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# Synthesis of Nanorattles Composed of Gold Nanoparticles Encapsulated in Mesoporous Carbon and Polymer Shells

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## ABSTRACT

In this study, we fabricated new spherical silica templates with submicrometer sized solid cores containing an encapsulated Au nanoparticle surrounded by a mesoporous shell structure. Hollow spherical carbon and polymer capsules, containing gold nanoparticles, were synthesized using these silica templates. The resulting carbon capsules inversely replicated the structure of the silica template and contained uniform pores with a narrow pore size distribution centered at 3.8 nm. These carbon capsules exhibited a BET surface area of  $>1000 \text{ m}^2 \text{ g}^{-1}$  and a total pore volume of  $>1.0 \text{ cm}^3 \text{ g}^{-1}$ . In addition, hollow polymer capsules having a well-defined pore size were fabricated using a similar synthetic procedure.

Since MCM-41 silica was synthesized by Mobil researchers in 1992, the construction of templates for advanced material preparation has become an area of intense activity.<sup>1</sup> These mesoporous materials have well-defined pore structures, extremely high surface areas, and precisely tuned pore sizes.<sup>2</sup> Due to these desirable properties, many mesoporous silica materials have been widely used as host materials for catalysts,<sup>3</sup> polymers,<sup>4</sup> metals,<sup>5</sup> semiconductor nanoparticles,<sup>6</sup> and carbon.<sup>7</sup>

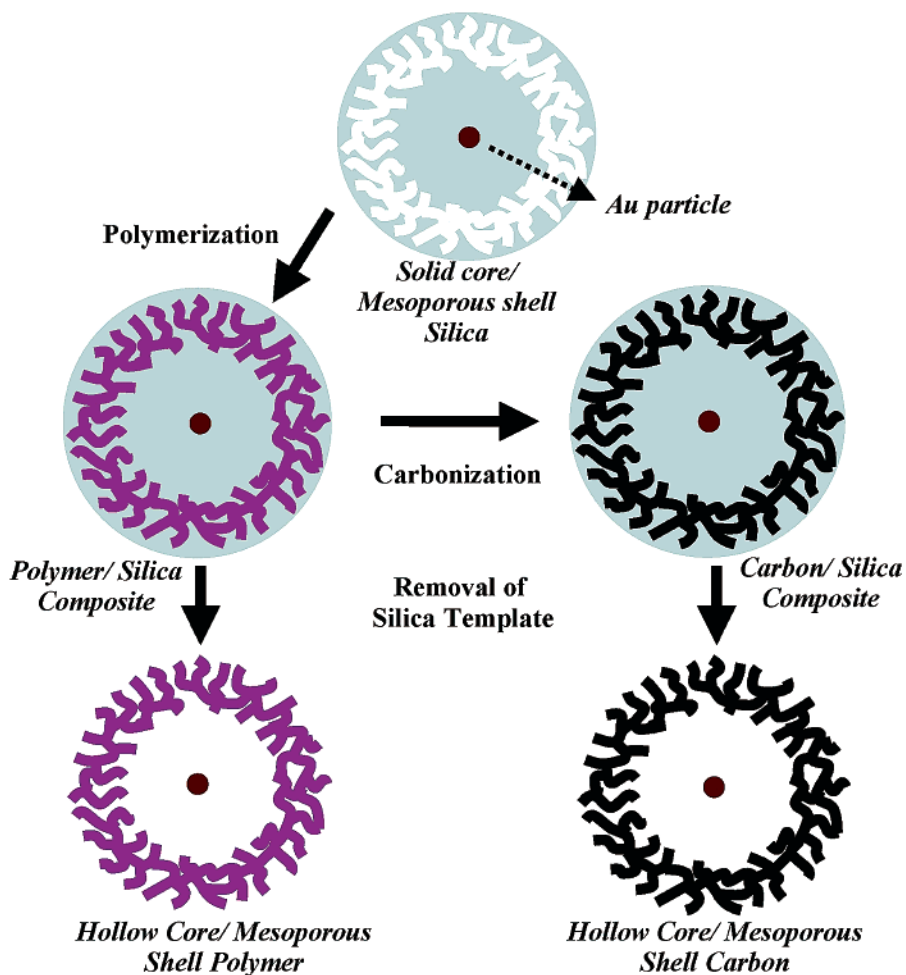
The fabrication of micro- and nanosized capsules, which allow the encapsulation of various materials, is of scientific and technological interest.<sup>8</sup> A variety of chemical and physicochemical methods have been employed to produce hollow spheres composed of polymer and ceramic materials. These include nozzle reactor approaches, such as spray drying or pyrolysis,<sup>9</sup> emulsion/phase-separation techniques,<sup>10</sup> emulsion/interfacial-polymerization strategies,<sup>11</sup> and self-assembly processes.<sup>12</sup> In particular, Caruso and co-workers introduced a layer-by-layer (LbL) self-assembly approach, which enables the fabrication of many different core-shell materials.<sup>13</sup> The alternating depositions of oppositely charged species have been applied to form shells composed of various materials, for example, silicas, titanias, polymers, silica-polymer nanocomposites, magnetic materials, and proteins. Solid core spheres or hollow core spheres may be produced, depending on core template removal.

