Mesoporous microcapsules with noble metal or noble metal oxide shells and their application in electrocatalysis

Nan Ren,a An-Gang Dong,a Wen-Bin Cai,*a Ya-Hong Zhang,a Wu-Li Yang,b Sheng-Juan Huo,a Ying Chen,a Song-Hai Xie,a Zi Gaoa and Yi Tang*a

aDepartment of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China
E-mail: yitang@fudan.edu.cn; wbcai@fudan.edu.cn; Fax: +8621 6564 1740;
Tel: +8621 5566 4125
bDepartment of Macromolecular Science of and Key Laboratory of Molecular Engineering of Polymers (Minister of Education), Fudan University, Shanghai 200433, P. R. China

Received 29th July 2004, Accepted 9th September 2004
First published as an Advance Article on the web 29th September 2004

A versatile peripheral-pore-nanocasting method is employed to fabricate a series of novel microcapsules with mesoporous shell of noble metal or noble metal oxides, including Pt, PdO, RuO2 and IrO2. The shell thickness of these hollow microcapsules can be adjusted by controlling the depth of 3-aminopyrrolyltrimethoxysilane (APS) modification. By pre-filling the guest species or their precursors into the 3-D pores of HMS (hexagonal mesoporous molecular sieves) spheres, an interesting material with a “sphere in shell” structure could be fabricated via the same method. Both the mesoporous platinum hollow microcapsules and carbon spheres encapsulated in platinum microcapsules have shown high mass-normalized activities as a catalyst in the oxidation of methanol, a fundamental reaction in direct methanol fuel cells (DMFC).

1 Introduction

With the development of nanoscience and technology, studies on hollow porous microcapsules deserve extra attention because of their distinct characteristics, such as a large void volume for the encapsulation of guest species and tunable porous shells which permit the selective permeation of gas or liquid molecules and protect the active ingredient in cavities from the environments, endowing them with a variety of potential applications as drug carriers, microcapsule-reactors, chemical sensors and so on. Up to now, hollow microcapsules with various types of shells, e.g., oxides,1 sulfides,2 zeolites3 and polymers4 have been synthesized through different approaches such as layer-by-layer fabrication, in-situ transformation, sonication etc. Among these materials, the hollow microcapsules made of noble metals5,6 (or their oxides) have aroused increasing interest because of their remarkable capabilities in catalytic, optical and electrochemical applications.7,8 The methods used for the preparation of these materials include layer-by-layer coating of metal nanoparticles (or their precursors) on sacrificial cores,9 reduction of PdCl2 by NaBH4 in the presence of the surfactant Bu4NBf8 and galvanic replacement reactions between nanoparticles with relatively lower reduction potential and metal ions with relatively higher reduction potential.7 However, a challenge in this work is to control the porosity in the shells of such materials, which dominates their applications in catalysis and adsorption. Another topic of interest in the field of porous microcapsules is the encapsulation of various guest species into porous microcapsules to functionalize their interior. Kim et al.9 have synthesized mesoporous polymers or carbon microcapsules with gold nanoparticle cores using solid core/mesoporous shell silica spheres as the template. In our previous work, a series of zeolite microcapsules encapsulated with Fe3O4, PdO, carbon and polymers has been prepared through in-situ transformation of guest-preloaded zeolite-seeded silica spheres.38,39,40 However, the methods for the encapsulation of guest species into mesoporous noble metals and their oxide microcapsules are still scarce.

2 Experimental

2.1 Materials

The APS was purchased from Aldrich. The noble metal precursors including H2PtCl6, RuCl3, H2IrCl6 and palladium(II) acetylacetonate (C5H8O2Pd) and KBH4 (94 wt.%) were obtained from Shanghai July Chemical Company. High purity grade sulfuric acid and methanol were supplied by Tianjing Chemical Reagent Company. All chemicals were used without any purification.
2.2 Preparation of noble metal and noble metal oxide microcapsules

