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Au–Pd/mesoporous Fe_2O_3: Highly active photocatalysts for the visible-light-driven degradation of acetone

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ABSTRACT

Three-dimensionally ordered mesoporous Fe_2O_3 (meso-Fe_2O_3) and its supported Au, Pd, and Au–Pd alloy (xAuPd$_y$/meso-Fe_2O_3; x = 0.08–0.72 wt.%; Pd/Au molar ratio (y) = 1.48–1.85) photocatalysts have been prepared *via* the KIT-6-templating and polyvinyl alcohol-protected reduction routes, respectively. Physical properties of the samples were characterized, and their photocatalytic activities were evaluated for the photocatalytic oxidation of acetone in the presence of a small amount of H_2O_2 under visible-light illumination. It was found that the meso-Fe_2O_3 was rhombohedral in crystal structure. The as-obtained samples displayed a high surface area of 111.0–140.8 m^2/g and a bandgap energy of 1.98–2.12 eV. The Au, Pd and/or Au–Pd alloy nanoparticles (NPs) with a size of 3–4 nm were uniformly dispersed on the surface of the meso-Fe_2O_3 support. The 0.72 wt.% AuPd$_{1.48}$/meso-Fe_2O_3 sample performed the best in the presence of 0.06 mol/L H_2O_2 aqueous solution, showing a 100% acetone conversion within 4 hr of visible-light illumination. It was concluded that the good performance of 0.72 wt.% AuPd$_{1.48}$/meso-Fe_2O_3 for photocatalytic acetone oxidation was associated with its ordered mesoporous structure, high adsorbed oxygen species concentration, plasmonic resonance effect between AuPd$_{1.48}$ NPs and meso-Fe_2O_3, and effective separation of the photogenerated charge carriers. In addition, the introduction of H_2O_2 and the involvement of the photo-Fenton process also played important roles in enhancing the photocatalytic activity of 0.72 wt.% AuPd$_{1.48}$/meso-Fe_2O_3.

Introduction

With industrialization and population growth, the environmental contamination induced by organic pollutants is becoming an overwhelming problem all over the world. Acetone is one of the most widely used organic solvents in industry, leading to serious water pollution. Wastewater containing acetone is a typical kind of wastewater emitted from electronics industries (Choi et al., 2013). Wastewater treatment requires novel techniques to degrade organics into small and non-toxic molecules. These techniques should be environmentally friendly and efficient enough to remove the organic pollutants completely. Photocatalytic oxidation is considered to be an effective pathway that is clean, non-hazardous, and environmentally benign, in which the key issue is the availability of high-efficiency photocatalysts. The photocatalytic purification of acetone-containing wastewater is an important pathway.

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Supported noble metal (Au, Pt, and Pd) catalysts are commonly used for photocatalytic degradation of organics. When the noble metals are loaded on the surface of a semiconductor, metal–semiconductor hetero-junctions are constructed. It was reported that a 0.5 wt.% Au–TiO_2 sample prepared by photodeposition showed excellent photocatalytic activity for phenol photodegradation (Hidalgo et al., 2011), which was due to the capacity of metallic gold to form a Schottky junction with TiO_2. Xue et al. (2015) pointed out that the a Au/p-g-C_3N_4 (p-type graphitic C_3N_4)/graphene hybrid structure could provide efficient light harvesting and effective separation and migration of photoinduced electrons, giving rise to a Methylene Blue (MB) degradation efficiency of 7.42 times higher than that over pure g-C_3N_4. In a study on the hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to *o*-chloroaniline (*o*-CAN) over 0.5 wt.% Pd/α-Fe_2O_3, Jiang et al. (2016) found that this catalyst showed a 100% *o*-CNB conversion and 91.4% *o*-CAN selectivity under the reaction conditions of 50°C, 2 hr, and 1 MPa hydrogen pressure.

It is well known that light irradiation can generate excited electron–hole pairs, which may migrate across the metal–semiconductor interfaces and result in the so-called Mott–Schottky effect. Photogenerated electrons migrate from the semiconductor with a higher Fermi energy to the metal with a lower Fermi energy until the energy level equilibrates, resulting in the effective separation of photoinduced electrons and holes. Also, the surface plasmon resonance (SPR) effect between the noble metal and the semiconductor can significantly improve the visible-light harvesting ability, facilitate the separation of photogenerated charge carriers, and synergistically contribute to the enhancement of photocatalytic activity. After investigating the preparation and characterization of Au–Pd/TiO_2 catalysts, Su et al. (2012) pointed out that the metal nanoparticles (NPs) could partially inhibit redox reactions and reduce the consumption of photogenerated radicals, thus improving the photocatalytic phenol degradation efficiency under ultraviolet (UV) irradiation; furthermore, the Au–Pd/TiO_2 photocatalyst showed stable activity with a phenol conversion of 90% in each cycle. Mizukoshi et al. (2010) fabricated the Au/Pd/TiO_2 catalyst *via* a sonochemical reduction route, and observed that this catalyst performed excellently for H_2 evolution from ethanol aqueous solution.