Recently, our group introduced a templating strategy that allows the fabrication of carbon capsules with hollow core/mesoporous shell (HCMS) structures from submicrometer-sized solid core/mesoporous shell (SCMS) silica spheres.<sup>14</sup>

Mesoporous and microporous materials are very useful hosts for the immobilization of various nanoparticles. Several methods have recently been proposed to form porous materials, which involve the incorporation of preformed nanoparticles within gels<sup>15</sup> and polymers.<sup>16</sup> Recently, much research has been undertaken on the fabrication of encapsulated and immobilized metal nanoparticles.<sup>17</sup> The encapsulation of these metal nanoparticles inside a capsule or in a capsule wall would lead to the creation of novel catalytic systems. Herein we report on the fabrication of new silica templates with a solid silica core/mesoporous shell, containing an Au nanoparticle within the silica core. Such templates were used as host materials to encapsulate Au nanoparticles. Moreover, hollow core/mesoporous shell capsules containing Au nanoparticles, which are inverse replicas of the silica sphere templates, were synthesized. The capsules possessed bimodal pore systems composed of uniform and tunable hollow macroscopic cores and mesopores in the shell.

Scheme 1 illustrates the procedure used for preparing hollow core/mesoporous shell (HCMS) carbon and polymer capsules containing a Au nanoparticle. The first stage involved the inclusion of divinylbenzene (DVB) or phenol resin in an Au@SCMS silica template. The pores of template were filled by capillary force with divinylbenzene (DVB) and azobisisobutyronitrile (AIBN) for the polymer shell, or phenol resin and paraformaldehyde for the carbon shell. The DVB monomers and AIBN and phenol and paraformaldehyde were polymerized within the pores of the template. Nanocomposites of phenol resin and Au@SCMS silica templates were further carbonized to obtain carbon/silica

