Applied Catalysis B: Environmental 156–157 (2014) 314–322

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Photocatalytic and antibacterial properties of Au-decorated Fe_3O_4@$mTiO_2$ core–shell microspheres

Cuiyan Li [a,c], Reza Younesi [a], Yanling Cai [b], Yihua Zhu [c], Mingguo Ma [d], Jiefang Zhu [a,*]

[a] Department of Chemistry - Ångström Laboratory, Uppsala University, Uppsala 75121, Sweden
[b] Division of Nanotechnology and Functional Materials, Ångström Laboratory, Uppsala University, Uppsala 75121, Sweden
[c] Key Laboratory for Ultrafine Materials of Ministry of Education, East China University of Science and Technology, Shanghai 200237, China
[d] Institute of Biomass Chemistry and Technology, College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China

ARTICLE INFO

Article history:
Received 17 January 2014
Received in revised form 4 March 2014
Accepted 11 March 2014
Available online 24 March 2014

Keywords:
Fe_3O_4 microsphere
Mesoporous TiO_2
Core–shell structure
Au nanoparticle
Photocatalysis
Antibacterial effect
Recycle

ABSTRACT

A facile approach for the fabrication of Au-decorated mesoporous Fe_3O_4@TiO_2 (Fe_3O_4@$mTiO_2$) core–shell microspheres is demonstrated. The protocol involved the coating of a successive layer of TiO_2 onto a magnetic Fe_3O_4 core *via* a *sol–gel* process, followed by TiO_2 crystallization and mesopore-formation by a hydrothermal treatment, and then the deposition of Au nanoparticles onto Fe_3O_4@$mTiO_2$ microspheres through an *in situ* reduction of perchloric acid. The mesoporous microspheres (Fe_3O_4@$mTiO_2$) showed stronger magnetic properties than the dense sample (Fe_3O_4@TiO_2) before the hydrothermal treatment. The size and loading amount of Au nanoparticles were controlled by the reduction temperature and concentration of Au salt, respectively. Compared to unmodified Fe_3O_4@$mTiO_2$ microspheres, Fe_3O_4@$mTiO_2$@Au microspheres showed higher photocatalytic activity for organic degradation and antibacterial action in water. These core–shell Fe_3O_4@$mTiO_2$@Au microspheres can serve as efficient and recyclable photocatalysts, which have promising applications in environmental treatment.

1. Introduction

During the past decades, photocatalytic degradation of organic pollutants in water by using semiconductor nanoparticles has attracted intense attention. Among various photocatalysts, titania (TiO_2) has been proven the most suitable for widespread environmental applications due to its high chemical stability, non-toxicity, and excellent degradation capacity [1,2]. However, on the basis of practicality, although monodispersed TiO_2 nanomaterials with high surface area and excellent photocatalytic activity have been successfully prepared [3–5], one of the major disadvantages for the application of such nanomaterials in water treatment is the inconvenience to recycle these photocatalysts due to their good dispersive properties. Conventional separation methods, including centrifugation and filtration, may lead to catalyst loss and energy consumption. Even though photocatalysts fixed on thin films allowing easy recovery have been successfully prepared [6–11], the activity of such photocatalysts is considerably reduced, because the effective surface area is significantly decreased.

In recent years, immobilizing catalysts onto magnetic nano- or microparticles has been adopted to solve the problem described above, as the catalysts can be easily collected from the solution with the help of an external magnetic field. There are two methods for immobilizing catalysts (e.g. TiO_2) onto magnetic nano- or microparticles (e.g. Fe_3O_4): indirect way and direct way. The indirect method has been developed to modify Fe_3O_4@TiO_2 microstructure with an intermediate layer (e.g. SiO_2), which is used as a barrier to avoid interactions between the magnetic core and the TiO_2 coating during calcination [12], while the superparamagnetic characteristic of the hybrid nanoparticles significantly decreased. In order to avoid this disadvantage, a direct way has also been adopted to directly deposit TiO_2 onto the magnetic cores. Xuan et al. have reported the fabrication of magnetically-separable photocatalysts with hollow nanostructures through a poly(styrene-acrylic acid) (PSA) template method at relatively low temperature [13], whereas, this method for preparing magnetic photocatalysts was relatively complicated. Therefore, the synthesis of magnetic photocatalysts has become a pressing need not only for fundamental interest but also for practical application.

