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Full Length Article

Au-CeO$_2$ Janus-like nanoparticles fabricated by block copolymer templates and their catalytic activity in the degradation of methyl orange

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ABSTRACT

A simple approach towards the fabrication of Au-CeO$_2$ Janus-like nanoparticles is presented. Composite micelles of polystyrene-*block*-poly (ethylene oxide) (PS-*b*-PEO)/Ce(NO$_3$)$_3$/HAuCl$_4$ with HAuCl$_4$ and Ce(NO$_3$)$_3$ precursors incorporated in the PEO domains are prepared first. By manipulating the pH value of the composite micelles solution, a redox reaction between Au(III) with Ce(III) in the PEO domains occurs and Au-CeO$_2$ Janus-like nanoparticles composed of a porous CeO$_2$ and an Au nanoparticle are generated. X-ray diffraction (XRD), UV–vis spectrum (UV), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) measurements are employed to characterize the Janus-like nanoparticles. The catalytic degradation of methyl orange dye (MO) under ultrasonic irradiation is chosen as the test reaction to examine the catalytic activity of the Au-CeO$_2$ Janus-like nanoparticles. It is found that Au-CeO$_2$ Janus-like nanoparticles show higher activity than that of CeO$_2$ nanoparticles or Au-CeO$_2$ composite nanoparticles. The increased catalytic activity of Au-CeO$_2$ Janus-like nanoparticles is attributed to the exposed Au core on one side of the Janus nanoparticles and the Au-CeO$_2$ heterointerfaces.

1. Introduction

Janus particles, initially named after the double-faced roman god Janus, are non-centrosymmetric particles with two distinct sides [1]. In the recent years, Janus particles have attracted increasing interests owing to their special structure-property relationship [2], and potential applications as optical and biological sensors, photocatalysts and two-phase stabilizers, or building blocks for complex hierarchical assemblies or novel materials [1a,3]. Recently, noble metal–metal oxide Janus nanoparticles have received great attention due to their optical, catalytic, and electronic properties, which originate from electron transfer across the nanometer contact at the interface of the two nanoparticles [4]. For examples, the Au-TiO$_2$ heterodimer nanoparticles displayed apparent photoluminescence that was ascribed to electronic transitions involving trap states of TiO$_2$ particles, and the enhanced photocatalytic performance, compared with that of P25 TiO$_2$ colloids, was ascribed to the charge separation of photogenerated electrons and holes at the Au-TiO$_2$ interface facilitated by the close proximity of the Au nanoparticles [5]. To date, various synthetic routes have been established to generate noble metal–metal oxide Janus nanoparticles, including the heterogeneous nucleation [6], asymmetric modification at interfaces [7a], and non-epitaxial deposition on the full surface of the first nanoparticle followed by thermal dewetting of the shell into a single domain [7b]. Au (Ag, Pt)-Fe$_3$O$_4$ Janus nanoparticles have been prepared using decomposition of Fe(CO)$_5$ on the surface of the noble metal nanoparticles [7,8]. Au@MnO heterodimers were prepared using preformed Au nanoparticles as seeds [9]. Janus-like Au-TiO$_2$ heterodimers have been prepared by using a block copolymer template, and exhibited apparent photocatalytic activity for efficient hydrogen generation under visible-light photoirradiation and methylene blue degradation [10,11], owing to their strong close to localization of plasmonic near fields to the Au-TiO$_2$ interface. Au-TiO$_2$ snowman-like heterodimer nanoparticles were prepared by a surface sol-gel process based on Au Janus nanoparticles whose surface-protecting mono-

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layers consisted of a hemisphere of hydrophobic 1-hexanethiolates and the other of hydrophilic 2-(2-mercaptoethoxy) ethanol.[5] Janus, eccentric core–shell, and concentric core–shell nanostructures were prepared by the anisotropic growth of TiO_2 onto Au nanorods, which can be used to catalyze 4-nitrophenol reduction with high cyclic stability [12].

CeO_2 has been attracted much attention due to the wealth of useful applications [13]. To improve the catalytic performance of CeO_2 materials, coupling CeO_2-based materials with noble metal nanoparticles has drawn continuous attention. In recent years, various noble metal nanoparticles/CeO_2 hybrid nanostructures with enhanced catalytic activity and selectivity have been fabricated [14–17]. For example, M@CeO_2 (M = Pt, Pd, Au, Ag, etc.) core-shell catalysts [14], the pomegranate-like Pt@CeO_2 multicore@shell nanospheres [16b], Pd@SiO_2@CeO_2 multisheath superstructures and multiyolk–shell nanostructures [17a], Au@CeO_2 multicore-shell hollow spheres [17b], and plum pudding-structured Pd@CeO_2 [18] have been fabricated. However, there have been very few reports of formation of Au-CeO_2 Janus-like nanoparticles.

The utilization of block copolymer micelles for the synthesis of metal and metal oxide nanoparticles has been extensively investigated [19]. Using block copolymer as surfactant CeO_2 nanoparticles can be synthesized [20]. We prepared arrays of titania or Au/titania nanoparticles using surface micellar films of poly(styrene-*block*-2-vinylpyridine) diblock copolymers (PS-*b*-P2VP) as reaction scaffolds [21]. Combining sol-gel process, organic-inorganic hybrid nanostructures can be fabricated with TiO_2 selectively incorporated into the PEO microdomains [22]. We also produced arrays of Au-TiO_2 nanobowls using Au precursor-loaded block copolymer micelles as templates [23]. Very recently, strawberry-like Au@CeO_2 nanoparticles were fabricated by assembly of PS-*b*-P2VP block copolymer composite micelles [24]. However, there is no previous work regarding the preparation of Janus-like Au-CeO_2 nanoparticles by using of block copolymer composite micelles as templates.

