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Marked capability for hydrogen occlusion of hollow silica nanospheres containing group 8–10 metal clusters

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Abstract

Hollow silica nanospheres containing various precious metal clusters such as Rh, Ir and Ru were synthesized by solubilizing corresponding metal ammine complexes into NP-6/cyclohexane reversed micelle system. The condensation and nucleation of the metal ammine complex in the reversed micelles took place and the resulting nanocrystals of the ammine complexes acted as a structure-directing agent for the formation of hollow cavity in silica spheres. The nano-hollow spheres were stable for thermal treatment up to 1073 K. By this method, bimetallic nanoparticles, i.e. Rh–Co–SiO_2 and Ir–Co–SiO_2, were also easily synthesized and both metal elements containing in the hollows may be alloyed after thermal treatment. The Ir– and Rh–SiO_2 nano-hollows exhibited excess hydrogen uptake. In particular, over Ir–SiO_2 sample, the H/Ir ratios reached 3.3 under 200 Torr of hydrogen at room temperature. At higher pressure, the H/M value reached 11.6 at 2.6 MPa.

Keywords: Nano-hollows; Silica; Iridium; Hydrogen occlusion; Reversed micelle

1. Introduction

Nano-sized silica particles are generally recognized as useful materials and utilized in wide varieties of industries, i.e. fillers for plastics, a high-precision abrasive for silicon wafers, and starting materials of sol–gel process for obtaining functional silicon oxide, column packing for chromatography, adsorbate and catalysts. The synthesis methods of those nano-size dense silica spheres have already been established until 1980s [1]. On the other hand, synthesis of hollow spheres with molecular dimensions is one of the most attractive studies to actualize photonic crystals [2,3], shape selective adsorbents [4,5], chemical sensors, controlled release capsules and catalysts. Many approaches have been carried out to synthesize such hollow materials by removing template cores surrounded by oxide shells to produce hollows. In many cases, molecular assembly [6], polystyrene latex spheres [7] and metal sulfide sols [8] are used as template cores. However, most of the investigations are concerned with the synthesis of micrometer-sized particles [7,9–11], because the synthesis of well-dispersed hollow particles with nanometer sizes is very difficult [3,7]. Furthermore, little is known about how to introduce foreign substances into their cavities giving some functionality to the hollow nanospheres [2,3]. Hippe et al. reported the novel preparation method of SiO_2 and TiO_2 nano-tubes encapsulating platinum nanoparticles inside their cavities by using a tetra-ammine platinum complex as structure-directing agent. By their method, the surface of ammine complex crystals was coated with silica layers formed by a sol–gel process, building up the nanometer walls. In the final step, the Pt-salt fibers are thermally decomposed and spontaneously reduced to metallic Pt nanoparticles [12]. We have studied adsorption and catalytic properties of the various metal containing oxide nano-tubes and nano-capsules synthesized by the similar manner with their report. From our study, remarkable selective hydrogen adsorption abilities of the metal–SiO_2 nano-tubes and capsules have been revealed [13,14]. Fine particles of precious metals and ultra micropores formed in the silica wall have an important role for the unique adsorption character. While the crystal template technique is the novel method for preparation of hollow oxide encapsulating metal nanoparticles, there is a disadvantage in this method, i.e. the difficulty in controlling the size and distribution of particles.

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We report here the synthesis of tailor-made hollow silica nanospheres containing ultrafine particles of precious metals in their cavities by using a crystal template method in a reversed micelle system. The preparation of ultrafine particles in a reversed micelle system has received considerable attention because of its possibility to obtain mono-dispersed particles of nm size [15,16]. In our previous work, we have employed a similar sol–gel process with crystal template in the inner cavity of reversed micelles and tried to achieve the synthesis of mono-dispersed metal encapsulating hollow structures [17]. The obtained metal silica nano-hollow showed very interesting properties for hydrogen adsorption. The Ir containing silica nano-hollows could adsorb 16 cm^3 (g-sample)$^{-1}$ of hydrogen gas at ambient temperatures and pressures which corresponds to more than three times the amount of total Ir metal atoms (bulk and surface). It was considered that such metal containing nano-cavities formed in silica spheres possess an anomalous affinity with hydrogen molecules and can occlude them like carbon nano-materials. In the present report, we investigated the synthesis of SiO_2 nano-hollows encapsulating various precious metals such as Ir, Rh and Ru and their combinations, e.g., Ir and Co, Rh and Co, in their cavities. The effect of preparation conditions on the morphologies of the nano-hollows and their chemisorption abilities are also discussed in depth.

