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Yolk–shell Au@CeO_2 microspheres: Synthesis and application in the photocatalytic degradation of methylene blue dye

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ABSTRACT

Porous micro- and nanostructured materials with the desired morphologies are of great interest because of their potential applications in environmental remediation. In this study, novel yolk–shell Au@CeO_2 microspheres were prepared from glucose and metal salt precursors via a one-pot hydrothermal synthesis followed by precipitation and calcination. These core/shell structure were characterized by scanning electron microscope, transmission electron microscope, X-ray diffraction, Fourier transform Infrared Spectrometer, X-ray photoelectron spectroscopy and N_2 adsorption–desorption techniques. These rattle-type spheres were found to compose of a porous CeO_2 shell (thickness ≈ 45 nm) and a solid gold core (diameter ≈ 50 ± 20 nm) with variable space between the core and the shell. The photocatalytic degradation of methylene blue dye was used as a catalytic test reaction revealing that the activity of the yolk–shell spherical products was substantially higher than that of their hollow counterparts. These new core/shell structures with encapsulated gold nanoparticles may exhibit potential applications in catalysis and adsorption.

1. Introduction

In recent years, the fabrication of inorganic micro- and nanosized hollow and rattle-type or yolk–shell core/shell materials has attracted substantial attention because of the versatile applications of these materials as catalysts, chemical sensors, drug carriers, drug/gene reservoirs, and adsorbents [1–3]. These core/shell composites often exhibit relatively low densities, large surface areas, excellent loading capacities, high permeabilities, and optical properties. Various methods including template-assisted synthesis and template-free routes have been proposed for hollow microsphere fabrication [4–7]. Recently, colloidal carbonaceous spheres were employed as green novel templates to synthesize hollow structures of a variety of materials [8–10]. After removing the template cores, hollow microspheres could be finally achieved.

Rattle-type or yolk–shell microspheres, which are considered a special class of core/shell particles, have been extensively studied because of their unique structural properties and potential catalytic applications [11–14]. The spherical shells in these materials can physically and thoroughly separate solid cores. Therefore, it is highly desirable to develop novel higher-order hollow nanostructures and rattle-type core/shell materials that could result in remarkable enhancements in catalytic activity, especially in combination with a relatively simple and practical preparation process. The incorporation of nanoparticles (NPs) as mobile cores into these hollow particles has been explored by several groups [15–17]. Notably, Kamata et al. reported that mobile Au NPs as cores within polymeric hollow spheres could act as optical probes for monitoring the diffusion of chemical reagents into and out of the shell [15]. Somorjai et al. demonstrated that the Pt cores in Pt@CoO yolk–shell structures could act as catalysts for ethylene hydrogenation [18]. Wang reported the synthesis and catalytic properties of yolk–shell mesoporous silica microspheres containing a single Au NP core [19].

CeO_2, as a technologically important rare earth material, has been widely used as an active component in three-way catalysts and is a promising candidate for applications in solid oxide fuel cells due to the redox activity between Ce^{3+} and Ce^{4+} [20–27]. Hollow CeO_2 microspheres, with open 3D hollow porous structures and high surface areas, large pore volumes, and marked hydrothermal stability, have received considerable attention recently [20–23]. Though the yolk–shell structured materials are expected to exhibit outstanding catalyst properties [28,29], work concerning the CeO_2 core/shell structures has been limited [20,22,30]. Yolk–shell Au@CeO_2 microspheres have not been synthesized to the best of our knowledge.

Herein, we report a simple and efficient route for the preparation of yolk–shell Au@CeO_2 microspheres using carbon microsphere templates in combination with a layer-by-layer (LBL) preparation strategy. The photocatalytic degradation of methylene blue dye (MB) was used as a catalytic test reaction revealing the very high activity of the yolk–shell spherical products.

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2. Experimental section

2.1. Starting materials

Analytical grade glucose (Fuchen Chemical Reagent Factory, Tianjin, China) was used as the core starting materials. A standard CeO_2 sample was prepared by calcining cerium nitrate at 600 °C for 2 h. $Ce(NO_3)_3 \cdot 6H_2O$ was purchased from Chengdu Chemical Corporation, China. Hexamethylenetetramine (HMT) was purchased from the National Pharmaceutical Industry of China. All the other reagents were analytical grade and used directly as received.

2.2. Synthesis

2.2.1. Preparation of hollow CeO_2 spheres

2.2.1.1. Carbon spheres. The monodisperse carbon particles used as templates were generated by the hydrothermal treatment of aqueous glucose solution (4 g in 30 mL H_2O) at 170 °C for 9 h [31].

2.2.1.2. Hollow CeO_2 spheres. $Ce(NO_3)_3 \cdot 6H_2O$ (0.36 g) and HMT (0.58 g) were added to distilled water (30 mL) with vigorous stirring to form a clear solution. Subsequently, the C microspheres (0.2 g) were added and well dispersed into the above solution with the assistance of ultrasonication for 20 min. Finally, the mixture was transferred into a round-bottomed flask and heated at 75 °C for 2 h with vigorous stirring. The precursor was collected by centrifugation, washed several times with deionized water and ethanol and dried at 60 °C in air. The final hollow CeO_2 yolk–shell microspheres were obtained through heat treatment at 600 °C for 2 h in air with a heating rate of 1 °C min^{-1}.

2.2.2. Synthesis of Au@CeO_2 yolk–shell spheres

2.2.2.1. Au@C microspheres. To a clear solution of glucose (4 g) in distilled water (30 mL) was added an $HAuCl_4$ solution (0.01 M, 1 mL) dropwise with stirring for 0.5 h. The solution was then sealed in a 50 mL Teflon-lined stainless steel autoclave and maintained at 170 °C for 9 h.

