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Short Communication

Synthesis of gold encapsulated in spherical carbon capsules with a mesoporous shell structure. A robust catalyst in a nanoreactor

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ABSTRACT

Core-shell templates containing an encapsulated Au nanoparticle in a mesoporous silica (Au@mSiO$_2$) or nonporous silica (Au@SiO$_2$) shell structure were made. The silicas were then covered with carbon by CVD using toluene and the silica was removed using HF. Au@mHCS and Au@HCS were both characterized by PXRD, HRTEM, TGA, BET and ICP-OES. The Au@mHCS yolk–shell composite exhibited excellent catalytic activity and reusability (10 cycles) for the reduction of *p*-nitrophenol with conversion of up to 97% in 8 min. Heat treatment of Au@mHCS at 800 °C/4 h/N$_2$ did not alter the morphology or the catalytic activity significantly.

1. Introduction

Many yolk–shell or rattle type nanostructures [1–3] with freely movable cores encapsulated inside an inorganic shell or a polymeric material have been synthesized [4–6]. These nanocomposite spheres not only modify the interaction between the metal core and the shell, limit physical and chemical contact in the structure and aggregation, but they also allow the encapsulated metal to exhibit a high catalytic activity in many reactions [7,8].

Interest in the use of yolk–shell nanostructures with the shell made of carbon has dramatically increased because of their excellent performance in catalysis and lithium ion batteries [9–11]. Coating the shell with carbon can be beneficial for the entrapped catalyst due to the thermal stability, chemical inertness and other useful physical properties associated with nanomaterial carbon [12–14].

Various methods have been demonstrated for preparing yolk–carbon shell capsules [15]. It is well-known that the preparation methods to make hollow nanostructures have an important effect on the physical and chemical properties of the resulting carbon framework. For example, SnO$_2$@hollow carbon spheres have been prepared by templating procedures using polystyrene spheres and simple hydrothermal methods [16,17]. Shi and co-workers [18] reported the preparation of Fe$_3$O$_4$@carbon with yolk–shell structures by a "ship in the bottle method". Liu et al. [9] synthesized Au@hollow carbon spheres via a one-step core shell–shell template using resorcinol-formaldehyde resin as carbon precursor. To explain the formation of some metal and semiconductor nanorattles, numerous mechanisms have been proposed to explain the fabrication of yolk–shell nanostructures [19–21]. In general, the synthesis of yolk–carbon shell nanostructures involves the synthesis of a spherical core-shell silica nanoparticles (M@SiO$_2$) coated with a carbon precursor to produce M@SiO$_2$@carbon nanoparticles. After carbonization, the template is selectively removed by chemical methods (acid or base etching) to obtain yolk–carbon shell nanostructures [9,22,23].

In many reactions catalysts may be subjected to high temperature conditions. In this study we have explored the stability of a yolk–carbon shell nanostructure after high temperature annealing. Here we report on an assembly route to prepare yolk–carbon shell catalytic nanoreactors by a chemical vapor deposition (CVD) method. As the CVD method is widely used in industry for carbon coating [24], the preparation of the catalysts described in this work can be used for the large scale synthesis of yolk–carbon shell nanostructures. Furthermore the catalytic reduction of *p*-nitrophenol to *p*-aminophenol was used as a benchmark reaction [25] to evaluate and compare the catalytic activity of Au@HCS and Au@mHCS (i.e. Au encapsulated in hollow carbon spheres (HCSs) that are non-porous or have mesopores) before and after heat treatment (800 °C/4 h/N$_2$). We have observed that Au@mHCS catalysts are recyclable and show

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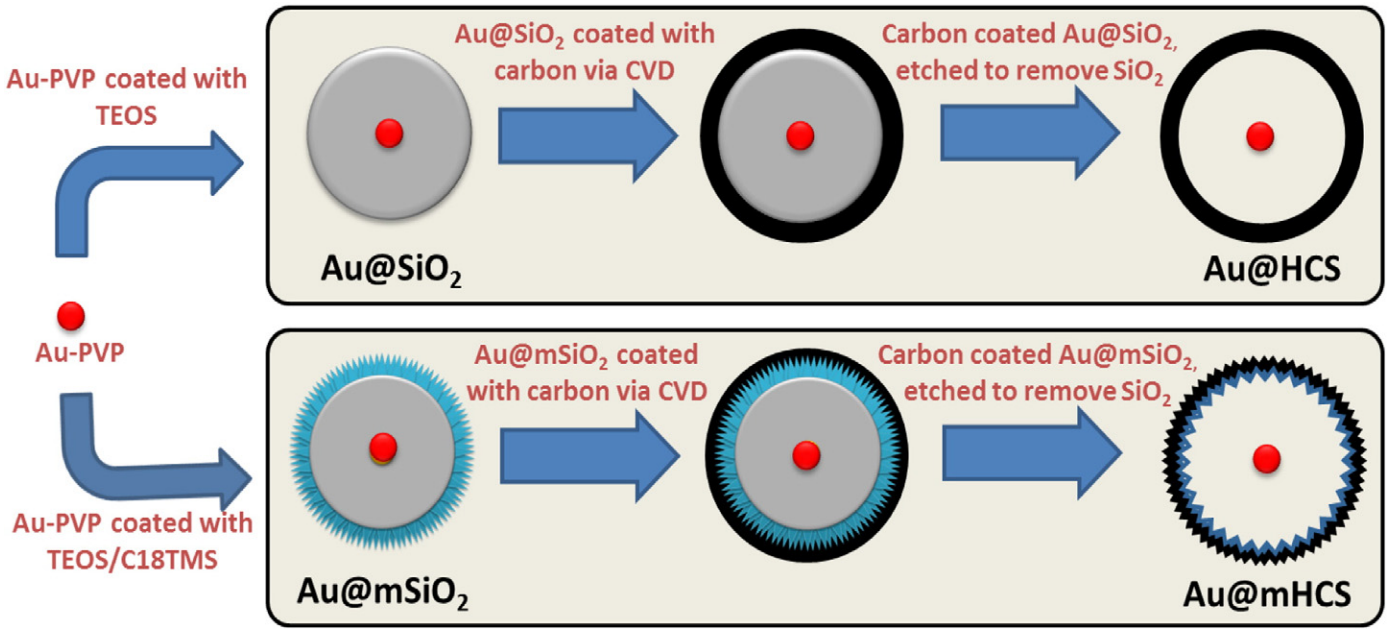

