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Fabrication of nanocapsules with Au particles trapped inside carbon and silica nanoporous shells†

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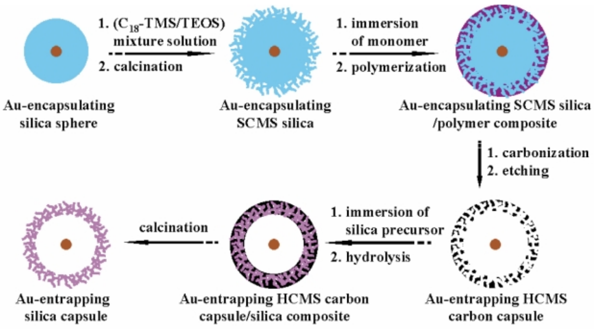
Carbon capsules with hollow cores and mesoporous shells (HCMS) containing entrapped Au particles were prepared by template replication from solid core/mesoporous shell silica spheres with encapsulated Au particles. The resulting HCMS carbon capsules were then nanocast one step further to generate Au-trapping hollow core silica capsules with nanostructured shells.

Various colloidal crystalline arrays have been used as templates for synthesizing new macroporous materials including metals,[1] inorganic materials,[2] polymers,[3] carbons[4] and SiC.[5] Core–shell composite materials and capsules with tailored properties have also been synthesized using various procedures including template surface modification with appropriate primers[6] and layer-by-layer adsorption of polyelectrolytes on charged nanoparticles.[7] Xia and coworkers reported the preparation of mesoscale hollow spheres of ceramic materials such as TiO_2 and SnO_2 templated from polystyrene crystalline arrays.[8] More recently, we reported a method for synthesizing different macroporous carbon networks by controlling the acid-polymerization sites over colloidal silica crystalline arrays.[9]

There has been also a great deal of interest in the synthesis of mesoporous silicas such as MCM-41, MCM-48, and SBA-15 *via* self-assembling surfactants. These mesoporous silica materials have been utilized as molds for the fabrication of new classes of highly ordered polymers[10] and other carbon frameworks.[11,12] It has been also reported that SBA-15 silica was regenerated from its mesoporous carbon replica CMK-3 by two-step replication.[13] Recently, the fabrication of carbon capsules with a hollow macroporous core/mesoporous shell[14] was reported using solid core/mesoporous shell (SCMS) silica particles as templates.[15] In this communication, we present the fabrication of the first nanocapsules containing Au particles entrapped in either carbon or silica nanoporous shells templated from solid core/mesoporous shell silica spheres with encapsulated Au particles. Metal nanoparticles entrapped in the nanoporous capsules could show novel selectivity in catalysis and chemical sensing.

Scheme 1 shows the schematic procedure for the fabrication of the nanocapsules. Silica-encapsulated Au particles were synthesized as reported previously.[16] A mixture of tetraethylorthosilicate (TEOS) and octadecyltrimethoxysilane (C_{18}-TMS) was added to a colloidal suspension of these silica spheres and allowed to react.[14] This resulted in nanocomposites of silica particles surrounded by mesoporous shells. The nanocomposites were retrieved by centrifugation and calcined at 823 K to generate SCMS silica spheres with encapsulated Au particles. A solution of divinylbenzene and a free radical initiator, azobisisobutyronitrile, was then incorporated into the mesopores of the Au@SCMS silica spheres, allowed to polymerize, and then carbonized to yield a carbon/silica nanocomposite. Dissolution of the silica template using 48 wt% HF generated hollow core/mesoporous shell (HCMS) carbon capsules with entrapped Au particles. The mesopores of the resulting Au-HCMS carbon capsules were then nanocast one-step further using TEOS as a silica precursor. Finally the carbon/TOES composite capsules were treated by two different methods to generate Au@silica capsules with either mesoporous or microporous shells. Experimental details are described in the ESI.†



Scheme 1 Schematic illustration for the fabrication of Au-entrapping carbon and silica capsules by nanocasting of Au-encapsulating SCMS silica spheres as template.

Fig. 1 shows the transmission electron microscope (TEM) images of the Au@SCMS silica spheres and the resulting Au@carbon and silica capsules and the scanning electron microscope (SEM) image of the Au@silica capsules. As shown in these images, these materials are composed of nearly uniform spheres with homogeneous shell thickness. The TEM image in Fig. 1a clearly shows Au particles of *ca.* 20 nm encapsulated in a silica core of *ca.* 200 nm diameter with a shell thickness of *ca.* 30 nm for the Au@SCMS silica spheres. Likewise, Fig. 1b and c show that the carbon and silica capsules with mesoporous shells possess a shell thickness of *ca.* 24 nm with hollow cores of *ca.* 195 and 190 nm in diameter, respectively. Fig. 1d shows the SEM image of the Au@silica capsules shown in Fig. 1c.

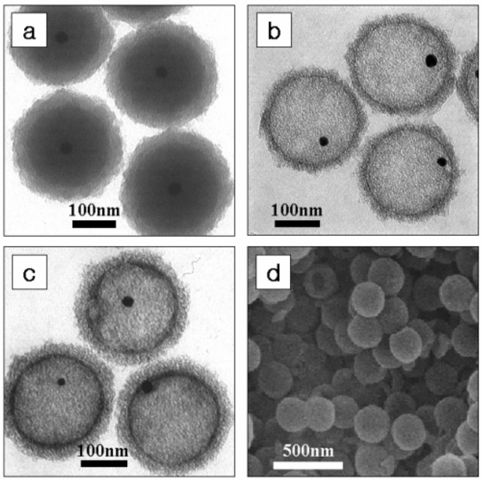


Fig. 1 TEM images of (a) Au-encapsulating SCMS silica spheres, (b) Au-entrapping HCMS carbon capsules, (c) Au-entrapping silica capsules with mesoporous shell, and (d) SEM image of the Au-entrapping silica capsules shown in (c).