**Scheme 1.** Schematic Illustration for the Synthesis of Au@HCMS Polymer and Carbon Capsules

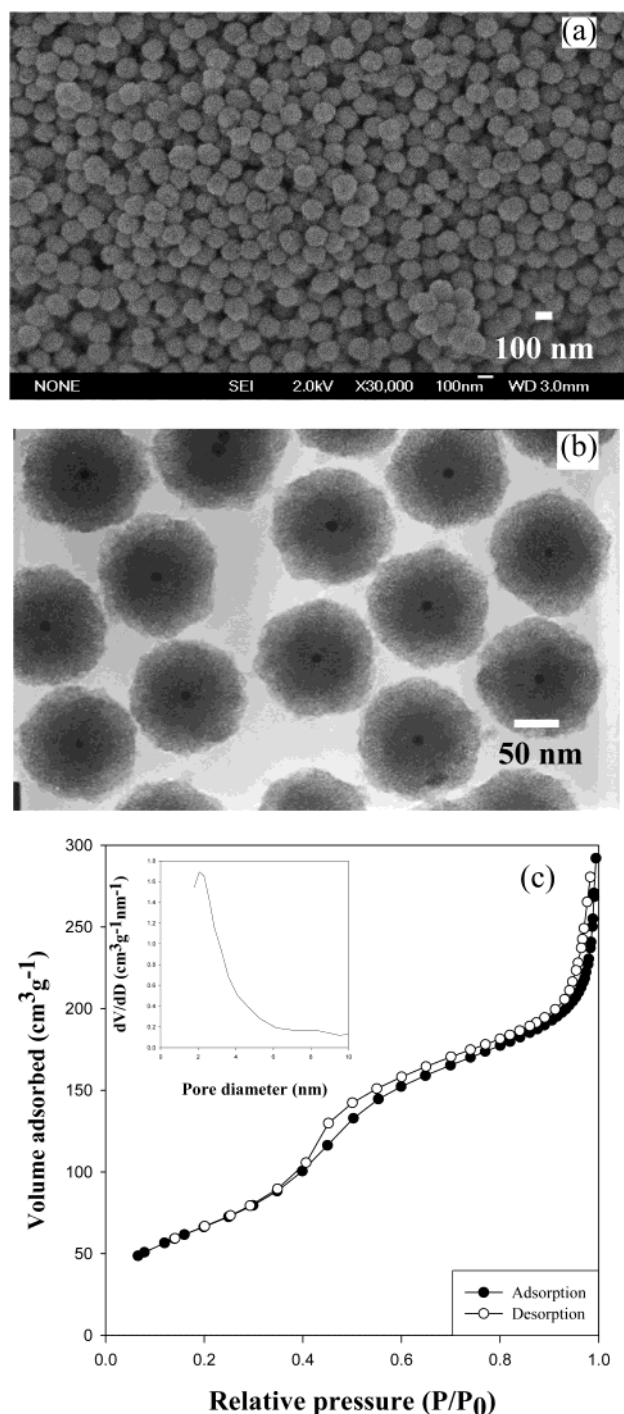


nanocomposites. Silicate template dissolution by HF solution generated Au@HCMS polymer and carbon capsules. The followings are the detailed synthetic procedures.

Gold nanoparticles encapsulated by a solid-core/mesoporous-shell (Au@SCMS) silica template were synthesized in three steps. The initial step involved the synthesis of the Au nanoparticles to be incorporated. Subsequently, the silica shells were grown on each gold nanoparticle, using a previously reported method.<sup>18</sup> The final step involved the formation of a mesoporous shell layer on the Au@SiO<sub>2</sub> core-shell particles. Gold sol was prepared according to the standard sodium citrate reduction method.<sup>19</sup> This method produces a stable deep-red dispersion of 13 nm gold particles. Subsequently, and according to a reported method,<sup>18</sup> a silica shell was formed on each gold nanoparticle. In a typical synthesis, an aqueous solution of aminopropyltrimethoxysilane (APS, 0.172 mL, 0.985 mM) was added to the gold sol with vigorous stirring. The mixture of APS and gold dispersion was allowed 15 min to enable the amine groups to complex with the gold surface. A dilute sodium silicate solution of pH 10–11 was then added to the APS-modified gold sol, again with vigorous stirring. Under these circumstances, the sodium silicate polymerizes onto the surface of the gold particles. This inner silica shell was thickened using the Stöber method. Finally, a mixture of 1.5 mL of