It is well known that the wide band gap and low quantum yield of TiO_2 limit its practical applications [14]. Improvement of the photocatalytic activity of TiO_2 is an important task in heterogeneous photocatalysis. Noble metals, such as Au, Ag, Pt and Pd deposited

---

* Corresponding author. Tel.: +46 18 4713722; fax: +46 18 153548.
E-mail addresses: jiefang.zhu@kemi.uu.se, jiefangzhu@hotmail.com (J. Zhu).

http://dx.doi.org/10.1016/j.apcatb.2014.03.031
0926-3373/© 2014 Elsevier B.V. All rights reserved.

on TiO_2 can achieve this goal, which is mainly due to the noble metals promoting the interfacial charge transfer processes in the composites [9,15–19]. Au-loaded TiO_2 photoreaction systems can work for long hours, since Au deposits are relatively stable. Several representative methods have been reported on the introduction of Au nanoparticles on TiO_2 such as electrodeposition [20], UV photoreduction [21], and chemical reduction [18]. However, most of the conventional methods failed to offer uniform distribution of Au nanoparticles on TiO_2, and the incorporated Au nanoparticles were usually loosely attached to TiO_2.

Although immobilizing TiO_2 onto Fe_3O_4 has been reported, as well as the deposition of Au nanoparticles on surface of TiO_2 powder or film, few works have been carried out to combine Fe_3O_4, TiO_2 and Au to obtain a multifunctional photocatalyst [22,23]. The aim of this work is to prepare magnetically separable, recyclable, efficient photocatalysts through a simple method. The Fe_3O_4@TiO_2 microspheres with a core–shell structure were fabricated by a direct deposition of titania *via* a *sol–gel* process. The mesoporous TiO_2 ($mTiO_2$) shell was obtained by hydrothermally treating the as-synthesized Fe_3O_4@TiO_2 microspheres in a mixed ethanol/water solvent, using $NH_3{\cdot}H_2O$ as a porosity modifier. The anatase TiO_2 nanoparticles on Fe_3O_4 microspheres exhibited considerable photocatalytic activity, due to their large surface area and high crystallinity. Au nanoparticles, which were well dispersed on the Fe_3O_4@TiO_2 microspheres by *in situ* reduction of Au^{3+}, combined with TiO_2 to form Au–TiO_2 heterostructure that can improve the separation of photogenerated electron–hole pairs, and thus enhance the photocatalytic activity of the Fe_3O_4@$mTiO_2$ microspheres. These Fe_3O_4@$mTiO_2$@Au microspheres possess unique multicomponent structures and multifunctional features, which could also have their potentials in other catalytic applications (e.g. CO oxidation) [24].

2. Experiment

2.1. Chemicals and materials

All chemicals, including $FeCl_3{\cdot}6H_2O$, NH_4Ac, sodium citrate, ethylene glycol, ethanol, acetonitrile, $NH_3{\cdot}H_2O$, tetrabutylorthotitanate (TBOT), $HAuCl_4{\cdot}4H_2O$, lysine, $NaBH_4$ and methylene blue (MB), were analytical grade reagents, purchased from Sigma-Aldrich, and used without further purification.

2.2. Methods

2.2.1. Preparation of Fe_3O_4 microspheres

The magnetite colloidal nanocrystal clusters were prepared through a modified solvothermal reaction [25,26]. Typically, 1.350 g of $FeCl_3{\cdot}6H_2O$, 3.854 g of NH_4Ac, and 0.400 g of sodium citrate were dissolved in 70 mL of ethylene glycol. The mixture was stirred vigorously for 1 h at 170 °C to form a homogeneous black solution, and then transferred into a Teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated to 200 °C, and maintained for 16 h; then it was cooled to room temperature. The black product was washed with ethanol and collected with the help of a magnet. The cycle of washing and magnetic separation was repeated several times.

To investigate the stability of the Fe_3O_4 microspheres in polar solvents, which is important for evenly coating TiO_2 onto them in the next step, 5 mg of the as-prepared Fe_3O_4 microspheres was dispersed in 20 mL of deionized water and ethanol after ultra-sonic treatment, respectively. After 24 h, a majority of the black Fe_3O_4 microspheres were still suspended, indicating that these Fe_3O_4 microspheres have a good stability in water and ethanol, due to the stabilization by citrate on the microsphere surface.