Hematite (α-Fe_2O_3) (Zhong et al., 2009) possesses a narrow bandgap energy (E_g = 2.20 eV) and can effectively absorb visible light. However, bulk α-Fe_2O_3 exhibits low surface area, high electron resistance, and a high charge recombination rate, thus limiting its applications. Ordered mesoporous materials offer an ideal support with high surface areas and large pore volumes (Castaño et al., 2009), favoring the improvement of catalytic activity. For example, the photocatalytic MB degradation efficiency increased in the order of α-Fe_2O_3 platelets (surface area = 1.98 m^2/g) < α-Fe_2O_3 NPs (surface area = 35.4 m^2/g) < porous α-Fe_2O_3 nanorods (surface area = 105.1 m^2/g) (Zhang et al., 2012), which was in good agreement with the surface area sequence.

Previously, our group prepared a number of mesoporous transition-metal oxides and their supported noble metal catalysts (*e.g.*, meso-CrO_x (Xia et al., 2009, 2010), Au/meso-Co_3O_4 (Liu et al., 2014), AuPd/meso-Co_3O_4 (Wu et al., 2015), and AuPd/meso-Cr_2O_3 (Wu et al., 2016)), investigated their catalytic performance for the oxidation of volatile organic compounds, and found that most of them performed well for the addressed reactions. To the best of our knowledge, there have so far been no reports in the literature on the preparation and photocatalytic applications of AuPd/mesoporous Fe_2O_3 (denoted as AuPd/meso-Fe_2O_3) for the degradation of acetone under visible-light illumination. Recently, we fabricated meso-Fe_2O_3 using three-dimensionally mesoporous silica (KIT-6) as a hard template, and adopted the polyvinyl alcohol (PVA)-protected reduction strategy to prepare the meso-Fe_2O_3-supported Au–Pd alloy NPs. In this work, we report the preparation and photocatalytic performance of AuPd/meso-Fe_2O_3 for acetone degradation under visible-light illumination. It was found that the loading of AuPd NPs significantly improved the photocatalytic acetone degradation activity under visible-light irradiation.

1. Experimental

1.1. Catalyst preparation

The meso-Fe_2O_3 was prepared using three-dimensionally ordered mesoporous silica (KIT-6) as a hard template and iron nitrate as the metal source. In a typical preparation, 1.0 g of KIT-6 powders was first dried in an oven at 100°C for 1 hr. Then, 2.0 g of $Fe(NO_3)_3·9H_2O$ was dissolved in 10 mL of ethanol. The dried KIT-6 powders were added to the Fe-containing ethanol solution and stirred at 60°C until dryness. The above mixture was placed in a crucible and calcined in a muffle furnace at a ramp of 1°C/min from room temperature (RT) to 350°C and kept at this temperature for 4 hr. The obtained red powders were leached twice with a hot NaOH aqueous solution (2.0 mol/L), followed by washing with deionized water and ethanol two times and drying at 60°C for 24 hr, thus obtaining the meso-Fe_2O_3 support.

The meso-Fe_2O_3-supported Au–Pd alloy samples were prepared *via* the PVA (10,000 g/mol)-protected reduction route with $NaBH_4$ as reducing agent. The typical preparation procedures were as follows: A desired amount of PVA (noble metal/PVA mass ratio = 1.0:1.5) was added to a 0.1 mol/L $HAuCl_4$ aqueous solution (Au/Pd molar ratio = 1.0:2.0) in an ice-bath under vigorous stirring for 10 min. Then, a certain amount of 0.1 mol/L $PdCl_2$ aqueous solution was added under stirring for 20 min, and a certain amount of 0.1 mol/L $NaBH_4$ aqueous solution (noble metal/$NaBH_4$ molar ratio = 1.5:1.0) was quickly added to the above noble metal- and PVA-containing aqueous solution, generating a dark brown noble metal solution. Finally, the desired amount of the meso-Fe_2O_3 support was added to the dark brown noble metal solution (theoretical Au–Pd loading = 0.1, 0.5, and 1.0 wt.%; theoretical Au/Pd mole ratio 1.0:2.0) under stirring for 6 hr. After that, the mixture was filtered, washed with deionized water, and dried at 80°C for 24 hr, thus obtaining the $xAuPd_y$/meso-Fe_2O_3 samples. The results of inductively coupled plasma atomic emission spectroscopic (ICP–AES) investigations revealed that the actual loading (*x*) of noble metals was 0.08, 0.37, and 0.72 wt.%; and the actual Pd/Au molar ratios (*y*) were 1.85, 1.57, and 1.48 in xAu_1Pd_2/meso-Fe_2O_3 (Table 1) respectively.

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