

$$Co(Ac)_2 + 2NaOH \rightarrow \beta\text{-}Co(OH)_2 + 2NaAc \quad (1)$$

$$SnCl_4 + 4NaOH \rightarrow SnO_2 + 4NaCl + 2H_2O \quad (2)$$

$$x\beta\text{-}Co(OH)_2 + (1-x)SnO_2 \rightarrow Sn_{1-x}Co_xO_{2-x} + xH_2O \quad (3)$$

A possible formation mechanism of the nanoring is proposed, as can be seen in Scheme 1a. Due to the intrinsic lamellar structures, most Co^{2+} ions existed in the form of β-$Co(OH)_2$ platelets in the alkaline precursor solution,[17] which are used as the sacrificial templates. It is known that the crystal planes located on the edge of the platelet have high surface energy.[18] Thus, under the hydrothermal conditions, the heterogeneous nucleation of SnO_2 mainly took place on the edges and subsequently accumulated there. Meanwhile, an interdiffusion between Sn^{4+} and Co^{2+} occurred to form solid solution. Co^{2+} ions accessed the SnO_2 lattice and SnO_2 migrated inward. The diffusion of Co^{2+} was faster than that of Sn^{4+}, resulting in the thinness in the center of the platelet, until a hole was formed. According to the classical nucleation theory, in a heterogeneous nucleation process, the bigger contact angle leads to higher free energy ΔG_s^*.[19] Therefore, SnO_2 crystallites continually accumulate on the outer loop of the platelet (Scheme 1b). The further reaction between SnO_2 and $Co(OH)_2$ led to further changes in morphology: the hole was enlarged and a ring structure was obtained. The formation process of the current nanorings is similar to that of hollow nanospheres or nanotubes through the Kirkendall effect.[4–7] With a low concentration of cobalt, *e.g.*, 50 atom%, nanorings with spokewise rods were obtained, because excess Sn^{4+} ions in the system tended to orientedly grow into SnO_2 nanorods under hydrothermal conditions.[20]

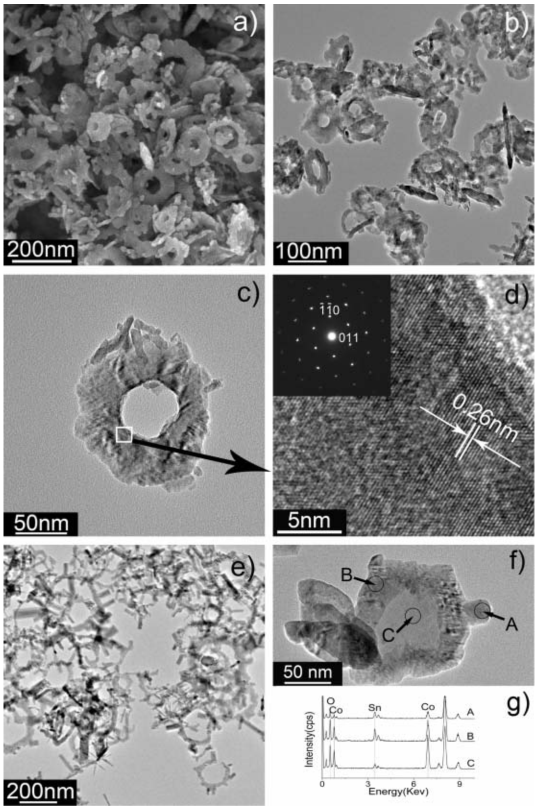
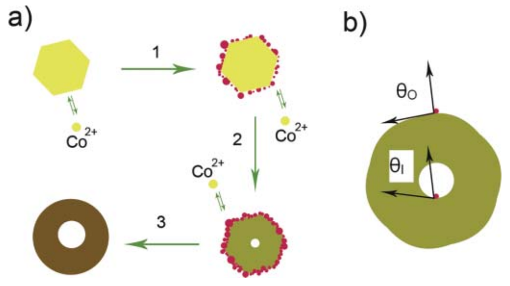


Fig. 2 (a) SEM image of the Co–Sn–O nanorings. (b) TEM image of the Co–Sn–O nanorings. (c) Enlarged TEM image of single nanoring. (d) HRTEM image of the Co–Sn–O nanorings. The insert is the SAED pattern. (e) TEM image of the rings with spokewise rods obtained at 50 atom% of cobalt. (f) TEM image of the nanoplatelets obtained by 10 h of hydrothermal treatment. (g) EDX spectra of the corresponding Co–Sn–O nanoplatelets.



Scheme 1 (a) Formation mechanism of Co–Sn–O nanorings: (1) heterogeneous nucleation process of SnO_2, (2) interdiffusion process, (3) formation of rings; (b) enlargement of the hole.

The above growth mechanism can be verified by the control experiment with a shortened treatment time, where nanoplatelets with thick edges formed and small particles were found on the edge (Fig. 2f). The EDX analysis of different regions of the platelets reveals that the center of the platelets contains the highest cobalt concentration, followed by the edge and the tiny particles (Fig. 2g). This evidently supports that the formation process of the rings is based on the interdiffusion of the two components, which is consistent with our proposition.