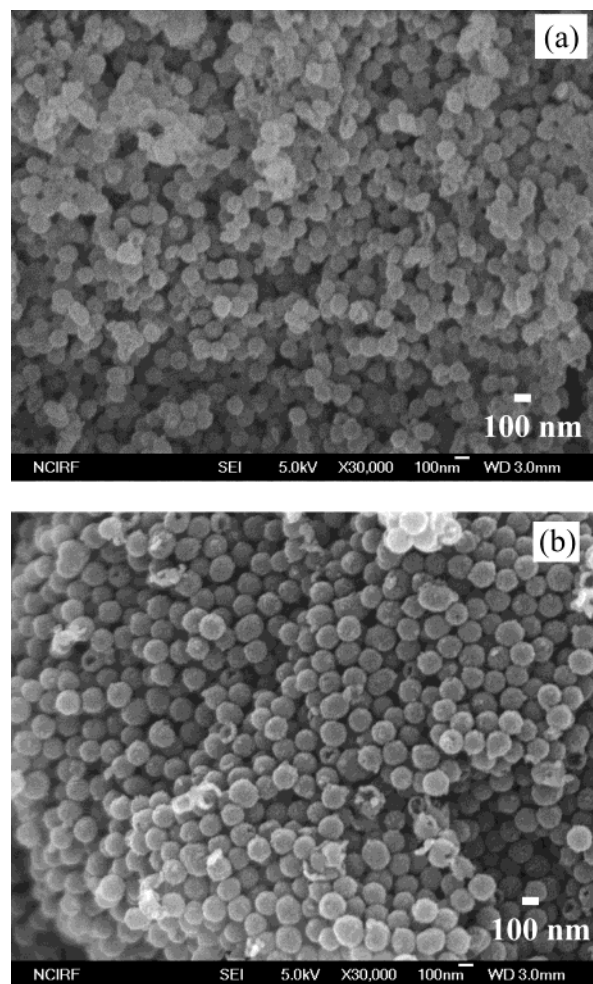
tetraethoxysilane (TEOS) and 0.5 mL of octadecyltrimethoxysilane (C18TMS) was added to a colloidal solution containing the Au@SiO<sub>2</sub> spheres and allowed to react for 3 h at room temperature to form a mesoporous layer. The resulting octadecyltrimethoxy-incorporated silica shell/solid Au@SiO<sub>2</sub> core nanocomposite was retrieved by centrifugation and further calcined at 823 K for 6 h in an oxygen atmosphere to produce the final Au@SCMS silica material.

The following describes the synthesis of Au nanoparticle-encapsulated polymer and carbon shells. Calcined Au@SCMS silica templates (1 g) were dehydrated in a vacuum at 473 K overnight, and the pores of the template were filled with divinylbenzene (DVB, 0.34 g) to produce the polymer capsules and phenol (0.4 g) to produce the carbon capsules by heating at 343 K for 12 h under a static vacuum. To produce the polymer capsules, the resulting DVB-incorporated Au@SCMS were polymerized with a free radical initiator, azobisisobutyronitrile (AIBN, 0.04 g), by heating at 343 K for 24 h in an argon atmosphere using a drying oven. For the synthesis of carbon capsules, the polymerization of phenol-incorporated Au@SCMS was performed with paraformaldehyde (0.25 g) by heating at 403 K for 24 h under a static vacuum in a drying oven. The resulting nanocomposite of phenol resin and Au@SCMS silica was heated at 1 K min<sup>-1</sup> to 433 K and maintained at this temperature



**Figure 1.** Characterization of Au@SCMS silica templates with core diameter of 80 nm and shell thickness of 25 nm: (a) SEM image, (b) TEM image, and (c) N<sub>2</sub> adsorption/desorption isotherms and the corresponding pore size distribution (inset).

