



Structure, morphology and photocatalytic activity of Cu₂O/Pt/TiO₂ three-layered nanocomposite films



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ABSTRACT

Novel Cu₂O/Pt/TiO₂ three-layered nanocomposite films were prepared by deposition on glass substrates using the magnetron sputtering method. Their structure, surface morphology as well as optical and photocatalytic properties were examined by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, UV–visible spectroscopy, and photoluminescence spectroscopy. As a comparison, Cu₂O/TiO₂ double-layer films were also investigated. The results show that Cu₂O/TiO₂ double-layer films have relatively smooth surfaces with agglomerated Cu₂O particle, whereas the surface layer of the Cu₂O/Pt/TiO₂ three-layered nanocomposite films was composed of fine nano-sized columnar Cu₂O and they had a rough surface morphology due to the insertion of the Pt layer. The photocatalytic activity of the three-layered films is significantly higher than that of the Cu₂O/TiO₂ double-layered composite films. Such enhancement is closely related to the presence of the Pt layer and the rough surface, which was composed of fine nano-sized Cu₂O columns; this increases the utilization of visible light as well as promotes the transfer of interfacial charge and the separation of photogenerated electron–holes.

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1. Introduction

The photocatalytic degradation of organic pollutants based on wide band gap semiconductors has attracted considerable attention during the past decades due to this method's capability to simultaneously harvest solar energy and drive chemical reactions via photo-excited charge carriers and activated electronic states [1,2]. Generally, the photo-catalysts are in powder form and placed in solutions that need remediation, which inevitably results in some disadvantages, such as difficult recovery, facile cohesion, low utilization rates, and secondary pollution [3]. In practice, the photocatalytic film is indeed more viable, and film-based

photocatalytic degradation has been rapidly developed in recent years.

TiO₂ has become the most promising photocatalytic material due to its chemical–physical stability, thermal properties, electrical properties, low cost, and excellent ability to degrade organic pollutants [4–6]. The photocatalytic effect on the degradation of organic compounds can be explained by the presence of electron–holes in the semiconducting material. However, due to the wide band gap, TiO₂ only absorbs in the near-UV region, which is only a small portion of the solar spectrum [7,8]. Due to this limitation, the development of photocatalysts that can be excited in the visible range is of great interest in order to further improve photocatalytic processes that use solar radiation for the degradation of organic pollutants [9,10]. Meanwhile, the significant recombination of the photogenerated electrons and holes is also a major

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obstacle inhibiting further increase in TiO₂ photocatalytic activity [11].

TiO₂ composited with other semiconducting materials with lower band gaps that can respond to visible light is one possible way to fix these issues. Recombination semiconductors can also increase the lifetime of charge carriers and the interfacial electron-transfer rate constant, which can improve the photoconversion efficiency for photocatalysis [12]. Cuprous oxide (Cu₂O), an important p-type semiconductor with a direct band gap of 2.0 eV, has attracted extensive attention for its applications in solar energy conversion, gas sensors, electronics, magnetic storage, etc. [13]. Recently, Cu₂O has been used as a visible-light-driven photocatalyst for splitting water and degrading organic contaminants [14–16]. However, pure Cu₂O has relatively low catalytic activity due to its faster recombination rate between the electron and hole. Thus, photocatalysts made of TiO₂ and Cu₂O composites have many potential applications [17–19]. When Cu₂O and TiO₂ nanoparticles are coupled together to yield nanocomposite oxides, efficient electron transfer from Cu₂O to TiO₂ in the nanocomposite occurs under visible-light irradiation [20].

In addition, the surface modification of TiO₂ may be achieved with noble metals [21]. Previous results have shown that noble metals can inhibit the charge recombination of photo-generated electron-hole pairs thereby enhancing the charge carrier density reaching the TiO₂/liquid interface and alter the surface work function of the catalyst [22–24]. Platinum is an important noble metal. Previous investigations confirmed that modified TiO₂ films with platinum were a promising way for preventing the recombination of the electron-hole pairs, and this led to improved photodegradation rates for various organic compounds under visible light irradiation [25].