2.2.2. Coating Fe_3O_4 microspheres by TiO_2 to obtain Fe_3O_4@TiO_2

The Fe_3O_4@TiO_2 core–shell microspheres were synthesized by directly coating a TiO_2 layer on the Fe_3O_4 in a mixed solvent of ethanol and acetonitrile by hydrolyzing TBOT in the presence of ammonia [27]. Briefly, 50 mg of the as-prepared Fe_3O_4 was dispersed in a mixed solvent containing 90 mL of ethanol and 30 mL of acetonitrile with the aid of ultrasound, and then 0.5 mL of $NH_3{\cdot}H_2O$ was added. Finally, 1 mL of TBOT was added to the above suspension under stirring. After 1.5 h reaction, the products were collected by magnetic separation and washed several times with ethanol and acetonitrile.

2.2.3. Hydrothermal treatment of Fe_3O_4@TiO_2 to obtain Fe_3O_4@$mTiO_2$

The mesoporous TiO_2 shells were achieved by a hydrothermal treatment of the obtained Fe_3O_4@TiO_2 microspheres in a mixed solvent of ethanol and deionized water, with $NH_3{\cdot}H_2O$ as a porosity modifier. Typically, 50 mg of the as-synthesized Fe_3O_4@TiO_2 microspheres was dispersed in 40 mL of ethanol and 20 mL of deionized water, and then a certain amount of $NH_3{\cdot}H_2O$ (1 mL, 2 mL, or 3 mL) was added to the above suspension. The mixture was then transferred to a Teflon-lined stainless-steel autoclave (100 mL capacity), which was heated to 160 °C and maintained for 20 h. Then the autoclave was cooled to room temperature, and the black product was collected with the help of a magnet, and washed with ethanol and water.

2.2.4. Loading Au nanoparticles to obtain Fe_3O_4@$mTiO_2$@Au

The deposition of Au nanoparticles onto Fe_3O_4@$mTiO_2$ was performed as follows. 20 mg of Fe_3O_4@$mTiO_2$ core–shell microspheres was dispersed into 5 mL deionized water by ultrasonication for 15 min, and followed by the addition of a certain amount (V) of 0.01 M $HAuCl_4$ (V is 1 mL, 2 mL, 3 mL, 4 mL, or 5 mL; the corresponding samples are denoted as Fe_3O_4@$mTiO_2$@Au_X mL or FTAX for short, where X presents the volume of $HAuCl_4$ solution used in preparation) and the double amount (2 V) of 0.01 M lysine solution. The dispersion was stirred for 30 min. 2 V amount of 0.1 M fresh $NaBH_4$ (excess) solution was added to reduce $HAuCl_4$ to Au nanoparticles, and then deionized water was added to make the total volume up to 30 mL. After the solution being stirred at a certain temperature (60 °C, 70 °C, 80 °C, or 90 °C) for 1 h, the precipitate was collected by magnetic separation, washed several times with deionized water and ethanol, dried at 70 °C, and calcined at 300 °C in air for 1 h to remove lysine.

2.3. Characterization

The crystal structure of samples was analyzed by an X-ray diffractometer (Bruker, D8 Advance Twin/Twin) with Cu Kα radiation ($\lambda = 1.54$ Å) at 45 kV and 40 mA. Transmission electron microscopy (TEM) micrographs were taken with a Tecnai F30 transmission electron microscope (FEI Company) using an accelerating voltage of 300 kV, which was equipped with an energy dispersive X-ray spectrometer (EDX) operated at 40 kV. For TEM observations, the sample powders were dispersed in ethanol by ultrasonic irradiation, and a drop of the suspension was placed onto a carbon-coated copper grid (Ted Pella, US). The deposit was dried in air prior to observation. In order to prove the core–shell structure of Fe_3O_4@TiO_2 composite, sample was analyzed by elemental mapping image analysis using electron energy loss spectroscopy (EELS). The XPS measurements were performed on a commercial PHI 5500 spectrometer, using monochromatic Al Kα radiation (1487 eV) and an electron emission angle of 45°. To reduce the effect of differential charging on samples, a flood gun was used during the measurements. All spectra were calibrated using the hydrocarbon peak