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† Electronic supplementary information (ESI) available: experimental section and TEM image of Au-entrapping silica capsules-1. See http://www.rsc.org/suppdata/cc/b2/b211714b/

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Some of the silica capsules were deformed and broken, but overall the capsules were roughly uniform and spherical with diameters of *ca.* 240 nm.

Fig. 2 shows typical nitrogen sorption isotherms at 77 K for the Au@SCMS silica spheres and the resulting Au@carbon and silica capsules along with their corresponding pore size distribution curves. The isotherms for the Au@SCMS silica spheres and the resulting Au@carbon and silica capsules can be classified as type IV isotherms characteristic of mesoporous materials according to IUPAC nomenclature.[17] In particular, the isotherm of the Au@silica capsules is very similar to that of the corresponding Au@carbon capsule template. Fig. 2 also shows another isotherm for silica capsules denoted Au@silica capsules-1, where the framework shrinkage was more severe. However, the Au@silica capsules-1 revealed an isotherm rather different from those of the starting SCMS silica spheres and the carbon capsules. Instead, it showed a type I isotherm, typically observed for microporous materials. The corresponding pore size distribution data calculated from the adsorption branches of nitrogen isotherms by the BJH (Barrett–Joyner–Halenda) method showed narrow pore size distributions centered at 2.9 nm, 4.3 nm, 2.6 nm, and 1.7, respectively. The calculated pore size of the Au@silica capsules-1 belongs in the microporous range, which is consistent with its isotherm appearance. A similar isotherm has been previously observed in other silica capsules with microstructured shells.[6a] While this manuscript was in preparation, a study was reported in which gold nanoparticles were encapsulated in mesoporous polymer and carbon shells.[18] Similar results were obtained for the carbon capsules. The present work makes an important step forward by the second inverse replication in order to obtain gold nanoparticles inside nanoporous silica shells. Both the carbon and the resulting silica capsules possess bimodal pore systems with the former having a hollow macropore as a core and a mesoporous shell and the latter having a hollow macropore and a mesoporous or microporous shell. The values for the BET surface area, total pore volume, pore size, and core diameter/shell thickness of the samples are summarized in Table 1.

In summary, a synthetic procedure has been described that allows the incorporation of preformed metal particles within uniform capsules with nanoporous shells. Gold-encapsulating SCMS silica spheres were fabricated and used as templates for the synthesis of Au-entrapping HCMS carbon capsules, which were nanocast one step further to form Au-entrapping hollow core/nanostructured silica capsules. The core sizes, shell thickness, and nanoporosity of the Au-entrapping carbon and silica capsules can be controlled by monitoring the size of the silica sphere core, the amounts and ratio of TOES and C_{18}-TMS added, and the thermal treatment. Furthermore, this method should be amenable to a variety of metal particles and inorganic capsule materials and investigations along this line are currently in progress.

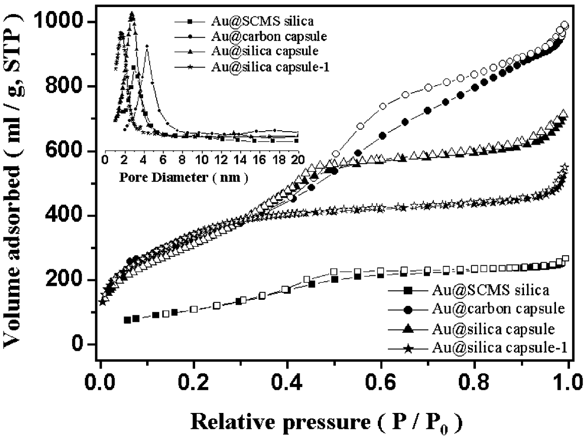

Fig. 2 N_2 sorption isotherms of the Au-encapsulating SCMS silica spheres and the Au-entrapping carbon and silica capsules, and the corresponding pore size distribution curves calculated from the adsorption branch of the nitrogen isotherm (insert). The isotherms were measured at 77 K on a Micromeritics ASAP 2000 Gas Adsorption Analyzer after each of the samples were degassed at 423 K to 20 μTorr for 4–6 h.

Table 1 Properties of the Au-encapsulating SCMS silica particle and the Au-entrapping carbon and silica capsules prepared in this work

	Particle size[a]				
Sample	Core diameter/ nm	Shell thickness/ nm	BET surface area/m^2 g^{-1}	Total pore volume/ml g^{-1}	Pore size[b]/nm
Au@SCMS silica	200	30	404	0.39	2.9
Au@carbon capsule	195	24	1166	1.47	4.3
Au@silica capsule	190	24	1134	1.07	2.6
Au@silica capsule-1	152	18	1256	0.85	1.7

[a] The particle size was determined from the electron microscopy data. [b] Maximum values of the BJH pore size distribution peak calculated from the adsorption branch of the N_2 isotherm.

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