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Letter to the Editor

Forming ceria shell on Au-core by LSPR photothermal induced interface reaction

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A B S T R A C T

A novel method for preparing core–shell structure of Au@ceria was presented, which is characterized with using photothermal effect from localized surface plasmon resonance (LSPR) to induce heat, and the heat can trigger the shell formation reactions confined on the surface of the Au nanoparticles (NPs). In short of the preparation procedure, aqueous sol of Au NPs, citric acid, ethylene glycol and cerous nitrate were irradiated with a Xe arc lamp, maintaining the temperature of the sol at 25 °C by cooling and stirring the sol. The Au NPs could generate heat from LSPR, and the heat induced polymerization reaction in the sol, resulting in cerium gel formation which enveloped each of the Au NPs, and the gel containing cerium formed only on the surface of the Au NPs. After calcination, Au@ceria was obtained. This method can be extended for preparing various core@shell nanocomposites in which metal cores possess LSPR effect and the shell formation can be induced by heat.

1. Introduction

The nanocomposite with a metal particle as the core and an oxide as the shell, generally signed as metal@oxide, has been attracted much attention for its wide range applications in electronic equipment [1], sensing devices [2], nanomedicine [3] and catalysis [4–6]. The metal@oxide nanocomposite favors the interaction enhancement between the metal core and the oxide shell as well as improves anti-sintering ability of the metal particles [7], both of which are very valuable for metal/oxide catalysts. One of the key challenges is how to prepare the nanocomposite.

Up to now, the accepted best way for preparing metal@oxide nanostructure is using an organic agent to link the metal nanoparticle (NP) with the shell of oxide precursor. As a typical example, Joo et al. used tetradecyltrimethylammonum bromide (TTAB) as the organic agent to prepare Pt@SiO_2. One side of the TTAB adsorbed on the surface of Pt NPs, and the other side bonded with the silica gel, thus coating silica shell on Pt NPs' surface [8]. Similarly, Sun et al. obtained Au@ZnO, Au@Fe_3O_4, Au@MnO, Au@Co_2O_3, Au@TiO_2 and Au@Eu_2O_3 by using polyvinylpyrrolidone (PVP) as the linking molecule [9]. In the preparation process, the oxide precursor gel was generated in the whole liquid, which brings difficulty to separate the core–shell NPs from the liquid containing gel. Besides, it was not an atom economy preparation method, considering that only a small portion of the gel was linked onto the metal NPs.

It is desirable that the chemical reaction of the shell formation can be confined only on the metal NPs' surface.

The localized surface plasmon resonance (LSPR) is the result of the interaction between plasmonic metal NPs and the light with resonant frequency, and LSPR can convert the energy of the light into heat, called photothermal effect [10,11]. As LSPR taking place, the surface of the metal NPs will be heated up to high temperature instantaneously due to the photothermal effect. A feature of the photothermal effect is that the heat is confined on the metal NPs' surface [10]. For the photothermal effect from LSPR, the intensity of the released energy is high, while the total capacity of the released energy is small, resulting in the heat confinement. The follow two examples are the application of the photothermal effect. An Au NP was delivered much close to a cancer cell, then the Au NP was irradiated with a laser to ignite LSPR, thus the cancer cell would be destroyed, without harming the adjacent normal cells [12,13]. In another example, Au nanorods were embedded in a polymeric material. By triggering LSPR-photothermal effect, the polymeric fibers on the surface of the Au nanorods were melted, while the other places of the polymeric material were unaffected [14].

Inspired by the interesting effect of LSPR stated above, we attempt to use LSPR-photothermal effect to induce interface-confined chemical reaction for forming oxide shell on the surface of metal NPs, which never been reported up to now. Core–shell composite of Au@CeO_2 was chosen, considering that Au is a well-studied metal for LSPR and Au/CeO_2 is a potential catalyst.

2. Experimental

2.1. Preparation of samples

2.1.1. Preparation of 17 nm Au NPs

A solution of 0.5 mL of $HAuCl_4$ (99.5%, Tianjin Guangfu Fine Chemical Institute) (24.28 mM) in deionized water (47.5 mL) was heated in a 100 mL three-necked round-bottomed flask under vigorous stirring. After the solution was heated to boiling under reflux, 2.4 mL solution of 1 wt.% sodium citrate (99.8%, Sinopharm Chemical Reagent limited corporation) was injected rapidly; the solution

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is further boiled for 30 min with stirring. After removing the heat sources and continuing to stir for 10 min, the solution was cooled slowly to room temperature and the Au NPs were obtained and their average particle diameter is about 17 nm [15].

2.1.2. Preparation of Ce^{3+} ions sol

$Ce(NO_3)_3$ (99%, Tianjin Guangfu Fine Chemical Institute, 0.1736 g), deionized water (100 mL), citric acid (99.5%, Tianjin Guangfu Fine Chemical Institute, 0.126 g), ethylene glycol (Tianjin Guangfu Fine Chemical Institute, 0.15 g) were mixed and stirred for 2 h at room temperature. The pH value of the solution was adjusted by adding dilute aqueous ammonia (1.5%, 4 mL) to 6.7, and then a clear solution was obtained.

2.1.3. Preparation of 17 nm Au@GCEC (GCEC: the gel of citric acid–ethylene glycol-Ce^{3+})

The experiment was carried out at a constant reaction temperature of 25 °C in a 300 mL quartz reactor system, a quartz jacket was coated on the reactor for cooling by circulating cool water. A 500 W Xe arc lamp was used as light source. The prepared sol containing Au NPs, citric acid, ethylene glycol and Ce^{3+} ions was added into the reactor, and then irradiated with light under stirring. The color of the solution was keeping shallow wine red in the whole irradiating period.

