

Novel hollow sub-microspheres with movable Au nanoparticles and excessive Pt nanoparticles in core and silica as shell

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ABSTRACT

A simple route has been designed for the syntheses of a kind of electrocatalyst, i.e., hollow spheres with Au and excessive Pt nanoparticles in core and silica as shell. The Au@carbon spheres synthesized by hydrothermal process can act as the transitional templates, and the carbonaceous matrix can in situ reduce $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ solution and load with Pt nanoparticles, and then a slightly modified Stöber process was applied to encapsulate the structures with silica shell. Further calcination at high temperatures removed the carbon matrix to form the hollow spheres with Au and excessive Pt nanoparticles in core and silica as shell. This new kind of structures shows excellent electrocatalytic properties compared with that of similar hollow spheres but only with pure Pt nanoparticles inside, and it might provide an efficient way to improve the electrocatalytic property of a bulk Pt/GC electrode.

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1. Introduction

A class of colloidal materials has been found widespread applications such as in the fabrication of photonic crystal, optical sensing, and drug delivery [1–4]. Recently, the engineering of movable cores inside hollow shells has also been achieved with a silica template method and a Kirkendall-type diffusion process [5–8]. If the shell is permeable to reactants, this new type of core–shell nanostructure can be considered in a wider sense as a tiny reactor containing a movable catalyst core. Xia has successfully synthesized monodisperse core–shell spherical colloids with movable cores [9]. A number of groups demonstrated the synthesis of core–shell particles consisting of metal shells and dielectric core by directly coating the surfaces of colloidal spheres with the metal [10,11].

Direct methanol fuel cell (DMFC) possesses excellent properties such as high energy transform level without pollution and no noise. Recent results indicate that the metal particles which are too huge or too small will not benefit for electrocatalysts [12]. Therefore it is of significance to synthesize the appropriate carriers embedded with metal nanoparticles with uniform sizes, which could contribute to prepare electrocatalysts with high activity for DMFC. For the development of methanol fuel cells, many investigations have been made on the catalytic activity of Pt–Ru alloy electrocatalysts [13,14], which perform as active anodes for methanol and carbon

monoxide-containing hydrogen. However, there is little research on bimetallic electrocatalysts, which could enhance the electrocatalytic activity.

Herein, we report a new route for the synthesis of hollow sub-microspheres with Au and excessive Pt nanoparticles in core and silica as shell, which show excellent electrocatalytic activity.

2. Experimental

2.1. Synthesis of Au@carbon spheres under hydrothermal conditions

Glucose 2.5 g was dissolved in 40 mL deionized water to form a clear solution under vigorous stirring, and then 1.2 mL HAuCl_4 (10 mM) was added to this solution drop by drop with vigorous stirring about 10 min to form a canary solution. Therefore, all solutions were transferred into a 50-mL Teflon-sealed autoclave and maintained at 160 °C for 20 h [16]. The brown black Au/carbon core–shell spheres precipitate was isolated by centrifugation, cleaned by three cycles of centrifugation, washed and redispersed in alcohol and in water, and then dried at 80 °C for more than 4 h.

2.2. Synthesis of Au and excessive Pt nanoparticles core/silica shell hollow nanospheres

About 0.1 g newly prepared Au/carbon core–shell spheres were dispersed in 25 mL deionized water with the aid of ultrasonication to form a homogeneous suspension, and then 2 mL $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ (0.1 mM) was added to the suspension solution. Subsequently, the solution was added into a refluxing flask for refluxing at 140 °C under continually stirring for about 8 h. Then silica coatings on the particles with different thickness can be achieved by directly using a slightly modified Stöber process [15]. The particles were again dispersed into 30 mL ethanol and 2 mL ammonia (37 wt%) mixed solution under ultrasonication about 20 min. And then 10 mL TEOS (10 mM) was injected into the above mixed solution very slowly. Thereafter, the final product was collected through three cycles of centrifugation, then was washed and

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Fig. 1. Illustration of the formation process of hollow nanospheres with Au and excessive Pt nanoparticles in core and silica as shell.

dispersed in alcohol and water. Finally, the product was collected, and dried at 80 °C, then calcined at 600 °C for about 2 h from room temperature with a heating rate of 1 °C min⁻¹ to remove the carbon layer.