The magnetic properties of the as-prepared samples were measured. The magnetic hysteresis curve of the nanorings is presented in Fig. 3, which illustrates the strong magnetic response of the material to a varying magnetic field. The saturation magnetization (M_S) value of the samples increases with the increase in cobalt concentration. When the cobalt concentration is beyond 50 atom%, the M_S value decreases, which might be due to the relatively lower crystallinity. The maximum M_S value is 15.7 emu g^{-1}, which is close to the M_S value of wurtzite CoO reported in the literature.[21]

In summary, a simple hydrothermal route was developed for the synthesis of Co–Sn–O nanoring structures with tetragonal SnO_2 crystal nature. The interdiffusion between CoO and SnO_2 is

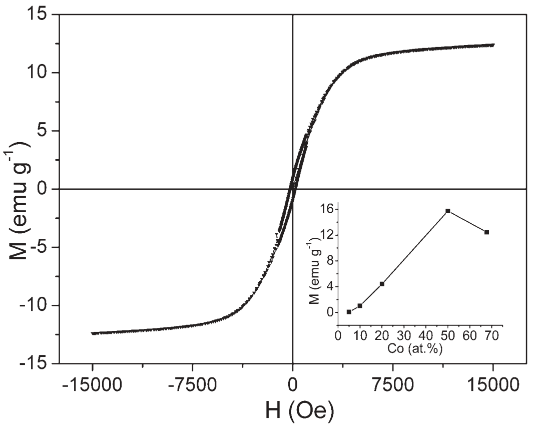


Fig. 3 The magnetic hysteresis curve of Co–Sn–O nanorings. The inset is the saturation magnetization value *vs.* cobalt concentration.

considered to be the main reason for the formation of such a nanoring structure. The Co–Sn–O nanorings show a strong magnetic response to a varying magnetic field. Other properties of the nanorings, such as gas sensing and solar cell performance are under investigation.

This work was financially supported by the National Basic Research Program (2005CB623605) and Shanghai Nanotechnology Promotion Center (0552nm045 and 0652nm022).

Notes and references

1 R. L. Penn and J. F. Banfield, *Science*, 1998, **281**, 969–971.
2 Z. Tang, N. A. Kotov and M. Giersig, *Science*, 2002, **297**, 237–240.
3 J. H. Yu, J. Joo, H. M. Park, S. I. Baik, Y. W. Kim, S. C. Kim and T. Hyeon, *J. Am. Chem. Soc.*, 2005, **127**, 5662–5670.
4 H. J. Fan, M. Knez, R. Scholz, K. Nielsch, E. Pippel, D. Hesse, M. Zacharias and U. Gosele, *Nat. Mater.*, 2006, **5**, 627–631.
5 Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai and A. P. Alivisatos, *Science*, 2004, **304**, 711–714.
6 Y. Wang, L. Cai and Y. Xia, *Adv. Mater.*, 2005, **17**, 473–477.
7 Y. Li, B. Tan and Y. Wu, *J. Am. Chem. Soc.*, 2006, **128**, 14258–14259.
8 W. Y. Li, L. N. Xu and J. Chen, *Adv. Funct. Mater.*, 2005, **15**, 851–857.
9 A. Rosental, A. Tarre, A. Gerst, J. Sundqvist, A. Harsta, A. Aidla, J. Aarik, V. Sammelselg and T. Uustare, *Sens. Actuators, B*, 2003, **93**, 552–555.
10 Y. Mao, T. Park and S. S. Wong, *Chem. Commun.*, 2005, 5721–5735.
11 U. A. Joshi and J. S. Lee, *Small*, 2005, **1**, 1172–1176.
12 J. J. Urban, J. E. Spanier, L. Ouyang, W. S. Yun and H. Park, *Adv. Mater.*, 2003, **15**, 423–426.
13 T. Park, Y. Mao and S. S. Wong, *Chem. Commun.*, 2004, 2708–2709.
14 S. B. Ogale, R. J. Choudhary, J. P. Buban, S. E. Lofland, S. R. Shinde, S. N. Kale, V. N. Kulkarni, J. Higgins, C. Lanci, J. R. Simpson, N. D. Browning, S. D. Sarma, H. D. Drew, R. L. Greene and T. Venkatesan, *Phys. Rev. Lett.*, 2003, **91**, 077205.
15 C. M. Liu, X. T. Zu and W. L. Zhou, *J. Phys.: Condens. Matter*, 2006, **18**, 6001–6007.
16 J. Fayat and M. S. Castro, *J. Eur. Ceram. Soc.*, 2003, **23**, 1585–1591.
17 Y. Hou, H. Kondoh, M. Shimojo, T. Kogure and T. Ohta, *J. Phys. Chem. B*, 2005, **109**, 19094–19098.
18 Y. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664–670.
19 W. D. Kingery, H. K. Bowen and D. R. Uhlmann, *Introduction to ceramics*, John Wiley & Sons, New York, 1976.
20 B. Cheng, J. M. Russell, W. S. Shi, L. Zhang and E. T. Samulski, *J. Am. Chem. Soc.*, 2004, **126**, 5972–5973.
21 A. S. Risbud, L. P. Snedeker, M. M. Elcombe, A. K. Cheetham and R. Seshadri, *Chem. Mater.*, 2005, **17**, 834–838.