2.2.2.2. Au@CeO_2 yolk–shell spheres. A similar process was employed to prepare hollow CeO_2 yolk-shell microspheress, except the C spheres were instead by Au@C microspheres.

2.3. Characterization

X-Ray diffraction (XRD) patterns of the synthesized samples were measured by X-ray powder diffractometry (Rigaku D/Max-3c, Japan). The particle morphologies of the yolk–shell Au@CeO_2 microspheres were investigated by scanning electron microscopy (SEM, Philips–FEI Quanta 200, America). Transmission electron microscopy (TEM) images of the synthesized samples were collected on a JEM-2100F instrument (Japan) operating at an acceleration voltage of 200 kV. IR spectra were recorded by using a Nicolet Avatar 360 E.S.P. Fourier transform IR spectrophotometer at room temperature. Particle size distributions were measured on a laser particle size analyzer (BI-90 Plus, Brookhaven, America). Thermogravimetry and differential scanning calorimetry (TG–DSC) analyses of the samples were carried out on an SDT Q600 instrument (TA instruments) at a heating rate of 5 °C/min from room temperature to 800 °C. The N_2 sorption measurements were performed on a Micromeritics ASAP 2020, and the specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method. Photocatalytic degradation was investigated using a photochemical reaction apparatus (BL-GHX-V, Xi'An Bilon, China).

The surface compositions of the samples were determined by X-ray photoelectron spectroscopy (XPS) in an ion-pumped chamber of an Axis Ultra (UK) spectrometer. The photoelectron emission spectra were recorded using an Al-Kα ($h\upsilon = 1486.6$ eV) monochromatized source operating at a pressure of 10^{-9} Torr. XPS analysis was implemented by first taking a wide scan using a 160 eV pass energy (150 W), after which narrow scan at a 20 eV pass energy (225 W) was taken. Spectra were corrected for charge shifting by using the carbon 1s value of adventitious carbon (284.8 eV) [32].

2.4. Evaluation of photocatalytic activity

Methylene blue (MB) was selected as model organic compounds to examine the photocatalytic activity of the Au@CeO_2 NPs. 10.0 mg of the Au@CeO_2 NPs was added to 100.0 mL of 2.0×10^{-2} M MB aqueous solution to get a suspension. The suspension was magnetically stirred for 30 min in the dark to establish an adsorption/desorption equilibrium between the dye and the photocatalyst. Then the mixed solution was irradiated with a 30 W medium-pressure mercury-vapor lamp at a distance of about 8 cm (XPA-7 photochemical reactor, Xujiang Electromechanical Plant, Nanjing, China). At a given irradiation time interval, 5 mL of sample was withdrawn from the test tube for analysis. Sample solutions were obtained by centrifugation, and their absorption spectra were measured by a Hitachi U-3900 spectrophotometer using deionized water as reference.

3. Results and discussion

3.1. Phase identification

The structures of the Au@CeO_2 microspheres were first investigated by XRD (Fig.1). We compared (a) the plain carbon spheres, (b) the Au NPs encapsulated by carbon spheres (Au@C), (c) the uncalcined precursor Au microspheres coated with the carbon and the CeO_2 composite (Au@C@CeO_2), (d) CeO_2 hollow spheres synthesized by a similar process, and (e) yolk–shell Au@CeO_2 sphere. The standard data for cubic phase CeO_2 (JCPDS File No. 43-1002) and Au (JCPDS File No. 04-0784) are also presented for reference. No obvious diffraction peak appears in Fig. 1(a); a broad hump at about $2\theta = 22°$ suggests the amorphous nature of the carbon sphere. For the Au@C spheres (Fig 1b), the main diffractions at $2\theta = 38.18°$, 44.40°, and 64.58° can be directly indexed to the cubic Au phase. Furthermore, the obvious broad hump at about $2\theta = 22°$ assigned to the amorphous carbon microspheres suggests that the sample is composed of Au and carbon spheres.

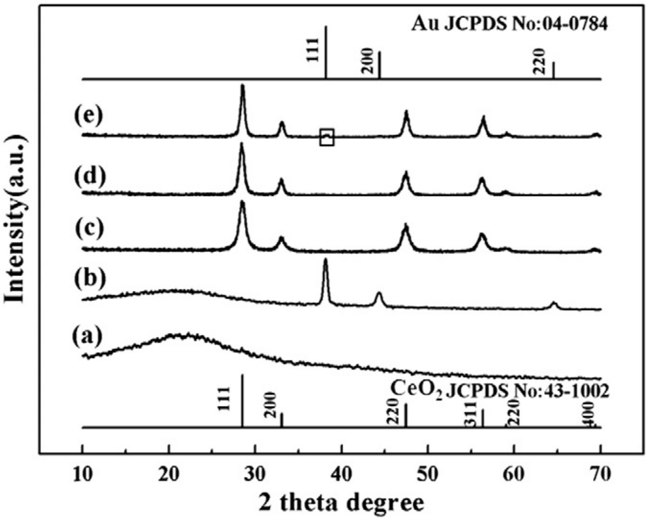

Fig. 1. XRD patterns of (a) carbon spheres, (b) Au NPs encapsulated with carbon spheres (Au@C), (c) uncalcined precursor Au microspheres coated with carbon and CeO_2 composite (Au@C@CeO_2), (d) CeO_2 hollow spheres, and (e) Au@CeO_2 hollow spheres, the samples in (d) and (e) were calcined at 600 °C for 2 h. Note: □ denotes the diffraction peaks of Au. Standard data for cubic CeO_2 and Au are also presented in the figure for comparison (JCPDS Files No. 43-1002 and No. 04-0784, respectively).