2.3. Characterization

The as-prepared products were characterized by X-ray power diffraction (XRD) analyses, which were carried out on a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and the operation voltage and current were maintained at 40 kV and 40 mA, respectively; field emission scanning electron microscopy (FESEM) was applied to investigate the size and morphology, which were carried out with a field emission scanning electron microscope (JEOL-6700F). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) (JEOL-2011) operated at an acceleration voltage of 200 kV. Energy dispersive X-ray (EDX) analysis was also carried out on high-resolution transmission electron microscope (JEOL-2011). All cyclic voltammogram (CV) measurements were performed in a conventional three-compartment glass cell by using an electrochemical workstation (CHI 631A, CH Instruments, Austin, TX).

3. Results and discussion

Monodisperse Au@carbon spheres were firstly prepared via hydrothermal method as described previously [16]. Secondly,

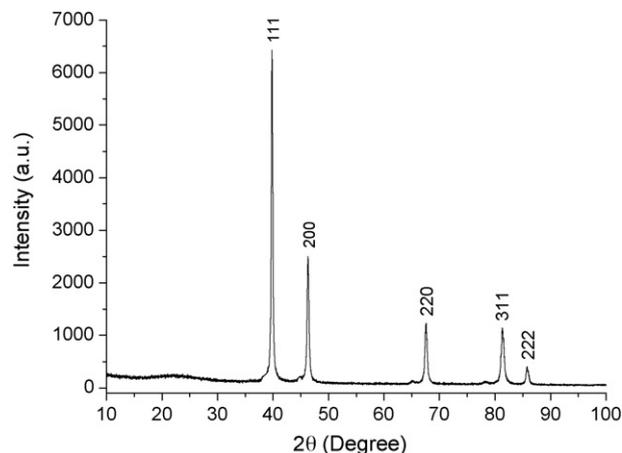


Fig. 2. XRD pattern of SiO₂ shell hollow spheres with movable Au and excessive Pt nanoparticles core.

monodisperse Pt nanoparticles were loaded on the carbonaceous spheres by in situ reducing H₂PtCl₆·H₂O solution. Thirdly, uniform SiO₂ coatings on Au and Pt/carbon core-shell structures can be achieved directly by a slightly modified Stöber process. The middle carbon shell can be removed by calcination. The main process can be illustrated in Fig. 1.

The XRD pattern of the as-prepared hollow nanospheres showed that all the diffraction peaks can be indexed as a cubic faced-

