doi:10.1246/cl.2011.106

Fabrication of Acid-tolerant Magnetic Co@SiO_2 Core–Shell Particles with Dense Silica Shell

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Cobalt particles occluded in hollow silica with dense shell were fabricated. Hollow polyalkylsiloxane microspheres containing cobalt oxide were prepared from W/O emulsion of aqueous cobalt nitrate and alkylsilyl trichloride isooctane solution. The particles were then reduced and finally heated in nitrogen. The resulting particles were magnetic and acid-tolerant.

Particles with core–shell structure, A@B (A: core of metal, metal oxide, etc.; B: shell of metal oxides, carbon, polymer, etc.), are of great interest as new materials in many current areas of separation, catalysis, transportation, biomedical sciences, and biomineralization. There have already been many reviews[1] in these areas. One important merit of the core–shell structure is protection of core substances from oxidation in air and dissolution in liquid phase by making a dense shell around the core. Such particles are of importance in various areas, for example, fabrication of acid- or base-tolerant magnetic particles. In general, a dense shell which interferes with passage of gases and liquids is necessary for the protection of core substances. However, there have been few studies of fabricating core–shell structures with dense shell. Lu et al.[2] fabricated Co@carbon, which is stable even in HNO_3 (53 wt %) for a long period (2 months). We reported that hollow microspheres with a dense shell of low specific surface area (ca. $10\,m^2\,g^{-1}$) is obtained by calcination of hollow polyalkylsiloxane particles at 873 K[3]. It is expected from this that a series of metal@SiO_2 of various metals can be fabricated by using polyalkylsiloxane as the precursor of SiO_2 shell. Here, we fabricated rattle-type acid-tolerant Co@SiO_2 particles with dense shell by using polymethylsiloxane as precursor of the shell.

Methyltrichlorosilane (MTCS) and octyltrichlorosilane (OTCS) were purchased from Shin-Etsu Chemical and Aldrich, respectively. A W/O emulsion was prepared by mixing 0.75 mL of 2.1 M aqueous $Co(NO_3)_2$ solution and 2.97 g of OTCS isooctane solution followed by ultrasonic agitation. Then 1.34 g of MTCS in 10 mL of isooctane was poured into the W/O emulsion under magnetic stirring. The mixture was stirred at room temperature for more than 3 h to make polymethylsiloxane shell around aqueous droplets. During the reaction, a large amount of air (ca. $3\,L\,min^{-1}$) was continuously supplied to remove evolved hydrogen chloride gas. Obtained solid was separated, washed thoroughly with isooctane, and dried. The sample was then calcined at 873 K for 3 h to convert $Co(NO_3)_2$ to its oxide, reduced in hydrogen gas at 673 K for 3 h, and subsequently heated at 973 K for 3 h in N_2 flow. Finally the sample was washed thoroughly with 1 M HCl. Characterization of the samples was performed by SEM, TEM, XRD, and N_2-adsorption. Saturation magnetization of the sample was determined by vibrating sample magnetometer. The amount of cobalt included in the particles was determined by ICP after converting to aqueous form by alkali fusion. The amount of cobalt leached during immersion in acid solution was also determined by ICP.

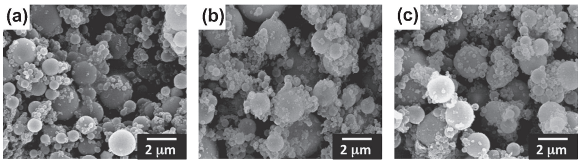

Figure 1. SEM images of the samples (a) after calcination at 873 K, (b) after reduction with H_2 followed by heat treatment in N_2 at 973 K, and (c) after washing with 1 M HCl.

The SEM image of samples after calcination at 873 K for 3 h is shown in Figure 1a. It is confirmed that spheres with various diameter are formed. During the calcination, changes in IR spectra showed that polymethylsiloxane phase turned to porous silica of $40\,m^2\,g^{-1}$ in specific surface area, and changes in XRD patterns showed that $Co(NO_3)_2$ was converted to Co_3O_4. The SEM image of particles once reduced in H_2 gas followed by heating in N_2 at 973 K is shown in Figure 1b. The shape of the particles remained the same even after heating at 973 K. On the other hand, specific surface area decreased from 40 to $5\,m^2\,g^{-1}$, suggesting that the silica shell turned to a dense nonporous phase. The change in XRD patterns showed that Co_3O_4 was reduced to metal cobalt after heating at 973 K, showing that hydrogen gas was effectively supplied through porous silica-shell during reduction at 673 K. After heat treatment at 973 K in N_2, the porous silica-shell turned to dense nonporous silica, but metal Co remained as it was. As shown in Figure 1c, the shape of the sample remained the same after washing with 1 M HCl. Average diameter of Co@SiO_2 was 1.5 µm obtained from the particle size distribution (see Figure S1 in Supporting Information; SI)[4] by SEM observation. It was confirmed from XRD pattern that Co remained in the sample even after washing with 1 M HCl (see Figure S2 in SI).[4]