2. Experimental

Silica nanospheres containing metal particles in their hollow structure (M–SiO_2(h)) were prepared by reversed micelle techniques as follows. An appropriate amount of $M(NH_3)_nCl_m$ aqueous solution (typically 360 μL, concentration of $M(NH_3)_mCl_n$ is 80 mM) was rapidly injected into 80 mL of 0.1 M NP-6 (hexaoxyethylene nonyl phenyl ether; supplied by Lion Corporation) cyclohexane solution. After stirring at room temperature for 12 h, 360 μL of 28% NH_3 aqueous solution was injected rapidly and after 2 h, 416 μL of tetraethoxysilane (TEOS) were added rapidly. The solution was transparent at the beginning but became slightly cloudy after 2 days stirring. The resulting solution was phase separated by the addition of 20 mL of methanol, followed by filtration and washing with cyclohexane and acetone. After drying in a desiccator overnight, the obtained dark gray fine powders were evacuated at 573 K for 5 h. The samples containing two different metal elements, e.g., Rh–Co, Ir–Co, were also synthesized employing mixed solution of both precursor salts. Hydrogen adsorption measurements were carried out using conventional volumetric adsorption equipment at 298 K after H_2 reduction at 573 K for 3 h followed by evacuation at 583 K. The morphology of the obtained particles was measured by using a transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer. Electronic states of the sample were measured by X-ray photoelectron spectroscopy equipped with an in situ pretreatment chamber. Before the XPS spectroscopy measurements, samples were reduced with 40 kPa H_2 in the in situ pretreatment chamber. The iridium content in Ir–SiO_2 was determined by ICP-AES techniques. Before ICP measurements, the sample was decomposed by fusion with Na_2O_2 according to the report of Danzaki [18].

3. Results and discussion

3.1. R_w dependence in the synthesis of various metal encapsulating silica spheres with hollow cavities

Fig. 1 shows the TEM images of various metal–SiO_2 particles obtained by the reversed micelle technique. As clearly shown in the photos, all of the SiO_2 spheres contain hollows in their center. Most of the spheres have only one hollow but a small number of spheres containing two or three hollows were observed in the same sample. Fine metal clusters of about 1 nm in diameter were observed in the hollow. During TEM measurement, those fine metal clusters rolled around freely inside the cavity by the irradiation of electron beam. This observation clearly shows that the hollow cavity really exists in the silica spheres. The average diameter of SiO_2 shell was about 40 nm and the size distribution was very sharp. The diameter of the hollow formed in the SiO_2 shell was around 10 nm. The size of both shell and hollow are controllable by water to surfactant ratios (R_w) in the reversed micelle. Fig. 2 represents changes in size of hollow and shell of Rh–SiO_2(h) with the R_w value observed by TEM. At lower R_w, the hollow was obscure and the shell size was below 35 nm. At $R_w = 5$, hollows were clearly observed but the shell size was almost the same as the one at lower R_w. At higher R_w, the shell size increased remarkably and the hollow size also increased. Since the micelle size is controlled by R_w value, it is considered that at higher R_w value more amount of metal ammine complex solution is contained in micelle particle.

3.2. Thermal stability of metal containing silica nano-hollows

The nano-hollow spheres were relatively stable for thermal treatment. Fig. 3 shows TEM images of Rh–SiO_2(h) after thermal treatment in air at different temperatures. The hollow structure is practically unchanged even after calcinations at 1073 K although the diameter of shell shrank slightly. Fig. 4 shows the effect of thermal treatment on diameter of shell and hollow as well as BET surface area. By the calcinations at 773 K, the diameter of shell decreased from 40 to 32 nm and the hollow size also decreased from 11 to 8 nm. Interestingly, after higher temperature treatment at 1073 K, both shell and cavity sizes were unchanged compared to those after 773 K calcined sample. On the other hand, the BET surface area of the Rh–SiO_2(h) remains unchanged until calcination at 773 K and decrease from 80 to 60 m^2 g^{-1} after calcination at 1073 K.

