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Coupling immobilized TiO_2 nanobelts and Au nanoparticles for enhanced photocatalytic and photoelectrocatalytic activity and mechanism insights

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HIGHLIGHTS

- The immobilized TiO_2 nanobelts and Au nanoparticles were coupled.
- This material showed high photocatalytic and photoelectrocatalytic activity.
- The introduction of Au nanoparticles facilitates the direct utilization of holes.

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ABSTRACT

A visible light responsive nanocomposite was prepared by depositing Au nanoparticles on the surface of immobilized anatase TiO_2 nanobelts (TiO_2 NBs/Au NPs). The designed materials were characterized by field-emission scanning electron microscopy, transmission electron microscopy, X-ray diffraction, diffuse reflectance UV–vis spectroscopy and photoluminescence spectra. The photoelectric properties were investigated by photoelectrochemical measurement. The results reveal that the Au NPs with diameter of 5–15 nm were uniformly deposited on the surface of TiO_2 NBs. Compared to bare TiO_2 NBs, a stronger visible light absorption and a higher photoelectrochemical response were achieved over TiO_2 NBs/Au NPs. The TiO_2 NBs/Au NPs nanocomposites exhibit higher photocatalytic activity than TiO_2 NBs under irradiation of simulated solar light and visible light, respectively. Moreover, the prepared photocatalyst exhibits its super reusability. The possible radical species involved in the degradation of Tetrabromobisphenol A (TBBPA) were analyzed by active species trapping. It is indicated that the degradation of TBBPA was primarily driven by hydroxyl radicals and holes. Meanwhile, it is interesting to find that the modification of Au NPs can contribute to enhancement of the direct utilization of photoexcited holes. The possible intermediates or products were identified by LC–MS, and the tentative degradation pathways of TBBPA were proposed. It is hoped that our work could offer valuable information on the design of efficient, recyclable and visible light responsive photocatalyst.

1. Introduction

TiO_2 has been regarded as one of the most promising semiconductors in the field of environmental pollution control and solar energy transformation because of its intriguing optical and electric properties, physical and chemical stability, nontoxicity, low cost, and ease availability [1–4]. Nevertheless, the low quantum efficiency for photocatalytic (PC) reactions results from the fast recombination of photogenerated electron–hole limits its applications to great extent. It is well known that the quantum efficiency of photocatalysts heavily relies on its microstructure [5,6], thereby, endeavors have been devoted to engineer novel TiO_2 photocatalysts, such as nanowires [7], nanotubes [8], nanorods [9], nanoparticles [10], which showed better separation of charge carriers and improvement in the PC degradation of pollutants. Therefore, it is important to fundamentally optimize the morphology of TiO_2 nanomaterials for effective separation and transportation of photoexcited charge carriers.

Another promising route to enhance the PC performance of TiO_2 photocatalysts is to decorate with noble metal nanoparticles (NPs) such as Ag, Au, Pt, and Pd [11–13]. Particularly, modification of TiO_2 with metallic Au has received much attention because of its unique catalytic and optical properties [14,15]. It has been shown

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that the loading of Au NPs can effectively shift the Fermi level to more negative potentials, resulting in the decrease of potential difference between the conduction band of TiO_2 and the Fermi level of Au NPs [16–18]. Consequently, the photogenerated electrons quickly transfer from TiO_2 surface to the Au NPs, which improves the electron–hole effective separation. Moreover, Au NPs can respond in the visible region based on surface plasmon resonance (SPR) result from the collective oscillations of the valence electrons, which can extend the absorption range of TiO_2 photocatalysts to visible light [19,20]. On the other hand, Au NPs-loaded TiO_2 photocatalysts were found to be advantageous as compared with other photosensitization systems using metal complexes or organic dyes [21].

However, in previous studies, the TiO_2 photocatalysts were usually used in the powdered form. Although photocatalysis is efficient, the large cost of separating TiO_2 powder from suspension is a major drawback that hinders the practical application of these PC processes in treating contaminants. The immobilized TiO_2 nanophotocatalysts provide an advantage over the drawback encountered with powder suspensions [6,22]. Thereby, recently, our group has prepared immobilized TiO_2 nanobelts (NBs) by a simple synthesis method [23], which exhibit convenient transfer of photogenerated charge carriers. The experiment results showed that as-prepared TiO_2 NBs are able to significantly enhance the PC and photoelectrocatalytic (PEC) properties compared with immobilized TiO_2 nanotubes which were studied extensively in previous researches [6]. Thus, to further improve the PC performance of TiO_2 NBs, combining Au NPs and TiO_2 NBs is expected to be worthy of intriguing exploration.

