Synthesis of Ordered Macroporous Co_3O_4 Microspheres via an Easy Melt Infiltration Route

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Uniform Co_3O_4 microspheres with ordered macroporous structure were synthesized via an easy melt infiltration method. Colloidal silica crystal was used as a hard template and $Co(NO_3)_2\cdot6H_2O$ as the precursor. The samples were characterized by X-ray powder diffraction, scanning electron microscopy, and transmission electron microscopy. A formation mechanism was also proposed.

Macroporous oxide materials prepared by using three-dimensional ordered organic or inorganic colloidal crystals as templates have attracted considerable attention in the past decade because of their potential applications in the fields of electrode materials,[1] catalyst,[2] storage,[3] and photonic band gap materials.[4] Up to now, most of the synthesized macroporous oxide materials are monoliths with three-dimensionally ordered macroporous (3DOM) structure. Macroporous oxides with microsphere structure have been rarely reported. Okuyama and co-workers synthesized macroporous silica and titania microspheres with the oxide nanoparticles forming the walls of the macropores via a spray-drying method.[5–7]

Recently, a new solid-liquid method for the preparation of mesoporous metal oxides by using KIT-6 and SBA-15 as templates has been developed.[8] The key to the success of the synthesis was that the melting point of the precursor must be lower than its decomposition temperature. In this letter, we report for the first time the synthesis of uniform Co_3O_4 microspheres containing ordered macropores via an easy melt infiltration route, which is based upon the fact that the melting point of the precursor is lower than its decomposition temperature. Colloidal silica crystal is used as the hard template and $Co(NO_3)_2\cdot6H_2O$ as the precursor. The ordered macroporous Co_3O_4 microspheres may serve as electrode materials, catalyst, and storage.

Nearly monodisperse silica spheres of 200 nm in diameter were synthesized by hydrolyzing tetraethyl orthosilicate (TEOS) under basic conditions according to Stöber's method.[9] Colloidal silica crystal was obtained by self-assembling silica spheres using a vertical deposition technique.[10] The colloidal crystal was sintered at 800 °C for 3 h in order to enhance the mechanical strength of the monolith. $Co(NO_3)_2\cdot6H_2O$ was melted at 55 °C and then the colloidal silica crystal monolith was immersed in the liquid to allow $Co(NO_3)_2\cdot6H_2O$ to infiltrate into the interspaces of the colloidal crystal by capillary action. After impregnation for 10 min, the impregnated composite monolith was carefully taken out and stood at room temperature. The resultant $Co(NO_3)_2\cdot6H_2O$/silica composite was calcined at 500 °C in air for 5 h with a heating rate of 1 °C min^{-1}. The silica template was removed by using a 10 wt % aqueous HF solution, followed by washing with distilled water six times and drying at 80 °C. The crystal structure of the sample was characterized by X-ray diffraction (XRD) (Bruker D8 advance). The microstructure of the samples was examined by scanning electron microscopy (SEM) (Gemini LEO1530) and transmission electron microscopy (TEM) (JEOL JEM-2100). The sample was dispersed in ethanol by ultrasonication for a few minutes before the TEM measurement.

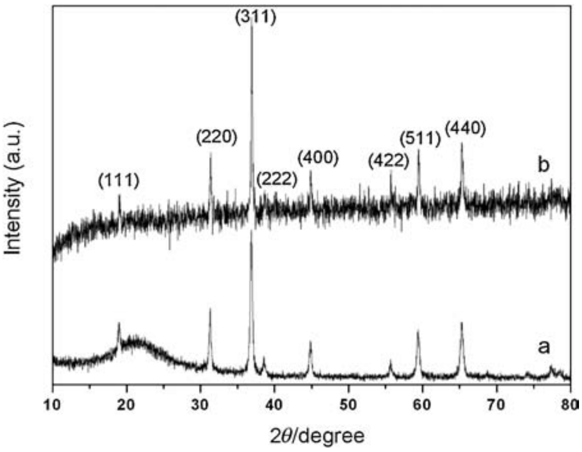


Figure 1. XRD patterns of the obtained samples.