3.3. The formation mechanism of hollow structure

The condensation and nucleation of metal ammine complexes in the reversed micelles may take place during the repeated collision and separation of micelles, which is believed to be responsible for the formation of nano-hollows. From the

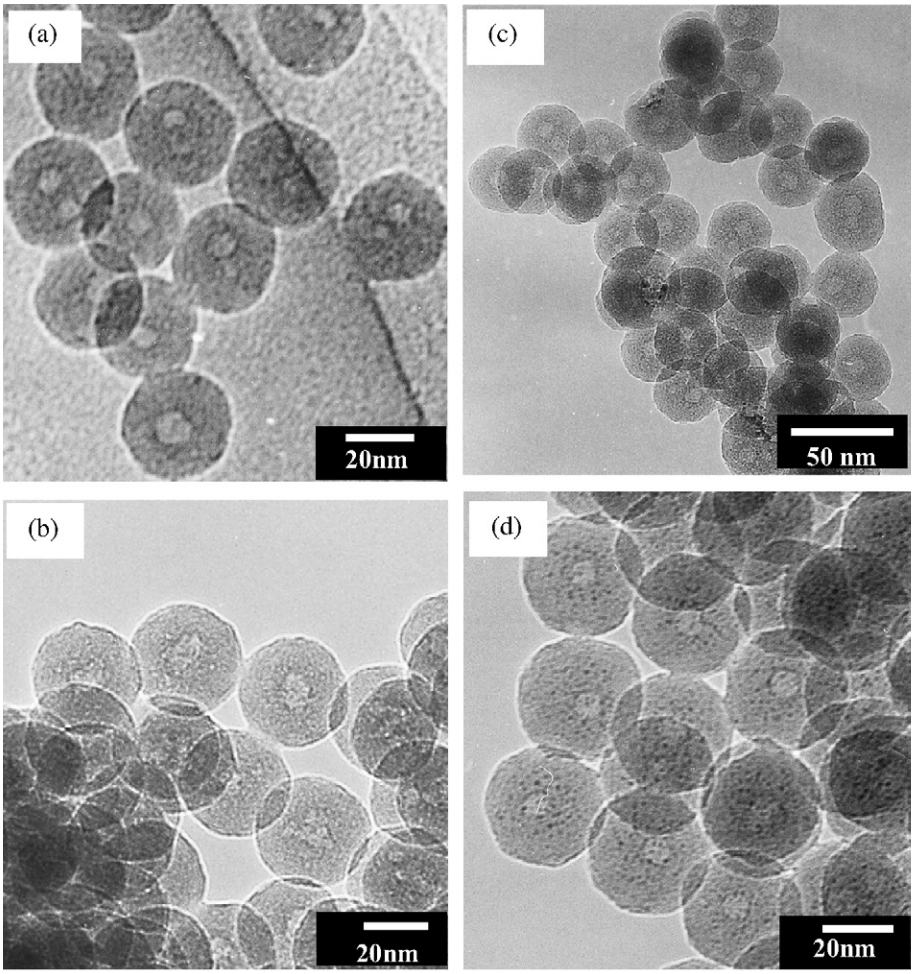

Fig. 1. TEM images of metal–SiO_2 nano-hollow spheres, after evacuation and reduction by hydrogen at 573 K: (a) Co–SiO_2(h), (b) Ru–SiO_2(h), (c) Rh–SiO_2(h), and (d) Ir–SiO_2(h).

