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Influence of Ag–Au microstructure on the photoelectrocatalytic performance of TiO_2 nanotube array photocatalysts

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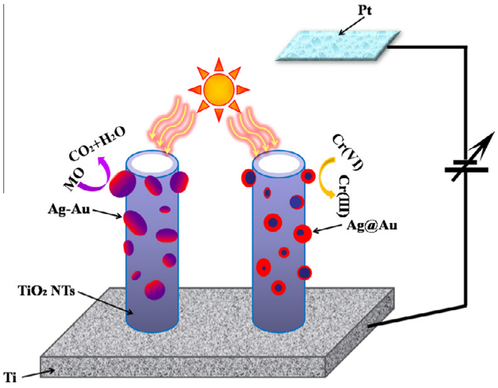
HIGHLIGHTS

- TiO_2 NTs/Ag–Au and TiO_2 NTs/Ag@Au were prepared by UV reduction and displacement reaction.
- Ag–Au alloy nanoparticles and Ag@Au core–shell nanoparticles grew on the walls of TiO_2 NTs.
- The plasmonic photocatalysts exhibited excellent photoelectrochemical properties.
- The TiO_2 NTs/Ag@Au showed higher photoelectrocatalytic removal of MO and Cr(VI).

GRAPHICAL ABSTRACT

The TiO_2 NTs/Ag–Au and TiO_2 NTs/Ag@Au were prepared by UV reduction and displacement reaction, respectively. Results indicated that the plasmonic photocatalysts exhibited excellent photoelectrocatalytic removal efficiency of MO dye molecule and Cr(VI) under solar illumination.



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ABSTRACT

In this work, vertically-aligned TiO_2 nanotube arrays (TiO_2 NTs) were grown on Ti substrates via a facile electrochemical anodization method followed by calcinations. Then, Ag–Au alloy nanoparticles and Ag@Au core–shell nanoparticles were deposited on the obtained TiO_2 NTs via UV reduction and displacement reaction, respectively. X-ray diffraction, scanning electron microscopy and transmission electron microscopy indicated that Ag–Au alloy nanoparticles and Ag@Au core–shell nanoparticles grew uniformly on the walls of TiO_2 NTs. Investigation results from removal of methyl orange (MO) and Cr(IV) ions indicated that the as-prepared bimetal plasmonic photocatalysts exhibited excellent photoelectrocatalytic (PEC) activities. The influences of Ag–Au alloy and core–shell microstructures on PEC properties of TiO_2 NTs were investigated and the TiO_2 NTs/Ag@Au photocatalyst showed more outstanding PEC removal efficiency than that of TiO_2 NTs/Ag–Au due to the regular core–shell microstructure and low recombination of photogenerated electrons and holes.

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1. Introduction

Recently, titania (TiO_2) has attracted immense attention because its unique physical and chemical properties make it suitable for the application in photocatalytic degradation of pollutants [1–3]. However, the low reusability and photogenerated electron utilization efficiency significantly limit the popularization of TiO_2 nanoparticles as photocatalysts [4]. Fortunately, self-organized TiO_2 nanotube array films show sustainability utilization and distinctive electronic properties of electron free transport along the axial direction [5]. Therefore, TiO_2 NTs are explored as outstanding photocatalysts to remove a wide range of pollutants, such as various dyes and heavy metal ions, as summarized in reported reviews [6,7]. Nevertheless, the intrinsic bandgap of TiO_2 (3.2 eV for anatase and 3.0 eV for rutile) limits their absorption in the ultraviolet region of solar spectrum. Moreover, the rapid recombination of photogenerated electrons and holes greatly lowers the PEC degradation efficiency.

Surface plasmon resonance (SPR) on noble metals, e.g. Ag and Au, has been successfully applied to photocatalysis under solar irradiation and it is proved to be a promising technique to enhance visible light response of TiO_2 NTs [8–10]. Consequently, when Ag, Au or their composite nanoparticles are deposited on TiO_2 NTs, photogenerated electrons could readily be excited under visible light irradiation, whereby SPR assisted photocatalytic reactions could significantly improve photocatalytic properties of TiO_2 NTs [11,12]. Our group investigated systematically photocatalytic performances of TiO_2 NTs/Ag photocatalysts prepared by a solvothermal method [13] and a successive ionic layer absorption and reaction method [14], and the sensitization of Ag nanoparticles greatly induced the photocatalytic decomposition of MO. However, the further improvement of photocatalytic activities of TiO_2 NTs was limited due to the weak visible light absorption. It has been shown that the incorporation of a second metal can effectively improve the photocatalytic performance of Ag-based plasmonic photocatalysts [15]. Investigations indicated the promising influences of bimetal Ag–Au compositions on photocatalytic activities of TiO_2 NTs, which caused immense attention of researchers to study the preparation methods of bimetal plasmonic photocatalysts. Compared with monometallic Ag nanoparticles, bimetallic Ag–Au nanoparticles particularly exhibit tunable SPR absorption by changing their compositions. In addition, a strong synergistic effect of Ag–Au nanoparticles facilates rapid transfer of photogenerated carriers, which reduces recombination chances of electron–hole pairs. Prof. Schmuki [16] prepared Ag and Au nanoparticles co-sensitized TiO_2 NTs by UV–light reduction followed by post-annealing treatment, and Ag–Au nanoparticles significantly enhanced the photocatalytic activity of self-organized TiO_2 NTs. Besides Ag–Au compositions, the microstructures such as Ag–Au alloy or core–shell structures also have significant influences on the photoelectrochemical performance. Despite the interest in the preparation and photocatalytic property of Ag–Au nanoparticles, there are only a few studies on the influences of Ag–Au nanoparticle microstructures on the PEC activity of TiO_2 NTs.