Figure 1 shows the XRD patterns of the samples prepared using the melt infiltration method with (Figure 1a) and without (Figure 1b) the colloidal silica crystal template. A broad diffraction peak at about $2\theta = 15$–$25°$ was observed in Figure 1a, indicating the amorphous nature of the silica.[11] All the peaks in Figure 1b can be indexed to the pure cubic phase of Co_3O_4 with lattice parameter $a = 8.084$ Å (JCPDS: 43-1003). No impurity peaks were detected, indicating the high purity of the sample.

Figure 2a shows the SEM image of the colloidal silica crystal template. Figures 2b–2d show the SEM images of the Co_3O_4 sample. The uniform Co_3O_4 microspheres with ordered macroporous structure can be clearly observed, indicating that the silica template was well replicated. The windows connecting the macropores are observed in Figure 2d, which corresponds to the contact points of the silica spheres.

Figure 2e shows the TEM image of the Co_3O_4 microspheres. The ordered macroporous structure collapsed partially due to the ultrasonic vibration in the preparation of homogeneous solution for TEM. Figure 2f indicates that the Co_3O_4 microspheres are composed of nanoparticles.

The formation mechanism of Co_3O_4 microspheres during the heat treatment is illustrated in Scheme 1. The scheme shows the two-dimensional cross section of a Co_3O_4 microsphere which is in the voids of the colloidal silica crystal template. $Co(NO_3)_2\cdot6H_2O$ is solid at room temperature. It turned into a liquid state when the temperature increased to its melting point

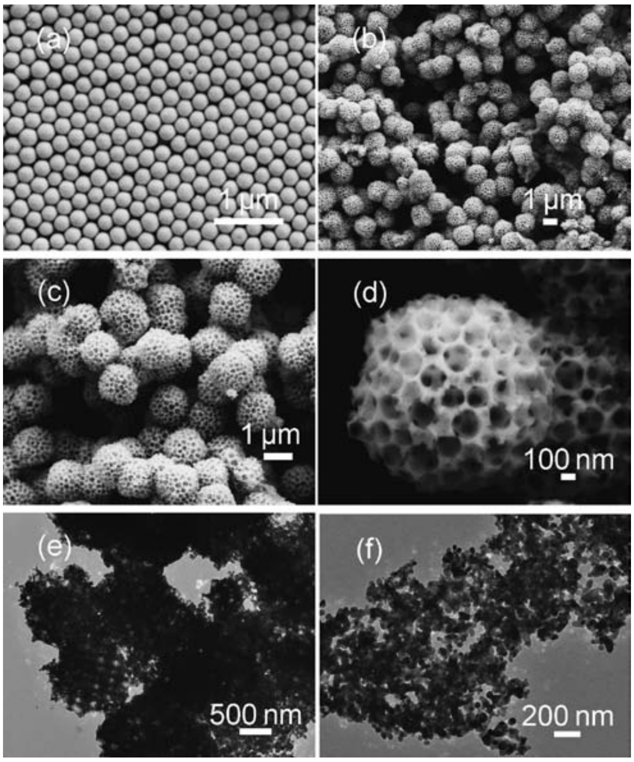
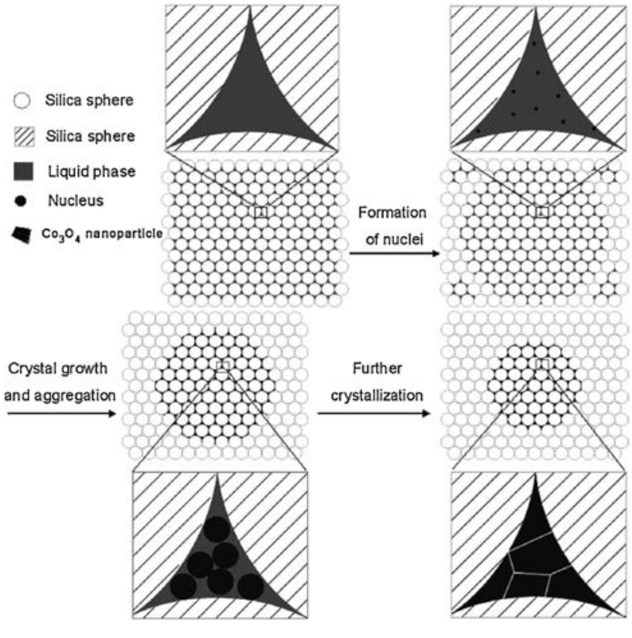