TEM observation, the formation of crystallized nuclei was confirmed at the initial stage after the addition of the aqueous ammine complex to the NP-6 cyclohexane solution. When the metal ammine complex was not present in the reversed micelle system, solid spherical silica particles without hollows were obtained. In the case of Ir–SiO_2(h), we have also employed hydrogen chloroiridate or iridium nitrate as Ir precursors. When those highly water-soluble Ir precursors were used, hollow structures could not be formed. Since the concentration of Ir ammine complexes is close to saturation, the water removal by the surfactant during these processes may cause the crystallization of the complexes from the water solution in the reversed micelle. When TEOS is added to this system, the hydrolysis of TEOS by water would proceed on the surface of the ammine crystals resulting in the encapsulation of the ammine crystals by a silica shell. It is reported that hydrolysis of TEOS proceeds selectively on the surface of metal ammine crystals by the electrostatic interaction between silicate anions and NH_3 ligands of $[M(NH_3)_n]^+$ complex cations [19]. After heat treatment, nano-hollows are generated in the SiO_2 spheres by the decomposition of the Ir ammine complex crystals. When hydrazine was added as a reducing agent after the introduction of aqueous Ir ammine complexes to the organic solution, the reduction of Ir ammine complexes in the reversed micelle took place and resulted in the disappearance of the nano-hollows.

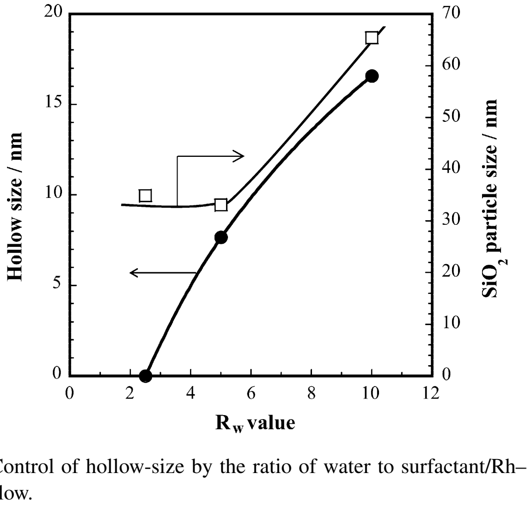

Fig. 2. Control of hollow-size by the ratio of water to surfactant/Rh–SiO_2(h) nano-hollow.

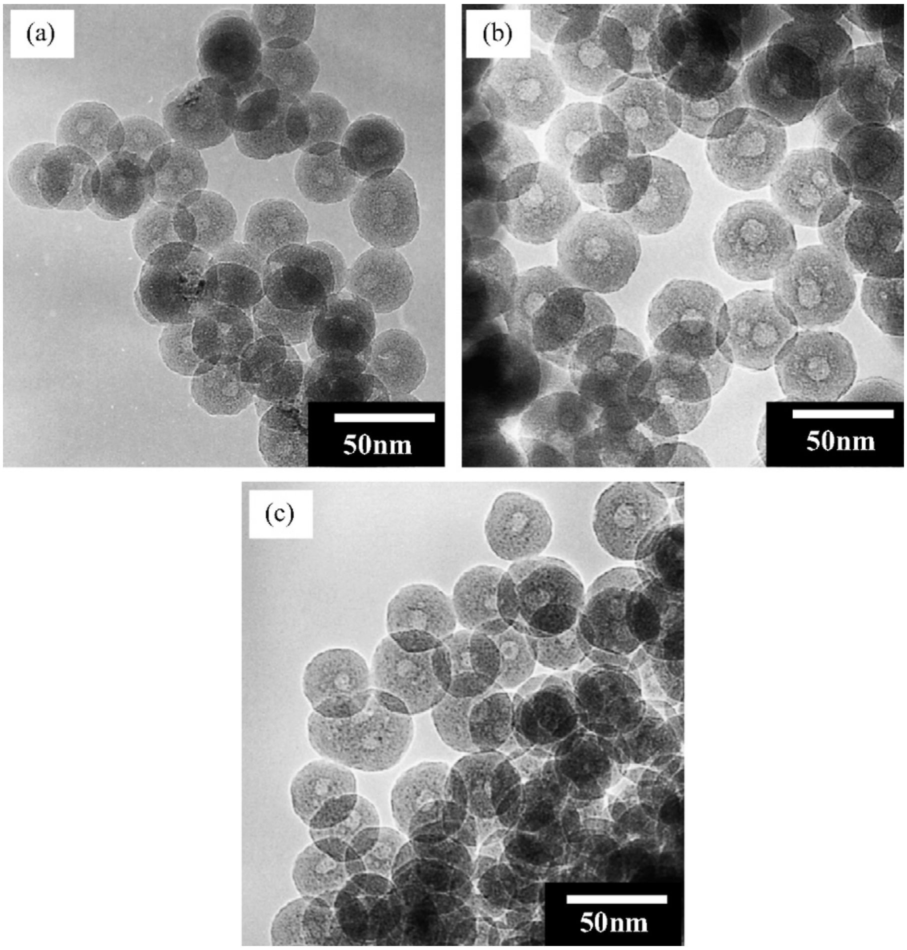

Fig. 3. Thermal stability of Rh–SiO_2(h): (a) 573 K, (b) 773 K, and (c) 1073 K.