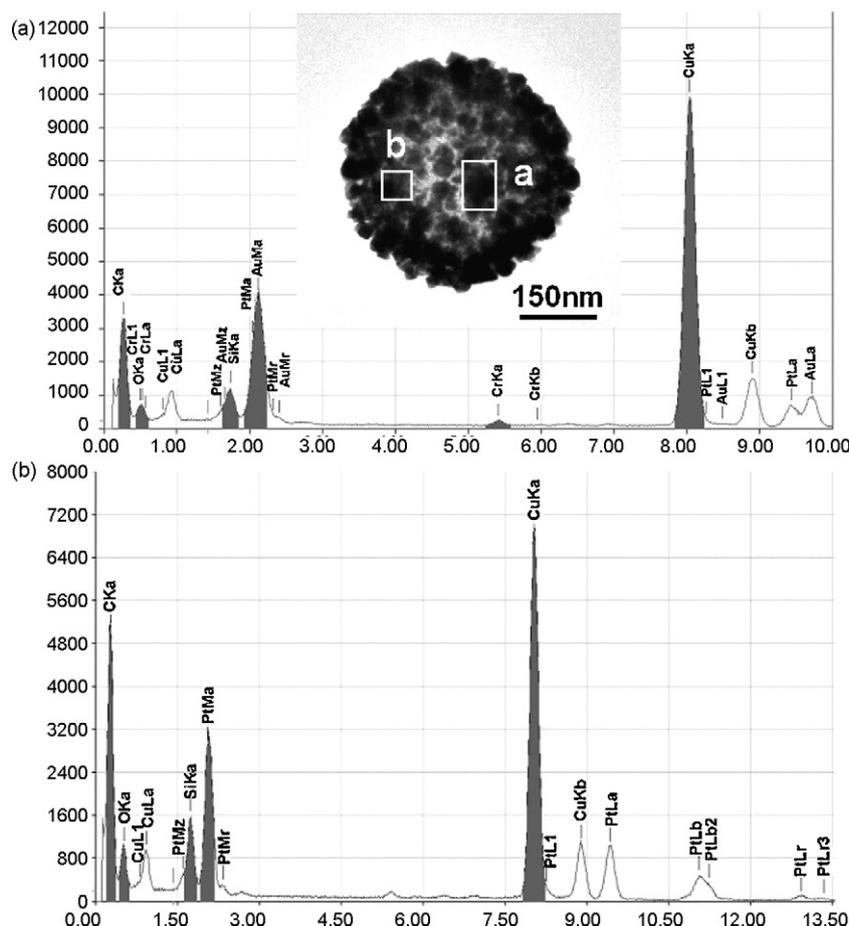


Fig. 3. The EDX spectra of the selected area as marked in the inserted TEM image. (a) The EDX spectrum measured in the selected area containing Au nanoparticle. (b) The EDX spectrum measured in the selected area which did not contain Au nanoparticle.

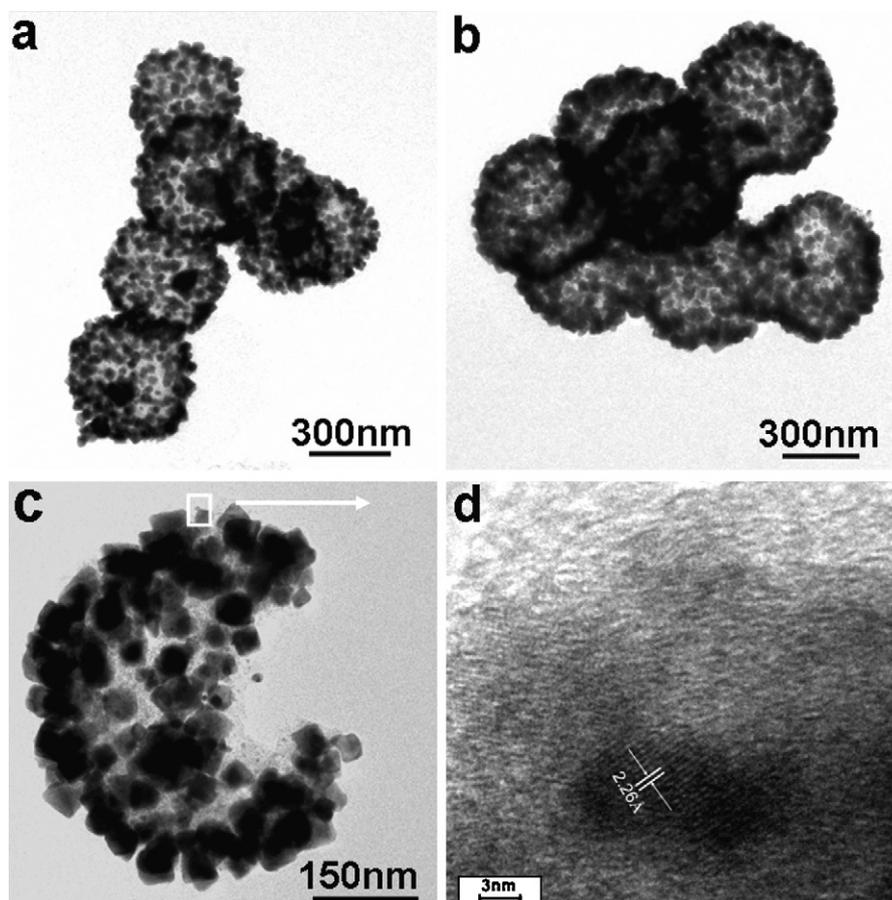


Fig. 4. TEM images of (a) and (b) the hollow spheres with Au and excessive Pt nanoparticles in core and silica as shell; (c) a broken sphere showing that it contains a lot of nanoparticles; (d) a HRTEM image taken on the selected area marked in (c).