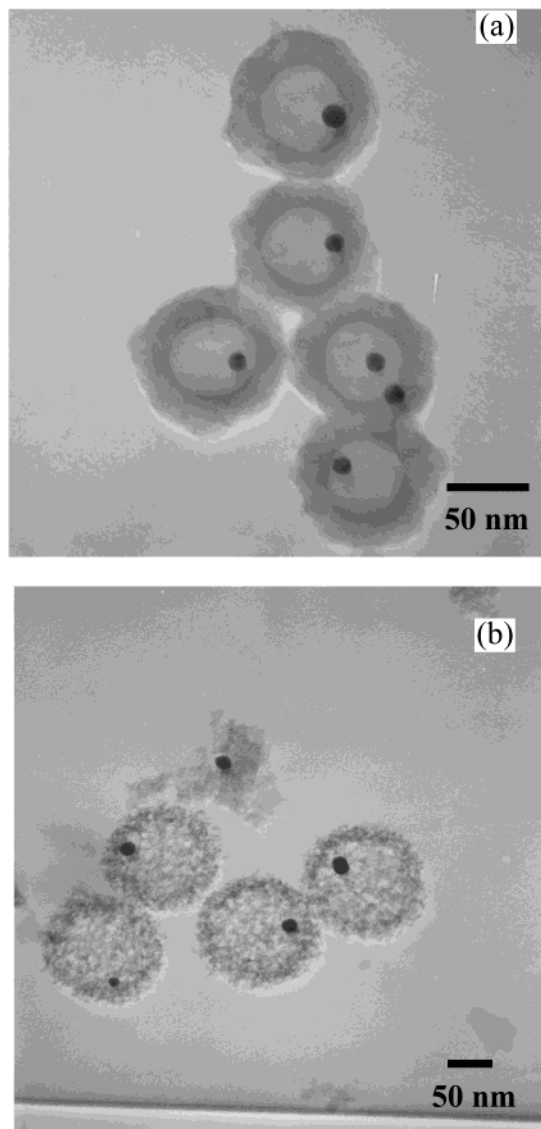
for 5 h in flowing nitrogen. The temperature was then ramped at 5 K min<sup>-1</sup> to 1123 K and maintained at this temperature for 7 h to carbonize the phenol resin within the mesopores of Au@SCMS silicate so as to obtain a carbon/silica nanocomposite. Gold nanoparticles encapsulated hollow-core/mesoporous-shell (Au@HCMS) polymer and carbon capsules were obtained after removing the silica templates by etching using 2 N HF solution in a 1:1 mixture of ethanol and water for 3 h.



**Figure 2.** SEM image of (a) Au@HCMS polymer capsules with diameters of 80 nm and (b) Au@HCMS carbon capsules with diameters of 130 nm.

The structures of the Au@SCMS silica template and Au@HCMS capsules were investigated by gas adsorption measurements, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The SEM image of the Au@SCMS silica sphere templates (Figure 1a) shows that the majority of particles are monodispersed and spherical with particle diameters of 130 nm. The TEM image of these templates reveals that they are composed of solid silica layers with thickness of 80 nm, and that they contain a 13 nm central Au nanoparticle and 25 nm thick mesoporous shells (Figure 1b). Typical nitrogen adsorption/desorption isotherms at 77 K for the Au@SCMS silica sphere templates and the corresponding pore size distribution (inset) are shown in Figure 1c. The nitrogen isotherms indicate a linear increase in the amount of adsorbed nitrogen at low relative pressures ( $P/P_0 = 0.4$ ). According to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature,<sup>20</sup> the resulting isotherm can be classified as a type IV isotherm with type H2 hysteresis. The corresponding pore size distribution data calculated from the adsorption branches of nitrogen isotherms by the BJH method shows that the pores are uniform and have a narrow pore size distribution, centered at 3 nm. The Au@SCMS silica templates exhibit a Brunauer–