TEM images of a representative Co@SiO_2 particle are shown in Figure 2. As shown in Figure 2a, a rattle-type core–shell structure is observed in the bright-field TEM image. The image shown in Figure 2b is a STEM dark-field image of the particle. Since lightness of the core is stronger than that of the shell, it is confirmed that the core and shell is composed of metal cobalt and silica, respectively. The images shown in Figures 2c and 2d show EDX elemental mapping images of Si and Co, respectively. It is obvious from the results that the major parts of Co are in the void space of the hollow silica. TEM observation (see Figure S3 in SI)[4] revealed that major parts of the Co@SiO_2

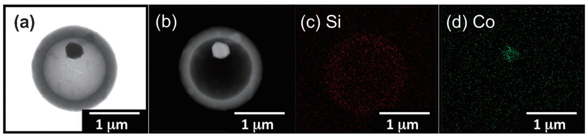

Figure 2. (a) Bright-field TEM image, (b) STEM dark-field image, (c) EDX elemental mapping images of Si, and (d) the same images of Co of a representative Co@SiO_2 particle.

Figure 3. The behavior of Co@SiO_2 to a magnet (right) after immersion in 1 M HCl for 1 year. Particles in the sample bottle are gathering near the magnet (left). The photograph also shows that the color of the pH indicator paper turned from yellow to red in the acid solution.

particles contain Co in the internal void space of the hollow silica with thin wall (0.03–0.5 μm). In addition, analysis by ICP showed that the amount of Co occluded in Co@SiO_2 was 3.6 mass % (the yield of Co was ca. 10%.). Thus it is concluded that rattle-type Co@SiO_2 particles have been fabricated by the method applied here.

In Figure 3 shows the response of Co@SiO_2 particles to a magnet (at right, surface magnetic field: 3.8 kOe) after immersion in 1 M HCl for 1 year.[5] Particles in the sample bottle gather near the magnet, so that Co@SiO_2 obtained here are acid-tolerant magnetic particles for a long period. The color change of the pH indicator paper (from yellow to red in acid solution) is also shown in the figure. Since metal cobalt is readily dissolved in 1 M HCl, this suggest that the metal cobalt was successfully shielded from the acidic solution by the dense silica shell.

Effect of acid-treating time on leaching of cobalt and saturation magnetization during immersion of Co@SiO_2 in 1 M HCl is exemplified in Table 1. As shown in the table, ICP analysis revealed that the amount of Co leached from Co@SiO_2 gradually increased over 2 weeks in the acidic solution, but the total leaching amount was less than 3% of total cobalt, suggesting that the Co@SiO_2 is acid-tolerant. Aslam et al.[6] fabricated Co@SiO_2 nanoparticles from tetramethylorthosilicate and $CoCl_2$ and found that the Co-core of the particle dissolved completely in 1 M HCl within 12 h. Their results suggest that the acid solution passes through the silica shell and that the Co-core is readily dissolved in aqueous HCl. Therefore, the acid-tolerant property observed here is ascribed to formation of dense nonporous shell which interferes with passage of acid solution. As shown in Table 1, the value of saturation magnetization was 2.7 emu g^{-1} for Co@SiO_2 before acid treatment, and the value was within 2.3–2.6 emu g^{-1} independent of immersion time, so that the major portion of metal cobalt existed in the particles even after the acid treatment.

Table 1. Effect of acid-treating time on leaching amount of Co and saturation magnetization during immersing Co@SiO_2 in 1 M HCl

Acid treating time /day	Leaching amount of Co /mol %	Saturation magnetization /emu g^{-1}
0	0	2.7
1	1.0	2.4
2	1.1	2.4
3	1.3	2.4
7	1.5	2.3
14	2.8	2.6

In conclusion, acid-tolerant rattle-type Co@SiO_2 was fabricated from hollow polymethylsiloxane particles occluding $Co(NO_3)_2$. The acid-tolerant property is ascribed to formation of dense nonporous silica shell. It is expected that various metal@SiO_2 can also be fabricated by applying the method developed here.

One of the authors (T. Okada) thanks MEXT of the Japanese Government (Grant-in-Aid for Scientific Research on Young Scientists B # 20750120) and Nippon Sheet Glass Foundation for Materials Science and Engineering.

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