Herein, the TiO_2 NBs decorated by Au NPs (TiO_2 NBs/Au NPs) have been synthesized via electrochemical deposition. The morphology of TiO_2 NBs/Au NPs was characterized by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The variations in the optical response before and after Au NPs modification was also investigated by UV–vis diffuse reflectance spectroscopy (UV–vis DRS) and photoluminescence (PL) spectra technologies. Moreover, the evolution of photocurrent (I_{ph}) and open-circle voltage (V_{oc}) response was measured through photoelectrochemical (PECH) experiments. Tetrabromobisphenol A (TBBPA), one of the most important brominated flame retardants, was chose as the probe reactant molecule to evaluate the PC and PEC activity of TiO_2 NBs/Au NPs. The reasons for the improvement of PC performance are also discussed in detail. Furthermore, the possible radical species involved in the degradation of TBBPA were analyzed by means of adding the corresponding scavengers, and the products and degradation pathway in such a system were proposed. We have also evaluated the reusability of the TiO_2 NBs/Au NPs. To our knowledge, immobilized TiO_2 NBs decorated by Au NPs for PC degradation of TBBPA have not been reported.

2. Experimental

2.1. Preparation

TiO_2 NBs were synthesized following a procedure proposed in our previous literature [6]. Typically, pure titanium sheets (10 mm × 90 mm × 0.5 mm, 99.8% purity) were ultrasonically cleaned in alcohol and acetone for 30 min before anodization. Then these sheets were chemically polished in a mixed acid ($HF:HNO_3:H_2O = 1:4:5$/vol) for 30 s to form a fresh metal surface, followed by a deionized water rinse and drying in air at 105 °C.

The potentiostatic anodization was carried out in a standard two-electrode electrochemical cell with titanium foil as a working electrode and platinum foil as a counter electrode. The electrolyte was ethylene glycol containing ammonium fluoride (NH_4F, 0.5 wt%) and water (5 vol%). All the anodization experiments were performed at 60 V and 25 °C for 3 h. After that, the as-anodized TiO_2 NBs samples were rinsed with deionized water and dried in air at 105 °C, then sintered in air at 550 °C for 2 h.

Au NPs were electrodeposited on a TiO_2 NBs electrode at −0.2 V (vs SCE) for 10 s in a 0.05 M Na_2SO_4 aqueous solution containing 0.1 mM $HAuCl_4$. The TiO_2 NBs electrode, platinum foil and saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode, respectively.

2.2. Materials characterization

The surface morphology of TiO_2 NBs/Au NPs and distribution of Au nanoparticles were characterized by FESEM (America QUANTA200F). TEM and high-resolution transmission electron microscopy (HRTEM) images were obtained on Tecnai F-30ST at an accelerating voltage of 300 kV coupled with an energy-dispersive X-ray (EDX) spectrometer. The crystal structure of synthesized samples was investigated by X-ray diffraction (XRD, Rigaku D/max-rb, Cu Kα, $\lambda = 1.5418$ Å). The accelerating voltage and applied current were 40 kV and 50 mA, respectively. UV–vis diffused reflectance spectra were obtained on a UV–vis spectrophotometer (UV2550, Shimadzu, Japan). PL spectra were recorded at room temperature using an FP-6500 Fluorescence Spectrophotometer (JASCO, Japan) with excitation wavelength of 570 nm.

2.3. PECH measurements

The I_{ph} and V_{oc} response were measured by a electrochemical workstation (AUTOLAB PGSTAT128 N, Metrohm) in a standard three-electrode system using a TiO_2 NBs/Au NPs electrode with an active area of 4 cm^2 as the working electrode, a Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Na_2SO_4 solution (0.5 mol L^{-1}) was used as the supporting electrolyte. A 35 W HID Xenon light (Philips) was employed as the exciting light source for simulated solar light irradiation, and which was filtered by an ultraviolet cutoff filter to provide visible light source ($\lambda > 400$ nm).

2.4. PC and PEC activity

The PC and PEC activity of TiO_2 NBs/Au NPs were evaluated by the degradation of TBBPA aqueous solution (5 mg L^{-1}, 35 ml). Prior to irradiation, the degradation cell was kept in dark for 30 min under stirring to obtain adsorption–desorption equilibrium. The TBBPA solution was collected at 20 min intervals for analysis. A constant potential of 1.5 V was applied for the PEC degradation of TBBPA with TiO_2 NBs/Au NPs as the anode and Pt foil as the cathode. The light source was identical with that used in the measurement of PECH performance. All experiments were performed at ambient temperature and pressure.

The concentration of TBBPA was determined by a High Performance Liquid Chromatograph (HPLC, Shimadzu LC-10A) equipped with a UV detector. The column was ZORBAX SB-C18 (4.6 mm × 150 mm, 5 μm) thermostatted at 30 °C. The mixture of methanol/water (80:20, v/v) was used as mobile phase at a flow rate of 1.0 mL/min. The ultraviolet absorbance was detected at 210 nm.

The degradation intermediates were analyzed by liquid chromatography/mass spectrometry (LC/MS, Finigan LCQ DEXP MAX) equipped with an electrospray ionization source that operated in positive and negative modes. Full scale MS spectra with a scan range m/z 50–700 were recorded. The mobile phase and flow rate was methanol/water = 80:20 and 0.3 mL min^{-1}, respectively. The