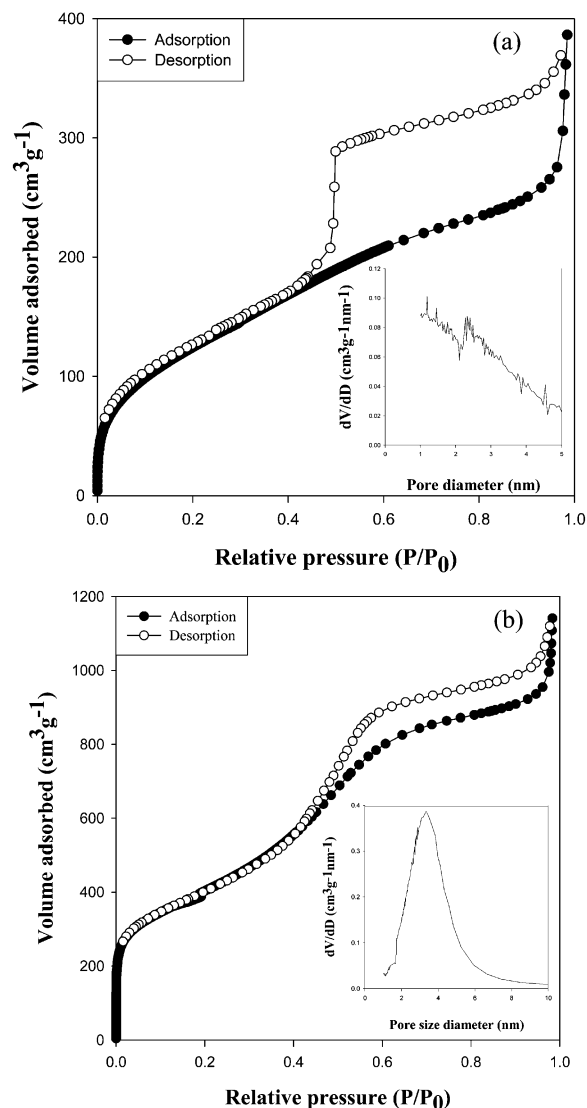




**Figure 3.** TEM image of (a) Au@HCMS polymer capsules with core diameters of 50 nm and shell thicknesses of 15 nm. (b) Au@HCMS carbon capsules with core diameters of 80 nm and shell thicknesses of 25 nm.

Emmett–Teller (BET) surface area of  $343 \text{ m}^2 \text{ g}^{-1}$  and a total pore volume of  $0.38 \text{ cm}^3 \text{ g}^{-1}$ .

The structures of the Au@HCMS polymer and carbon capsules are inverse replicas of the SCMS silica sphere templates. The SEM images of the Au@HCMS polymer (Figure 2a) and carbon capsules (Figure 2b) show that most particles are nearly uniform and spherical with particle diameters of 80 and 130 nm, respectively. Some particles are deformed by shrinkage. The TEM images of the polymer and carbon capsules are displayed in Figure 3. The Au@HCMS polymer and carbon capsules are found to have hollow cores of 50 and 80 nm in diameter, which contain one or two gold nanoparticles and mesoporous shells of thickness 15 and 25 nm, respectively. The fabricated polymer shells are a little thinner than the template shell thickness of 25 nm to 15 nm, but the spherical shape of the template particles are preserved. Figure 4 shows the nitrogen adsorption/desorption isotherms and the corresponding pore size



**Figure 4.**  $\text{N}_2$  adsorption/desorption isotherms and the corresponding pore size distributions (insets) of (a) Au@HCMS polymer capsules and (b) Au@HCMS carbon capsules.

distribution (inset) of the polymer capsules (Figure 4a) and carbon capsules (Figure 4b). The resulting isotherms can be classified as type IV isotherms with type H2 hysteresis. Their corresponding pore size distribution data calculated from the adsorption branches of nitrogen isotherms by the BJH method shows that the pores are uniform, and that the pore size distribution is narrow and centered at 3 nm for polymer capsules and 3.8 nm for carbon capsules, respectively. The Au@HCMS polymer and carbon capsules exhibit Brunauer–Emmett–Teller (BET) surface areas of  $492 \text{ m}^2 \text{ g}^{-1}$  and  $1415 \text{ m}^2 \text{ g}^{-1}$  and total pore volumes of  $0.48 \text{ cm}^3 \text{ g}^{-1}$  and  $1.53 \text{ cm}^3 \text{ g}^{-1}$ , respectively.

In conclusion, we fabricated hollow spherical polymer and carbon capsules encapsulating gold nanoparticles. These materials could find many advantages for their applications. The presence of a shell with mesopores leads to size selectivity in catalyzed reactions and the mesoporous shell can also serve as a protective shield, which protects the catalyst from hazardous environments. Furthermore, this shell structure can prevent Au nanoparticle aggregation. Moreover,

it is suggested that the hollow core/mesoporous shell structure containing encapsulated metal nanoparticles can be used as a microreactor to selectively conduct reactions within the capsules.

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