In this work, we suggest a simple approach towards the fabrication of Au-CeO_2 Janus nanoparticles. This approach involves the preparation of the PS-*b*-PEO/$Ce(NO_3)_3$/$HAuCl_4$ composite micelles solution by dissolving the PS-*b*-PEO block copolymers, $Ce(NO_3)_3 \cdot 6H_2O$ and $HAuCl_4$ in a mixed solvent of toluene and ethanol. $HAuCl_4$ and $Ce(NO_3)_3$ are incorporated in the PEO domains. Specifically, by addition NaOH solution to the composite micelles solution, the reaction between Ce^{3+} and NaOH to form $Ce(OH)_3$, and the redox reaction between Au(III) with Ce(III) to Au(0) and Ce(IV) took place successively; eventually, Au-CeO_2 Janus-like nanoparticles are obtained. It is found that the catalytic activity of the Janus-like Au-CeO_2 nanoparticles in the degradation of MO under ultrasonic irradiation is enhanced as compared to that of CeO_2 or Au-CeO_2 composite nanoparticles. To the best of our knowledge, the present work is the first example of the preparation of Au-CeO_2 Janus nanoparticles.

2. Experimental section

2.1. Materials

PS-*b*-PEO was purchased from Polymer Source Inc., Dorval, Quebec, Canada. The molecular weight of the PS block was 20,000 and of the PEO block 14,000, M_w/M_n was 1.05. The volume fraction of PS block in the copolymer was 0.59. Tetrachloroauric (III) acid ($HAuCl_4 \cdot xH_2O$, $M_w = 333.79$), $Ce(NO_3)_3 \cdot 6H_2O$ and methyl orange (MO) were purchased from Alfa Aesar. Toluene, ethanol and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

2.2. Sample preparation

Au-CeO_2 Janus nanoparticles were synthesized as follows. PS-*b*-EO/$Ce(NO_3)_3$/$HAuCl_4$ composite micelles solution was prepared with PS-*b*-PEO solution in toluene (0.03 wt%, 5.0 ml), $Ce(NO_3)_3$ solution in ethanol (0.25 M, 33.75 μl), and $HAuCl_4$ solution in ethanol (0.25 M, 5.625 μl). The NaOH solution (0.5 M, 26.875 μl) in ethanol was added into the composite micelle solutions prepared above and stirred for 1 h at room temperature. The molar ratios of $HAuCl_4$/EO, $Ce(NO_3)_3$/$HAuCl_4$, NaOH/$Ce(NO_3)_3$ were 1/10, (3–9)/1, and 8/5, respectively. After the addition of ethanol, the mixture was centrifuged and the obtained precipitate was washed with ethanol for three times, dried at 25 °C in vacuum. The dried sample was further washed with pure water for three times to remove $NaNO_3$ completely, dried at 110 °C overnight in air. Pure CeO_2 and Au-CeO_2 composite nanoparticles were prepared simply by addition of NaOH solution to $Ce(NO_3)_3$ and $Ce(NO_3)_3$/$HAuCl_4$ solutions under the identical conditions.

2.3. Characterization

UV–vis spectra were acquired with a UV2450 spectrometer (Shimadzu Co., Japan). Transmission electron microscopy (TEM) measurements were performed on a JEM-2100 TEM microscope (JEOL Ltd., Japan) operated at 200 kV. The samples were prepared by mounting a drop of the dispersions on a carbon-coated Cu grid and allowing it to dry in air. The average particle size was determined by counting particles from the TEM pictures. X-ray diffraction (XRD) was performed using a D8 FOCUS diffractometer (Bruker-AXS, Germany) with Cu Kα radiation (λ = 1.5418 Å). The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 with Al Ka excitation. Photoluminescence (PL) spectra were measured using FLS920 instrument (Edinburgh Instruments, UK) with an excitation wavelength of 380 nm.

2.4. Catalytic activity measurements

The decomposition experiments were carried out in a multiwave ultrasonic generator (Sonicator KQ3200DA; Kunshan Ultrasonic Instrument Co., China) with a frequency of 40 kHz and maximum output power of 150 W. Before used, the prepared catalysts were calcined at 400 °C for 2 h in N_2. In a typical reaction, MO solution (48 ml, 10 mg/L), Au-CeO_2 catalyst (6 mg) were placed in a flask, which was then treated by ultrasonication in a water bath (25 °C) for different times. Prior to ultrasonic treatment, the suspension was equilibrated for 40 min in the dark. To avoid the effect of visible light irradiation, the degradation reaction was carried out in the dark. For comparison, control experiments in the absence of catalyst, in the presence of CeO_2 catalyst prepared without using block copolymer and $HAuCl_4$, and in the presence of Au-CeO_2 composite nanoparticles were also conducted. After the degradation experiment, the treated MO solution was centrifuged at 10,000 rpm for 5 min and then filtered to remove the catalyst powders. The change of absorption at 464 nm was measured to identify the concentration of MO using a UV–vis spectrophotometer. A calibration curve obtained using standard MO solutions was used to estimate the initial (C_0) and instant (C) (at reaction time t) concentrations of MO, respectively.

3. Results and discussion

It has been reported that PS-*b*-PEO block copolymers form reversed micelles composed of a soluble PS corona and an insoluble PEO core in toluene above the critical micelle concentration [22]. The PS-*b*-PEO micelles have been used to generate various TiO_2 nanostructures [23]. When $HAuCl_4$ and $Ce(NO_3)_3$ precursors