Scheme 1. Synthetic procedures of Au@HCS and Au@mHCS catalyst.

excellent stability after the treatment at high temperature under inert conditions.

2. Experimental

The $Au@SiO_2$ was prepared by routine procedures. The core shell $Au@mSiO_2$ was synthesized according to previously published procedures (using octadecyltrimethoxysilane ($C_{18}TMS$) as porogen) with some minor modifications [26]. The gold particles modified by PVP with a diameter of 15 ± 3 nm were prepared through reduction of chloroauric acid with sodium citrate [27]. Details are given in the Supplementary material.

Deposition of carbon (from toluene) onto $Au@mSiO_2$ and $Au@SiO_2$ was carried out using a CVD method and after removal of the silica with HF solution, gave Au encapsulated hollow carbon spheres (Au@mHCS and Au@HCS). Details of the synthesis, the standard

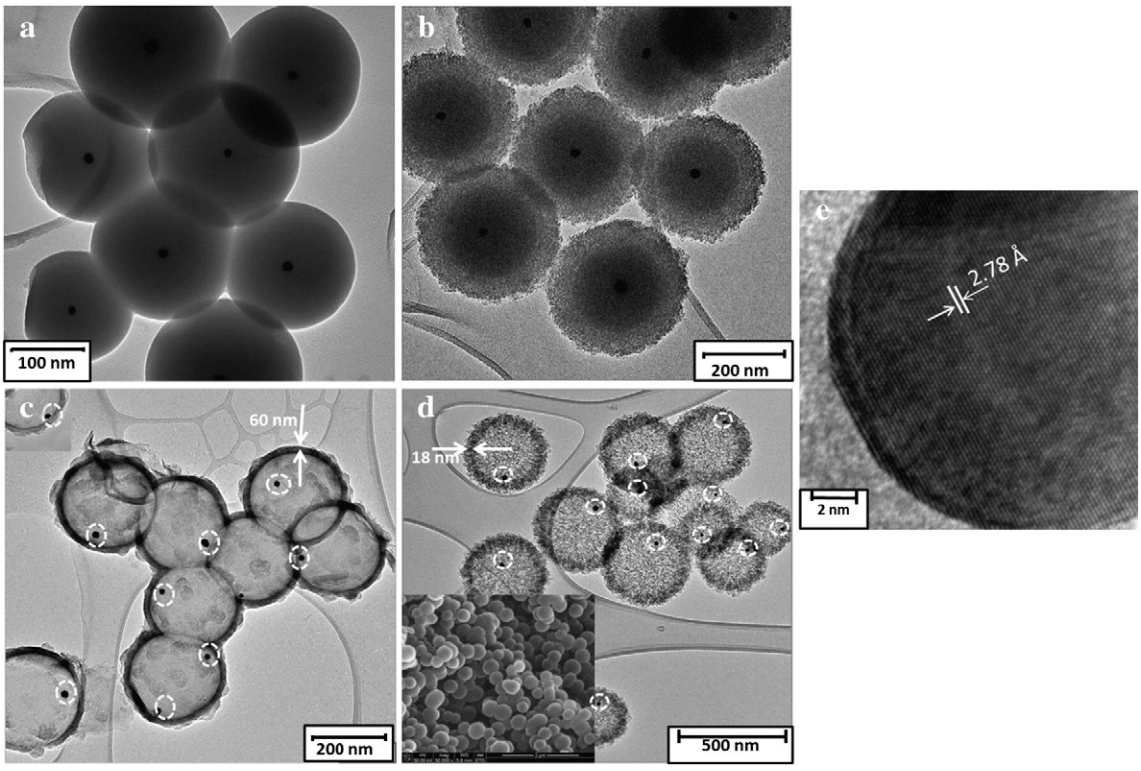

Fig. 1. TEM images of (a) $Au@SiO_2$, (b) $Au@mSiO_2$, (c) Au@HCS, and (d) Au@mHCS (inset SEM image of Au@mHCS); (e) HRTEM image of an encapsulated Au particle.