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Short Communication

Hollow hybrid titanate/Au@TiO_2 hierarchical architecture for highly efficient photocatalytic application

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ABSTRACT

Hollow hybrid titanate/Au@TiO_2 hierarchical architecture consisting of titanate and anatase titanium dioxide (TiO_2) loaded with Au nanoparticles was prepared via a sol-impregnation method combined with a hydrothermal etching process. The titanate/Au@TiO_2 architecture possesses unique hollow spherical configuration with Au nanoparticles loaded in the middle of titanate and TiO_2 shells and allows to be used as a microreactor for photocatalytic application. The hybrid titanate/Au@TiO_2 photocatalyst shows significantly enhanced photocatalytic activity on degradation of methylorange (MO) under UV light irradiation due to the lower electron–hole pairs recombination rate arisen from the synergistic effect of titanate-Au-TiO_2 in hybrid hierarchical architecture.

1. Introduction

Heterogeneous photocatalysis is a potential approach to solve worldwide environmental and energy-related issues with great promise [1]. Recently, titanium dioxide (TiO_2) materials have attracted great attention due to their high surface-to-volume ratio, lower density, better permeation, and wide potential applications in solar energy conversion and environmental purification [2–6]. It is generally accepted that the catalytic performance of TiO_2 materials is largely correlated with their size, morphology, and surface state. It is revealed that the catalytic performance of TiO_2 materials can be improved by loading noble metals (Ag, Au, Pt, or Pd) on TiO_2 to form noble metal supported TiO_2 catalysts [7–11]. Besides, the catalytic performance can also be enhanced by incorporating other semiconductor oxides (CdS, SnS_x, Ag_2O, WO_x, Bi_2O_3, $ZnMn_2O_4$, $FeTiO_3$, or $LaVO_4$) into TiO_2 to form hybrid composite catalysts [12–16]. In addition, it is also proven that the modification of TiO_2 surface to obtain specifically functionalized TiO_2 can further enhance the catalytic performance [17]. Furthermore, the creation of high-energy exposed facets of TiO_2 to enhance the catalytic performance of TiO_2 materials was greatly focused [18–20]. Lately, it was further suggested that that TiO_2 materials with hierarchical structures may show improved catalytic performance. As it was demonstrated by previous reports [21,22], the hollow architectures possessed low density, high surface area, and good stability and permeability and can be used as microreactors with the confinement effects for gathering the reactants and making them closely contact with the catalyst during the catalytic reaction process, which may eventually improve the catalytic activity. To this aspect, hierarchical TiO_2 architectures constructed by unique individual building block are highly desired because of their more efficient light harvesting due to excellent incident light scattering within the structures, unique hierarchical characteristics, and high organic dye or pollutant adsorption [12,23–27].

In this paper, we developed a facile sol-impregnation method combined with a hydrothermal etching process to create hollow hybrid titanate/Au@TiO_2 hierarchical architecture composed of internal titanate and external anatase TiO_2 shells anchored with noble metal Au nanoparticles in the middle. The aim of such design is to hybridize the energy levels of titanate-Au-TiO_2 to improve the photocatalytic activity while endowing the hierarchical architecture hollow microreactor configuration to enhance photocatalytic performance. It is proven that the obtained hybrid titanate/Au@TiO_2 architecture shows significantly enhanced photocatalytic activity on degradation of methylorange (MO) under UV light irradiation in comparison with the commercial bench material of P25. The obtained hybrid titanate/Au@TiO_2 hierarchical architecture may find potential application in photocatalytic degradation of organic dyes.

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2. Experimental

2.1. Synthesis of SiO_2@TiO_2 spheres

Monodispersed SiO_2 spheres used as templates were synthesized by a Stöber sol–gel method according to the previous report [22]. The SiO_2 spheres (1 g) were dispersed into absolute ethanol (30 mL). After that, aminopropyl triethoxysilane (ATPES, 1 mL) was added and the solution was stirred at room temperature for 12 h to ensure the amino groups modified on the surface of SiO_2 spheres. The amino-modified SiO_2 spheres were collected by centrifugation and dried at 65 °C. Then to achieve the SiO_2@TiO_2 spheres, the amino-modified SiO_2 spheres (50 mg) were then dispersed in a mixed solvent containing 90 mL of ethanol and 30 mL of acetonitrile under ultrasonication. The suspension was mixed with 0.5 mL of ammonia solution at room temperature, and tetrabutyl titanate (TBOT, 1 mL) was added under stirring. After reacting for 3 h, the SiO_2@TiO_2 spheres were collected by centrifugation and washed with ethanol several times.

2.2. Synthesis of hollow titanate spheres

The SiO_2@TiO_2 sphere (0.5 g) were mixed with an aqueous NaOH solution (20 mL, 1.0 M) and stirred for 10 min, then placed in a 30 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 150 °C for 24 h and then allowed to cool to room temperature. The obtained products were then immersed in HCl aqueous solution (100 mL, 0.1 M) for 20 min and subsequently washed with deionized water until the solution reached the neutral pH, and then dried at 60 °C to achieve hollow titanate spheres.

2.3. Synthesis of SiO_2/Au and hollow titanate/Au spheres

$HAuCl_4$ solution (1 g/L, 12.6 mL) and polyvinyl alcohol solution (PVA, 1 wt%, 0.75 mL) were diluted to 100 mL with deionized water under vigorous stirring. After 30 min, $NaBH_4$ solution (0.1 mol/L, 1.5 mL) was injected into the above solution, and a dark orange-brown solution was obtained. After another 30 min, SiO_2-NH_2 or hollow titanate (0.2 g) was added immediately. After stirring for 12 h, the Au colloids were completely absorbed. The SiO_2/Au or hollow titanate/Au was collected by centrifugation and washed for several times with deionized water to completely remove the chloride ion.