2.1.4. Preparation of SiO_2 support

The preparation of poly styrene (PS) foams was stated in detail in our previous work [16]. The resulted PS foam was used as template, and silica gels were impregnated on the pore of the PS, details were stated in our previous work [17]. This impregnation was repeated for 7 times until the weight of the sample was no longer increase. The resultants were dried at 60 °C for 24 h and then calcined in N_2 for 4 h at 600 °C to remove the templates, finally calcined in air for 4 h at 750 °C.

2.1.5. Preparation of $Au@CeO_2/SiO_2$ catalyst

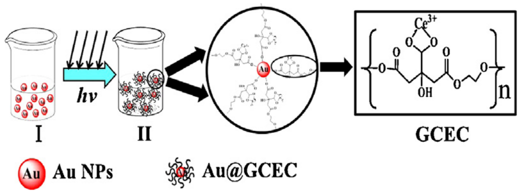
The obtained Au@GCEC with irradiating time of 2 h was concentrated by centrifugation at 10,000 rpm/min for 15 min, and then mixed with the solid SiO_2 under ultrasound vibration. The impregnated samples were dried at 120 °C for 12 h, and then calcined at 350 °C for 4 h in air with a heating rate of 2 °C min^{-1}.

2.2. Characterization of samples

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 F20 transmission electron microscope at 200 kV. The chemical compositions of the samples were investigated by an energy dispersive spectrometer (EDS) analysis. The size distribution of Au NPs was analyzed via least 100 particles on the TEM images. Ultraviolet visible (UV–vis) absorption spectra were acquired with a Perkin Elmer Lambda 750S UV–vis spectrometer. The solution was placed in a Quartz cuvette, and spectral analysis was performed in the range of 200–800 nm at room temperature. The powder X-ray diffraction (XRD) measurements were performed on a Bruker D8-Focus X-ray diffractometer with Ni-filtered Cu Kα radiation source ($\lambda = 0.15406$ nm). The spectra were collected from 10° to 80° (2θ degree) at a scanning rate of 5° min^{-1}.

2.3. Catalytic performance tests

CO oxidation reactions were carried out in a fixed-bed continuous-flow reactor coupled with on-line gas SP-3420 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a column packed with 5A molecular sieve. For the purpose of detecting the CO concentration at ppm level, FID was used as the detector. In each run, 160 mg catalyst was put into the reactor, and the reaction gas mixture composed of 1% CO, 1.6% O_2 and N_2 balance gas with a total gas flow rate of 40 mL min^{-1}, corresponding to the volume space velocity of 15,000 mL h^{-1} $g_{cat}{}^{-1}$, with a heating rate of 1.25 °C min^{-1}.



Scheme 1. (I) Au NPs dispersed in an aqueous solution containing Ce^{3+} ions, citric acid and ethylene glycol. (II) Au@GCEC dispersed in the aqueous solution (GCEC: the gel of citric acid–ethylene glycol-Ce^{3+}).

3. Results and discussion

3.1. Shell formation mechanism of Au@GCEC

An illustration for preparing Au@GCEC ($Au@CeO_2$ precursor) is shown in Scheme 1. Firstly, aqueous sol of Au NPs with uniform particle size distribution was prepared. Then, citric acid, ethylene glycol and cerous nitrate were added into the sol. After that, a Xe arc lamp was used to irradiate the sol; meanwhile the temperature of the system was kept constant at 25 °C by cooling and stirring the sol. It is known that only heated to certain high temperature, citric acid, ethylene glycol and Ce^{3+} ions can undertake polymerize reaction [18], as indicated in Eq. (1). The reaction product is shorted as “GCEC”, which is the gel of citric acid-ethylene glycol-Ce^{3+}, to see the last formula in Scheme 1.

$$HOOCCH_2C(OH)(COOH)CH_2COOH + CH_2(OH)CH_2(OH) + Ce^{3+} \rightarrow GCEC \qquad (1)$$

Where the heat came from to trigger the polymerize reaction in our preparation process? The heat was converted from the light of the Xe arc lamp via LSPR induced photothermal effect on the Au NPs. As stated above, the heat was confined on the surface of Au NPs, or in another words, the heat was confined at the interface between the Au NPs and the aqueous sol medium. So, GCEC should be generated only on the interface; while in the bulk aqueous medium, GCEC was not formed. The generated GCEC was coated on the surface of Au NPs and enveloped Au NPs, forming Au@GCEC.

3.2. Structure and morphology of Au@GCEC

The transmission electron microscopy (TEM) images of the resultant Au@GCEC are shown in Fig. 1. As shown in Fig. 1(a), the as-synthesized Au NPs are uniformly dispersed and in spherical shape with the average diameter of 17 nm.

As can be seen from Fig. 1(b)–(f), the GCEC shells were formed only on the surface of the Au NPs, in other words, no GCEC could be observed in the aqueous medium except the interface of Au NPs. Fig. 1(i) and (j) show the energy dispersive spectrometer (EDS) line scanning curve of a representative nanocomposite, it is seen that the prepared nanocomposite is Au@GCEC.

In Fig. 1 from (b) to (g) and the insets, it can be noted that the shells’ thickness increased from 1 to 13 nm with the increase of the irradiating time from 15 min to 2 h. It is known that GCEC could not be generated in the aqueous medium temperature of 25 °C in the process [19]. This implies that the shell formation was induced by the irradiating. For comparison, the same aqueous sol of (I) in Scheme 1 was maintained for 3 h under the same conditions without irradiation. As a result, there is indeed no GCEC could be detected. So, GCEC could not be produced without irradiation.

As the irradiating time was 2 h or longer, see Fig. 1(g) and (h), it can be seen that the GCEC was not only formed at the