The HMS sphere was synthesized according to the procedure reported by Unger’s research group. The fabrication of metal and metal oxide microcapsules (shown in Scheme 1, route a) was conducted as follows: 0.5 g of the as-synthesized HMS spheres was immersed in 30 ml of 1.0 wt.% APS ethanolic solution, and stirred for 30 min at room temperature or refluxed for 1.0 h to obtain NH$_2$-modified HMS spheres. After washing with pure ethanol, 0.1 g of APS-modified HMS spheres were mixed with 10 ml of 0.04 M aqueous solution of H$_2$PtCl$_6$, RuCl$_3$, or H$_2$IrCl$_6$, or ethanolic solution of palladium(ii) acetylacetonate under vigorous stirring at room temperature and then treated with 12 ml of 10$^{-3}$ M K$_2$B$_4$H$_6$ solution until no more bubbles were observed. After being centrifuged, washed and dried, the sample was calcinated in flowing air at 550 °C for 3 h with a ramp of 1 °C min$^{-1}$. The hollow microcapsules were finally obtained after etching the sample with 25 wt.% HF.

2.3 Encapsulation of mesoporous carbon guests

The infiltration of carbon species into the inner part of the mesopores in HMS spheres was carried out according to the literature. After that, 0.1 g of carbon infiltrated sample was immersed into 30 ml of 1.0 wt.% APS toluene solution and refluxed for 3.0 h. After washing with toluene and separation by centrifugation, the APS-modified samples were impregnated with platinum salt and reduced with the same procedures as those for the fabrication of hollow noble metal microcapsules. Afterwards, the metal loaded sample was calcinated in nitrogen at 550 °C for 2 h with a ramp of 1 °C min$^{-1}$. The etching process is the same as that for the hollow noble metal or noble metal oxide microcapsules.

2.4 Electrochemical measurement

The working electrode was prepared by dip-coating the suspension of various Pt-containing catalysts in Millipore water onto the glassy carbon (GC) electrode (3 mm), dried under a stream of high-purity nitrogen. Before each catalyst loading process, the GC was polished with Al$_2$O$_3$ paste with sizes down to 0.05 μm and washed ultrasonically in ultrapure Milli-Q water. The loading qualities of all the catalysts on GC are ~0.0885 mg cm$^{-2}$ for the purpose of comparison. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrolyte solution was 1 M CH$_3$OH in 0.5 M H$_2$SO$_4$, which were prepared from super-pure sulfuric acid, methanol and Milli-Q water. The electrochemical experiments were made on a CHI 630 electrochemical system at room temperature in a three-electrode cell containing the supporting electrolyte and reactants. Before a measurement, the solution was degassed by bubbling argon for 30 min.

2.5 Characterization

XRD patterns were taken on a Rigaku D/MAX-IIB diffractometer using Cu Kα radiation. SEM and TEM studies were performed on Philips XL 30 and JEOL 200 instruments with the accelerating voltage of 20 and 200 kV, respectively. The selected-area electron diffraction (SAED) patterns were obtained via the electron diffraction instrument attached to TEM.

3 Results and discussion

3.1 Fabrication strategy

Scheme 1 illustrates the strategy of peripheral-pore-nanocasting methods for the synthesis of noble metal or their oxide mesoporous microcapsules. Route (a) depicts the fabrication of the target hollow microcapsules. After treating as-synthesized HMS spheres with APS, the surfactant (n-hexadecylamine) in the peripheral pores are substituted and the APS is anchored on the pore wall in the meantime. The substitution and modification occur only in the peripheral pores due to the strong diffusive restriction in the pores of as-synthesized HMS spheres, and the residual surfactant in the inner parts of HMS spheres would act as a protector for the inner pores in the following process of introducing the metal species. After partial reduction of the metal species (ca. 50%) and subsequent calcination, a continuous metal or metal oxide shell is formed inside the peripheral mesopores of HMS spheres. The mesoporous microcapsules with hollow interiors are obtained by etching silica ingredients in the sample. The shell thickness of such material could be adjusted by control of the APS-modified depth in the spheres simply via variation of the substituent temperature and time. Another important advantage of this method is that it could be employed to prepare metal microcapsules with guest cores (route (b)). When the inner part of the mesopores in the surfactant-removed HMS spheres is pre-filled with a guest phase or their precursors before the introduction of the metal species, a microcapsule with a unique “sphere in shell” structure could be generated through this method. In this paper, the fabrication of mesoporous platinum microcapsules with a mesoporous carbon sphere inside is presented to demonstrate the feasibility of this idea. In this strategy, the capillary shrinkage of the guest carbon spheres during the carbonization process is crucial for the formation of such structure, which provides peripheral free channels for the modification of amino groups as well as the

Scheme 1 Schematic illustration of the peripheral-pore-nanocasting method for the fabrication of hollow mesoporous noble metal or noble metal oxide microcapsules (a) and mesoporous noble metal microcapsules with mesoporous carbon core (b).
further introduction of metal species for the formation of metal or metal oxide shells.