centered Pt phase with cell constant $a = 3.92 \text{ \AA}$, which is in good agreement with the value in the literature (JCPDS card No. 040802) (Fig. 2). The presence of a broadening peak at about 25° indicated the formation of amorphous silica.

Energy dispersive X-ray analysis shows the selected area pane which contains SiO_2 shell hollow spheres with movable Au and excessive Pt nanoparticles core indeed composed of Au, Pt, and Si elements (Fig. 3a). In contrast, the spectrum taken in the area where no Au is presented did not show any Au signal (Fig. 3b). Due to the use of Cu foils and C film as the sample substrate in the measurement, the signals from Cu and C elements were observed in the EDX spectrum.

The hollow structures were also characterized by high-resolution transmission electron microscope. Fig. 4a and b

clearly demonstrated that the hollow signal Au and excessive Pt nanoparticles@ SiO_2 hollow spheres with movable Au and Pt nanoparticles in core. The hollow particles have a size of 450 nm and are of a wall thickness of 30 nm. The strong contrast between the dark edge and grayish center shows an evidence of hollow nature of the spheres. And the black dots in the interior were the speckles of Au and Pt nanoparticles, which were not in the center as before. It is obvious that the Au and Pt particles cores could be moveable within the hollow structures. SEM images in Fig. 5a and b show that the outside surface of the spheres is coarse.

The cyclic voltammograms of hollow spheres with Au and excessive Pt nanoparticles in core and silica shell/GC electrode in 0.5 M H_2SO_4 are shown in Fig. 6A. The upper potential limit for Au and Pt core-silica shell/GC electrode was selected to avoid significant

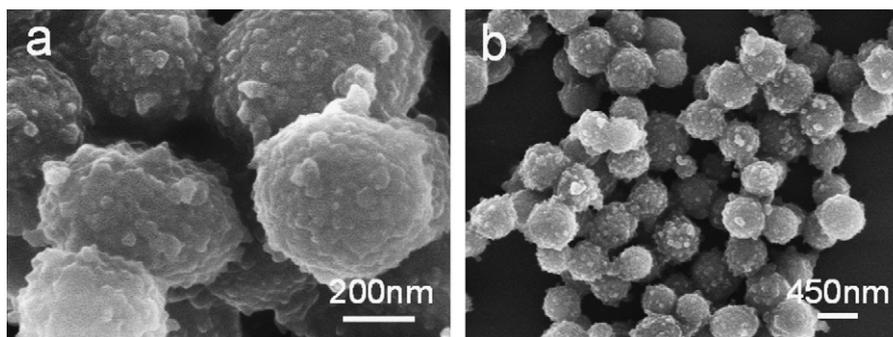


Fig. 5. SEM image of hollow spheres with Au and excessive Pt nanoparticles in core and silica as shell.