In this paper, Ag–Au alloy nanoparticles and Ag@Au core–shell nanoparticles with high PEC performances were successfully deposited on the surface of TiO_2 NTs using UV reduction and displacement reaction methods, respectively. The alloy and core–shell microstructures of Ag–Au nanoparticles on TiO_2 NT walls were confirmed, whereas the PEC properties were explored. TiO_2 NTs sensitized by Ag–Au alloy (TiO_2 NTs/Ag–Au) and Ag@Au core–shell (TiO_2 NTs/Ag@Au) could significantly enhance the photoabsorption and PEC activities compared with those of TiO_2 NTs alone under solar irradiation.

2. Experimental

2.1. Preparation of TiO_2 NTs sensitized by Ag–Au nanoparticles

2.1.1. Preparation of TiO_2 NTs sensitized by Ag–Au alloy nanoparticles

TiO_2 NTs were prepared by a two-step anodization method, which was similar with our previous reports [17–19]. TiO_2 NTs sensitized by Ag–Au alloys were prepared by a UV light reduction method [20]. In brief, TiO_2 NTs were soaked into 0.1 M $HAuCl_4{\cdot}3H_2O$ solution for 3 h, and the film was rinsed with distilled water and exposed subsequently to UV light illumination for 0.5 h. In addition, the TiO_2 NTs/Au were treated in 0.1 M $AgNO_3$ solution with the same progress to prepare TiO_2 NTs/Ag–Au.

2.1.2. Preparation of TiO_2 NTs sensitized by Ag@Au core–shell nanoparticles

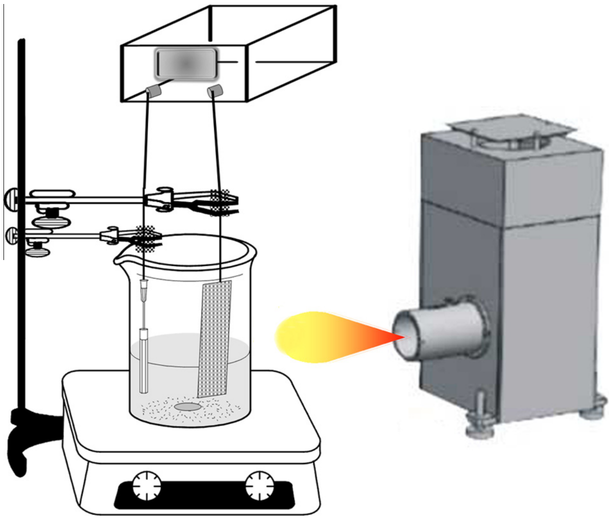
The TiO_2 NTs/Ag@Au photocatalyst was prepared by UV light reduction followed by metal displacement reaction. First, TiO_2 NTs/Ag were prepared by a UV light reduction method, and then immersed into 0.1 M $HAuCl_4{\cdot}3H_2O$ at 25 °C for 12 h. The film was taken out, washed with ethanol for several times and dried in room temperature for characterization

2.2. Characterization

The phase compositions of samples were determined by a Rigaku D/Max 2400 X-ray diffractometer (XRD) equipped with graphite monochromatized Cu Kα radiation. The morphologies of the prepared samples were observed using scanning electron microscopy (SEM, Quanta 200 FEG) at an accelerating voltage of 10 kV and transmission electron microscopy (TEM, Tecnai-F30) at an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) of samples were recorded on a UV-2550 UV–vis spectrophotometer with an integrating sphere attachment.

2.3. Photoelectrocatalytic activity test

The PEC degradation of MO was measured with a 500 W Xe lamp (CEL-S500) to provide solar light (AM 1.5). The geometry of PEC devices is shown in Scheme 1. The photocatalyst with an active area of 1.8 cm^2 was placed as the working electrode and a platinum electrode served as the counter electrode. 0.1 M K_2SO_4 solution



Scheme 1. Geometry of the reactor in the PEC test.