3.4. Synthesis of bimetallic clusters in the silica nano-hollows

In this study, bimetallic clusters in the hollow silica spheres, e.g., Rh–Co–SiO_2(h) and Ir–Co–SiO_2(h) were synthesized. A mixture of two kinds of metal ammine complexes solution was injected into a reversed micelle solution followed by ammonia and TEOS addition and hydrolysis. Other procedures were the same as the normal preparation method. The shape and morphologies of hollow spheres are similar to those of M–SiO_2(h) samples containing mono-metal complex (Fig. 5). Careful EDS analysis of bimetal–SiO_2(h) samples by using nano-size spot measurements revealed the successful formation of bimetallic clusters in the hollow cavities. The drastic change in chemisorption properties by mixing of two kinds of metals also supported the formation of bimetallic alloy. The chemisorption properties of these bimetallic nano-hollows will be discussed in Section 3.5. In general, a preparation of alloy is sometimes difficult when physical properties of the component are different from other ones, e.g., melting point, temperature of

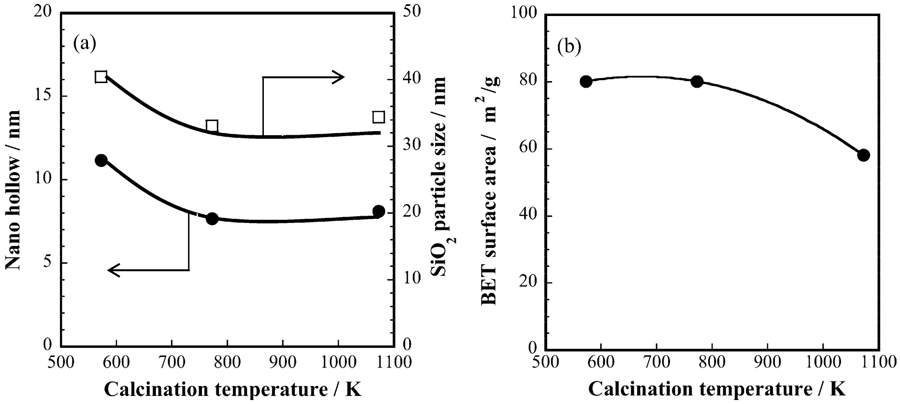

Fig. 4. Change in size and surface area with calcination temperature of Rh–SiO_2(h): (a) diameter, and (b) surface area.

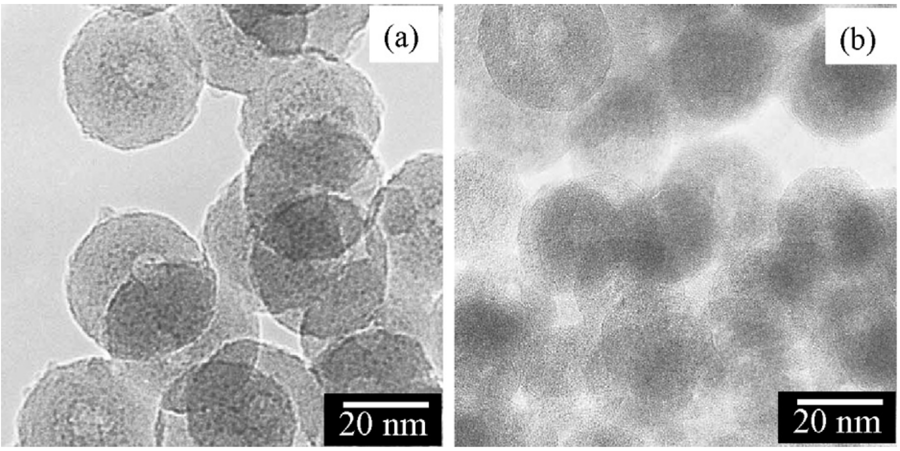

Fig. 5. TEM images of bimetal–SiO_2(h): (a) Ir–Co–SiO_2(h) and (b) Rh–Co–SiO_2(h).