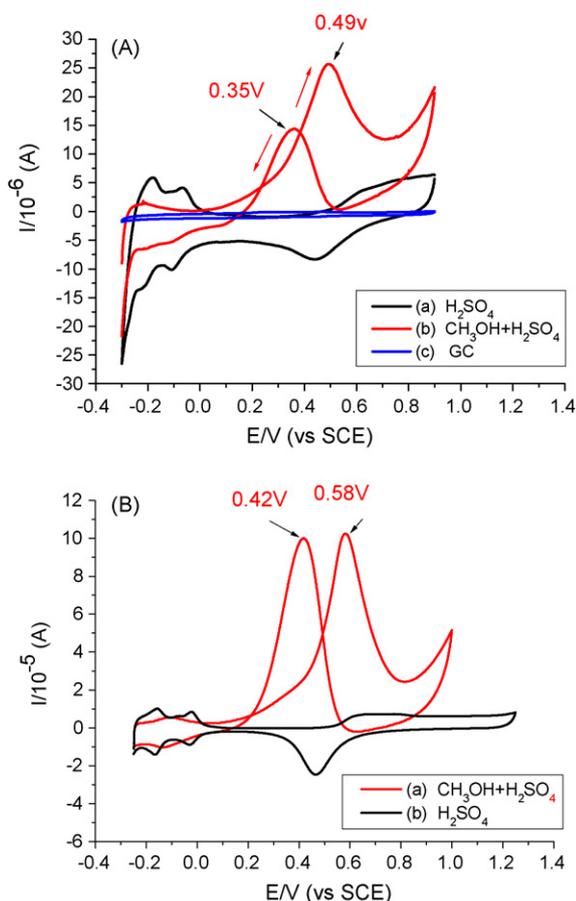
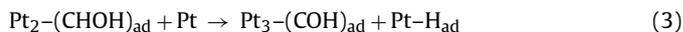
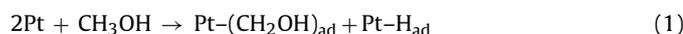


Fig. 6. (A) Cyclic voltammograms of Au and excessive Pt nanoparticles core-silica shell hollow spheres assembled on a surface in (a) 0.5 M H_2SO_4 and (b) 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ (c) cyclic voltammograms of normal GC electrode in 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ mixed solution. (B) Cyclic voltammograms of hollow spheres with excessive Pt nanoparticles in core and silica as shell assembled on a surface in (a) 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ and (b) 0.5 M H_2SO_4 . Scan rate: 50 mV s^{-1} .

oxygen evolution which is catalyzed by the Pt nanoparticles. When Au and excessive Pt nanoparticles core-silica shell hollow spheres are assembled on the GC surface in the 0.5 M H_2SO_4 solution, the CV shows typical surface oxidation and reduction current peaks similar to those of a bulk Pt/GC electrode [17,18].

To investigate the more catalytic behaviour of the hollow spheres with Au and excessive Pt nanoparticles in core and silica shell, we examined the oxidation of methanol in view of its important role in methanol fuel cells. The cyclic voltammogram recorded in 0.5 M $\text{CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ solution shows an oxidation peak at around 0.49 V in the anodic scan direction, which is lower than that commonly observed on a bulk Pt electrode [19,20] (Fig. 6B). These results show that the hollow spheres with Au and excessive Pt nanoparticles in core and silica as shell have stronger electrocatalytic activity than the hollow spheres with only Pt nanoparticles inside silica shell toward methanol oxidation and stronger dissociation of methanol spontaneously to produce CO.

The initial reaction on the electrode at reasonable anodic potentials in acid solution is believed to involve the dissociative absorption of methanol to give a Pt_3COH species in a three-step process [21], which are shown in Eqs. (1)–(3):



At the same time, the $\text{Pt}-\text{H}_{\text{ad}}$ species are lost to the solution as H^+ , which is shown in Eq. (4).

Generally, the high electrocatalytic activity can be attributed to the following reasons: (1) the improved dispersion degree of the deposited Pt and Au nanoparticles, and (2) the collaborative effect from the Au and the Pt. Biswas et al. reported that the Au nanoparticles with a size of less than 20 nm exhibits high electrocatalytic activity to CO and CH_3OH [22–24]. The uniform Au nanoparticle cores could effectively enhance the electrocatalytic activity of the hollow spheres with Au and excessive Pt nanoparticles in core and silica as shell.

4. Conclusion

In summary, a kind of novel hollow sub-microspheres with movable Au and excessive Pt nanoparticles in core and silica as shell has been successfully fabricated via simply templating against Au@carbon spheres synthesized from a hydrothermal process. This new kind of structures shows excellent electrocatalytic properties compared with that of similar hollow spheres but only with pure Pt nanoparticles inside, which might provide an efficient way to improve the electrocatalytic property of a bulk Pt/GC electrode.

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