2.4. Synthesis of hollow titanate/Au@TiO_2 and @Au/TiO_2 spheres

Hydroxypropyl cellulose (HPC, 400 mg) was dissolved in deionized water (30 mL) under ultrasonication. Then titanate/Au or SiO_2/Au (0.2 g) was added into the solution. After stirring for 12 h, the products were collected by centrifugation and washed with ethanol several times to obtain the HPC-modified hollow titanate/Au or SiO_2/Au. The obtained HPC-modified h-titanate/Au or SiO_2/Au was re-dispersed in mixed solvent of ethanol (95 mL) and H_2O (0.4 mL). The reaction mixture was stirred for 30 min and tetrabutyl titanate (TBOT, 2 mL) dissolved in ethanol (20 mL) was slowly added to using a syringe pump (0.5 mL min^{-1}). The solution was stirred for 100 min under reflux conditions. The hollow titanate/Au@TiO_2 or SiO_2/Au@TiO_2 was collected by centrifugation and washed with ethanol. The SiO_2 templates were further removed with NaOH to obtain @Au/TiO_2. In order to improve the photocatalyst crystallinity, the obtained @Au/TiO_2, SiO_2/Au@TiO_2, and hollow titanate/Au@TiO_2 were calcined at 500 °C for 2 h. The characterization and the photocatalytic test sections are supplemented in the supporting information.

3. Results and discussion

3.1. Synthetic process

The synthetic procedures for hybrid titanate/Au@TiO_2 hierarchical architecture involve several steps (Scheme 1). Uniform SiO_2 spheres were used as templates, and then a compact TiO_2 layer was deposited directly on the surface of SiO_2 spheres. The resulting SiO_2@TiO_2 spheres were hydrothermally etched in NaOH solution at 150 °C to remove the SiO_2 cores and achieve hollow titanate spheres. After that, Au nanoparticles were loaded on the surface of hollow titanate spheres to obtain hollow titanate/Au spheres. The hollow titanate/Au spheres were further coated with a TiO_2 layer to obtain the hybrid @titanate/Au@TiO_2 hierarchical architecture. For comparison, hollow @Au/TiO_2 microsphere without titanate shells was also prepared.

3.2. Phase structure

Fig. 1A comparatively shows the XRD diffraction patterns SiO_2/Au, SiO_2/Au@TiO_2 (calcined at 500 °C), @Au/TiO_2 (calcined at 500 °C), SiO_2@TiO_2, hollow titanate, hollow titanate/Au, and hollow titanate/Au@TiO_2 (calcined at 500 °C). It is revealed that the diffraction patterns for the obtained architectures can be well indexed, and their crystalline phase structure can be perfectly identified. As indicated Fig. 1A(a), the SiO_2/Au shows a board diffraction peak located at around 23° indexed to amorphous SiO_2, and a characteristic diffraction peak around 38.2° corresponding to Au nanoparticles (JCPDS no. 04-0784) is also observed, suggesting that Au nanoparticles are loaded on the SiO_2 surfaces. After coating a layer of TiO_2 and being calcined at 500 °C following the removal of SiO_2 with NaOH, the SiO_2/Au@TiO_2 and @Au/TiO_2 are obtained and their XRD patterns are shown in Fig. 1A(b and c). The diffraction peaks appeared at 25.4°, 37.8°, 48.1°, 54.0°, and 55.2° are assigned to the lattice planes of (101), (004), (200), (105), and (211) of anatase TiO_2 (JSPDS no. 89-4921), respectively, suggesting the formation of well-crystallized TiO_2 layer. To obtain the final hollow titanate/Au@TiO_2, the SiO_2@TiO_2 is first synthesized, as its XRD pattern is illustrated in Fig. 1A(d). The TiO_2 layer is coated via a sol–gel method without calcination; thus, the TiO_2 layer is amorphous and no diffraction peaks assigned to crystallize TiO_2 are observed. After hydrothermally etching the SiO_2@TiO_2, the hollow titanate is obtained, as its XRD pattern is shown in Fig. 1A(e). It is found that the XRD diffraction peaks located at 25.7°, 48.8°, and 63.2° are assigned to titanate [28], indicating that the hydrothermal etching treatment with NaOH can make the amorphous TiO_2 layer transform into titanate while removing the SiO_2 to form hollow titanate. After the loading of Au nanoparticle, the hollow titanate/Au shows the similar diffraction pattern as hollow titanate, as shown Fig. 1A(f), and no diffraction peaks attributed to Au is observed probably due to the low loading content and the well dispersion of small Au nanoparticles. After coating the final layer of TiO_2 and calcining at 500 °C, the titanate/Au@TiO_2 architecture is obtained, as its XRD pattern is shown in Fig. 1A(g). The diffraction peaks located at 25.4°, 37.8°, 48.1°, 55.2°, and 60.0° can be assigned to the lattice planes of (101), (004), (200), (105), and (211) of anatase TiO_2 (JSPDS no. 89-4921), respectively. The board diffraction peak located at 23° is indexed to amorphous SiO_2. The characteristic diffraction peaks corresponding to Au nanoparticles appeared at 38° (JCPDS no. 04-0784) illustrate that Au nanoparticles have been successfully loaded on the surface of SiO_2 spheres.

3.3. Surface area and porous structure

Fig. 1(B and C) shows the N_2 adsorption/desorption isotherms and the corresponding pore size distribution of hollow titanate, hollow titanate/Au, hollow titanate/Au@TiO_2 spheres, and P25. It is found that hollow titanate, hollow titanate/Au, and hollow titanate/Au@TiO_2 exhibit a type IV isotherm, indicating the mesoporous characteristics of the hollow spheres [29], in consistence with the TEM results shown