decomposition of the precursor, and surface tension. In such cases, separation of two components takes place during decomposition of precursor and reduction into metal phase. By the present method, synthesis of bimetallic particle is easily achieved because the hollow cavity in the silica spheres can act as nano-size crucible for the formation of bimetallic particles. It is thought to be one of the great advantages of this method and may be applicable for wider variation of elements including difficult elements to form bimetallic alloys by the ordinal technique.

3.5. Hydrogen occlusion properties of M–SiO_2(h)

The amount of hydrogen uptake on various metal containing hollow silica samples was summarized, together with diameters of SiO_2 spheres and hollows in Table 1. The ratio of adsorbed hydrogen to bulk metal atom (H(a)/M) varied significantly with the kind of metal elements contained in the cavities of the hollow SiO_2. The H/M ratio on Co–SiO_2(h) and Ru–SiO_2(h) samples are 0.08 and 0.14, respectively. The ratio of CO chemisorbed on Ru–SiO_2(h) is significantly larger than stoichiometric value. This means Ru has strong affinity with CO molecules. It is worth noticing that the Ir and Rh–SiO_2 samples show excess of H/metal ratio. In particular, over Ir–SiO_2 sample, the H/Ir reached 3.3 at 200 Torr of equilibrium pressure of hydrogen. Fig. 6 demonstrates the adsorption isotherms of hydrogen over 10 wt% Ir–SiO_2(h) at 298 K. At higher pressure, the H/M value increased dramatically and reached 11.6 at 2.6 MPa. Since the amount of H_2 adsorption over non-hollow sample (Ir–SiO_2(h), prepared by the addition of reducing agent) was 70% of the hollow sample, nano-hollows may play an important role in the excess hydrogen adsorption. When Co was added to Rh–SiO_2(h) and Ir–SiO_2(h) samples which shows large amount of hydrogen uptake, the amount of hydrogen uptake decreased significantly. This means the properties of elements are also significant factor for the hydrogen occlusion ability. In the case of Ir–SiO_2(h), it is difficult to suppose that the excess hydrogen adsorption proceeds via formation of Ir hydride clusters because such clusters with coordination number beyond 3 has not been reported in any previous literatures. We conclude that hydrogen molecules can permeate the silica shell and be absorbed in the hollow by the affinity with iridium particles contained in the cavity. In addition, spillover of hydrogen from the cluster into the hollow cavities may increase the occlusion amount of hydrogen.

Table 1
Chemisorption over various M–SiO_2(h) samples

Samples	Chemisorption		Diameter (nm)	
	H/metal	CO/metal	SiO_2	Hollow
Rh–SiO_2	1.11	1.22	40.5	11.2
Ir–SiO_2	3.27	1.95	39.6	8.7
Ir–SiO_2[a]	2.20	–	30.0	–
Co–SiO_2	0.08	0.06	33.4	7.7
Ru–SiO_2	0.14	1.20	33.0	7.5
Rh–Co–SiO_2	0.24	–	35.8	7.4
Ir–Co–SiO_2	0.56	–	32.8	8.3
Ir–Rh–SiO_2	1.31	0.97	32.4	8.5

[a] Non-hollow sample.

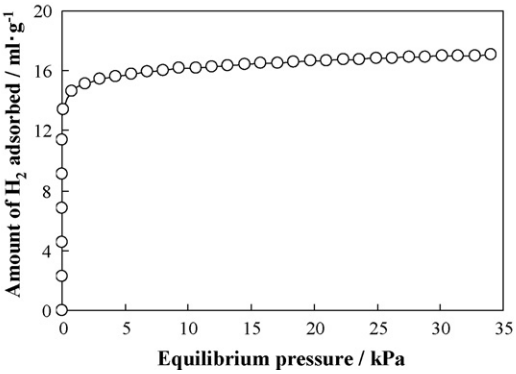

Fig. 6. H_2 isotherms over 10 wt% Ir–SiO_2(h) measured at 298 K.

Acknowledgement

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