3.2 Fabrication of mesoporous noble metal and oxides hollow microcapsules

Fig. 1 shows the SEM and TEM images of platinum hollow microcapsules prepared through the peripheral-pore-nanocasting method, in which the spherical morphology (Fig. 2a), the hollow interior (Fig. 1b), and the worm-like mesoporous shell (Fig. 1c) are clearly observed. The diameter of the spheres is mainly around 1.3 μm, somewhat smaller than that of the original HMS spheres (ca. 1.5 μm), which can be assigned to the capillary effect of the metal precursors inside the pore channels during drying and calcination of shell formations, resulting in the diameter shrinkage of the microcapsules. The polycrystalline structure of the hollow platinum nanoparticles in the shell is verified by the ring-like SAED pattern (inset of Fig. 1c) and the XRD pattern (Fig. 2). The average size of the nanocrystals on the shell is ca. 6.1 nm, calculated from the width of Pt (111) peak using the Scherrer formula. It is found that the partial reduction of the metal species plays an important role in the fabrication of platinum mesoporous microcapsules. When an excessive amount of reductant is introduced, only discrete platinum nanoparticles are obtained. On the contrary, if the pre-reduction step is omitted, large platinum crystals are formed. This suggests that the small platinum crystallites generated during partial reduction may serve as crystallization nuclei while the unreduced platinum particles for the formation of metal precursors inside the pore channels during drying and calcination of shell formations, resulting in the diameter shrinkage of the microcapsules. The polycrystalline structure of the hollow platinum nanoparticles in the shell is verified by the ring-like SAED pattern (inset of Fig. 1c) and the XRD pattern (Fig. 2). The average size of the nanocrystals on the shell is ca. 6.1 nm, calculated from the width of Pt (111) peak using the Scherrer formula. It is found that the partial reduction of the metal species plays an important role in the fabrication of platinum mesoporous microcapsules. When an excessive amount of reductant is introduced, only discrete platinum nanoparticles are obtained. On the contrary, if the pre-reduction step is omitted, large platinum crystals are formed. This suggests that the small platinum crystallites generated during partial reduction may serve as crystallization nuclei while the unreduced platinum particles generated during partial reduction may serve as crystallization nuclei while the unreduced platinum nanoparticles in the shell are verified by the ring-like SAED pattern (inset of Fig. 1c) and the XRD pattern (Fig. 2). The average size of the crystallites of the corresponding noble metal oxides.

3.3 Control of the shell thickness

The shell thickness of the prepared mesoporous microcapsules can be adjusted by changing the APS modified conditions before the introduction of the noble metal salt. Here, platinum microcapsules with different shell thickness are presented as an example. When the APS exchange is conducted under reflux, the shell thickness is considerably increased (Fig. 4b) because higher temperature favors the substitution of APS with the surfactant in the HMS spheres and profits the introduction of platinum species into deeper parts of the mesopores in succession. On the other hand, if the surfactant in the HMS spheres is removed completely by calcination before amino-modification, nearly all the pores of the HMS spheres could be filled with the metal precursor, and solid platinum spheres are obtained (Fig. 4c). It could be found that the solid metal spheres have a much smaller diameter than that of the hollow spheres, which could be attributed to a stronger capillary effect of the platinum species in the pores of the surfactant-free HMS spheres during the drying and calcination processes.

3.4 Encapsulation of the mesoporous carbon guests

The encapsulation of guest species into microcapsules might greatly broaden their application range because of their unique structure with porous shell outside and functional core inside. Here, as an example, the mesoporous carbon spheres were encapsulated into the hollow platinum microcapsules as guest cores by prefilling the 3-D interconnected pore system of HMS spheres with carbon before peripheral-pore-nanocasting (Scheme 1, route b). The SEM and TEM images of the resulting mesoporous platinum microcapsules with mesoporous carbon spheres are shown in Fig. 5. The product (Fig. 5a) well retained the spherical morphology of the HMS template but with a slightly smaller diameter (ca. 1.0 μm). The cross-sectional SEM image (Fig. 5b) and the TEM image (Fig. 5b, inset) clearly demonstrate the “sphere in shell” structure of the material. The platinum quantity in this material is 8.9 wt.% determined by the inductively coupled plasma (ICP) analysis. The SEM and TEM images in Fig. 5c display the morphology and the mesoporosity of the carbon spheres before metal shell formation (the silica ingredient brought from HMS template...
has been removed through HF-etching. It shows that the diameters of the carbon cores have shrunk to ca. 690 nm after carbonization due to the capillary effect, which provides the required empty peripheral pores for the following nanocasting procedure to form the metal shells.