Figure 2. SEM images of (a) colloidal silica crystal and (b)–(d) Co_3O_4 microspheres. TEM images of (e) Co_3O_4 microspheres and (f) Co_3O_4 nanoparticles.



Scheme 1. Schematic illustration for the formation of macroporous Co_3O_4 microspheres.

and infiltrated into the interspaces of the silica template by capillary action. The liquid $Co(NO_3)_2{\cdot}6H_2O$ solidified again when the impregnated composite monolith was cooled at room temperature. During the further heat treatment, with the increase of the temperature, $Co(NO_3)_2{\cdot}6H_2O$ which has infiltrated into the interspaces of the silica template turned into a liquid phase before decomposition. When the temperature increased to its decomposition temperature, a number of dispersed nuclei were generated in the interspaces of the silica template. With further increase of temperature, the crystal growth occurred in the limited space between the silica spheres. During the crystal growth, in order to have a stable equilibrium configuration with a minimal energy in thermodynamics, the nanocrystals aggregated into spherical structure. The spherical structure shrunk gradually during the crystallization. After the crystallization was completed, the microspheres composed of Co_3O_4 nanoparticles were formed in the interspaces of the silica template. After removal of the silica template, uniform Co_3O_4 microspheres with ordered macropores were obtained.

In summary, uniform Co_3O_4 microspheres with ordered macropores were prepared by using colloidal silica crystal as the hard template and $Co(NO_3)_2{\cdot}6H_2O$ as the precursor via an easy melt infiltration method. The microspheres are composed of Co_3O_4 nanoparticles. It is expected that this method can be extended to the preparation of other macroporous oxide microspheres.

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References and Notes

1 H. Yan, C. F. Blanford, B. T. Holland, M. Parent, W. H. Smyrl, A. Stein, *Adv. Mater.* **1999**, *11*, 1003.
2 Z. Wang, M. A. Al-Daous, E. R. Kiesel, F. Li, A. Stein, *Microporous Mesoporous Mater.* **2009**, *120*, 351.
3 O. D. Velev, E. W. Kaler, *Adv. Mater.* **2000**, *12*, 531.
4 G. Subramanian, V. N. Manoharan, J. D. Thorne, D. J. Pine, *Adv. Mater.* **1999**, *11*, 1261.
5 F. Iskandar, Mikrajuddin, K. Okuyama, *Nano Lett.* **2001**, *1*, 231.
6 F. Iskandar, Mikrajuddin, K. Okuyama, *Nano Lett.* **2002**, *2*, 389.
7 F. Iskandar, A. B. D. Nandiyanto, K. M. Yun, C. J. Hogan, Jr., K. Okuyama, P. Biswas, *Adv. Mater.* **2007**, *19*, 1408.
8 W. Yue, W. Zhou, *Chem. Mater.* **2007**, *19*, 2359.
9 W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.
10 P. Jiang, J. F. Bertone, K. S. Hwang, V. L. Colvin, *Chem. Mater.* **1999**, *11*, 2132.
11 K. M. S. Khalil, A. A. Elsamahy, M. S. Elanany, *J. Colloid Interface Sci.* **2002**, *249*, 359.
12 The detailed experimental conditions in preparation of silica spheres and colloidal silica crystal, SEM images of the cross section of colloidal silica crystal, SEM images of the Co_3O_4 microspheres, and a color schematic illustration for the formation of macroporous Co_3O_4 microspheres are given in the Supporting Information those are available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.