3.5 Electrocatalytic activity

Platinum nanoparticles exhibit special catalytic effects towards the electrooxidation of methanol, a fundamental reaction involved in DMFC.\textsuperscript{18} The dispersion of Pt nanoparticles greatly affects their activity and/or utilization in such a reaction. The electrocatalytic activity of Pt microcapsules with a hollow interior (Fig. 1, shell thickness of \~{}50 nm) and carbon cores (Fig. 5) was studied using the oxidation of methanol as the prototype reaction. For comparison, the electrooxidation of methanol on a GC electrode modified with Pt nanoparticles was also measured. The Pt nanoparticles were prepared through vigorously grinding the hollow platinum spheres or poly(N-vinyl-2-pyrrolidone) (PVP) protecting\textsuperscript{17} methods. The loading quantity of each synthesized Pt-containing material on a bare GC electrode was kept to be 0.0885 mg cm\textsuperscript{-2}. As shown in Fig. 6, all the materials show catalytic behavior for the electrooxidation of methanol by the appearance of an oxidation peak at ca. 0.65 V (vs. SCE) in the forward half scan, in accordance with the literature report.\textsuperscript{19} It is believed that the improved activity of an electrocatalyst could be judged either through the negative shift of the oxidative peak\textsuperscript{18a} or the enhanced mass-normalized oxidative current.\textsuperscript{19b} Both of the hollow Pt microcapsules and carbon/platinum “sphere in shell” type microcapsules have much higher oxidative peak currents (113.2 mA mg\textsuperscript{-1} Pt and 290.5 mA mg\textsuperscript{-1} Pt, respectively) than the platinum nanoparticles (20.2 mA mg\textsuperscript{-1} Pt and 13 mA mg\textsuperscript{-1} Pt for the nanoparticles prepared from grinding and PVP protecting routes, respectively). The remarkable high catalytic efficiency of platinum microcapsules may be directly related to their unique microcapsule structure with thin mesoporous shells and large hollow cavity, which could increase the surface fraction of Pt atoms accessible to methanol, as well as facilitate the transport of reactants/products. Interestingly, the Pt microcapsules encapsulating carbon spheres show both the highest mass-normalized oxidation and largest double layer currents, probably attributable to the existence of mesoporous carbon spheres in the porous platinum shells which further facilitates the transport of the reactant. The relatively lower activity of both Pt nanoparticles is mainly caused by the decrease of effective surface area and loss of diffusion paths derived either from heavily breaking the specific porous (mesopores and cavities) structure of the hollow microcapsules or the close-packing of the Pt nanoparticles on the surface of the electrode.

4 Conclusions

Hollow mesoporous microcapsules of noble metal or noble metal oxide such as Pt, PdO, RuO\textsubscript{2}, IrO\textsubscript{2} with tunable shell thickness have been successfully fabricated through a peripheral-pore-nanocasting method. Guest species (e.g., carbon) can be encapsulated into the hollow microcapsules by prefilling them or their precursors in the inner pores of HMS spheres before nanocasting the metal shell. The platinum-based microcapsules showed a high activity in the electrocatalysis of methanol oxidation reactions because of their special microcapsule structure and high mesoporosity. Such novel hollow and “sphere in shell” mesoporous microcapsules with variable compositions are expected to have more promising applications in a wide variety of fields including microreactors, electrochemical devices and so on.

Acknowledgements

The authors thank the NSFC (20273016, 20303003, 20325313, 20233030) and the SNPC (03DJ14004, 0249nm028) and the Major State Basic Research Development Program (2003CB615807, 200007750) for financial support.

References


\textsuperscript{3} (a) X. D. Wang, W. L. Yang, Y. Tang, Y. J. Wang, S. K. Fu and Z. Gao, \textit{Chem. Commun.}, 2000, \textit{261}; (b) A. G. Dong, Y. J. Wang,