To the best of our knowledge, a metal combined with two semiconductors that is to be utilized as a photocatalyst has very rarely been reported. Photocatalytic films for this application indeed are more viable due to their easy separation recovery and a simple post-treatment process. In this work, Cu₂O/Pt/TiO₂ three-layered nanocomposite films with rough surfaces composed of fine nano-sized Cu₂O columns were prepared by magnetron sputtering. The influences of the Pt metal layer on the structure, surface morphology, optical properties and photocatalytic activities of these three-layered composite films were investigated and discussed. It has been shown that the optical absorption property and the photocatalytic activities of the three-layered composite films are significantly higher than those of the Cu₂O/TiO₂ double-layered composite films.

2. Experimental procedures

2.1. Preparation of films

The Cu₂O/Pt/TiO₂ three-layered composite films were prepared by magnetron sputtering. Prior to deposition, the glass substrates (6 × 6 cm²) were ultrasonically cleaned with acetone, absolute ethyl alcohol, and de-ionized water for 10 min. TiO₂ single films were deposited on glass substrates by a high vacuum multifunctional magnetron

sputtering equipment (JGP560I, Shenyang Scientific Instrument Co., China) using TiO₂ ceramic targets at room temperature. During sputtering, the argon gas flow rate was kept at 30 sccm, the chamber pressure was maintained at 4.3 Pa, and the sputtering power was 100 W. After deposition the films were annealed at 500 °C for 2 h in an ambient atmosphere so as to form the anatase phase of TiO₂. Cu was deposited onto the anatase-TiO₂ films and annealed in an ambient atmosphere at 200 °C for 2 h to form Cu₂O/TiO₂ double-layered composite films. Cu₂O/Pt/TiO₂ three-layered composite films were prepared by depositing Pt and Cu onto the anatase-TiO₂ films in sequence, followed by annealing at 200 °C for 2 h in an ambient atmosphere. The reactive DC power for both the Pt and Cu targets were 100 W. During sputtering, the argon gas flow rate was kept at 30 sccm, and the chamber pressure was maintained at 6 Pa for Cu and 4.3 Pa for Pt. The thickness of the films was measured with a scanning electron microscope (JSM-6700F), and the corresponding deposition rates of the TiO₂, Pt, and Cu films were then calculated to be about 10, 12, and 16 nm/min, respectively. In the three-layered structure, the thicknesses of the TiO₂ and Cu₂O layers were 100 nm and 90 nm, respectively, while the intermediate Pt layer was about 10 nm. For comparison, TiO₂ (100 nm) single films, Pt (10 nm) single films, and TiO₂ (100 nm)/Cu₂O (90 nm) double-layered composite films were also investigated.

2.2. Film characterization

The crystal structures of the films were analyzed with the Cu K α line from a Rigaku D/max 2500 X-ray diffractometer (XRD) with patterns recorded in a range of 20–80° (2 θ). The Raman spectra were collected on a laser micro-Raman spectrometer (Renishaw inVia) at a wavelength of 514 nm at room temperature. A scanning electron microscope (SEM) (JSM-6700F) operated at 10 kV was employed to investigate the morphologies of the films. Optical absorption of the composite films in the wavelength range of 300–800 nm was measured using a UV/vis spectrophotometer (Perkin-Elmer Lambda 750). The photoluminescence emission spectra of the samples were measured at room temperature with a Cary Eclipse Fluorescence Spectrophotometer (VARIAN). The binding energy was determined by X-ray photoelectron spectroscopy (XPS) (Escalab250).

2.3. Photocatalytic properties

The photocatalytic activities of samples were evaluated by measuring the degradation rates of methylene blue (MB) in aqueous solution under visible light irradiation. The test samples were added to 10 ml MB aqueous solutions with concentrations of 5 mg/L in cylindrical glass reactors. Before the photocatalytic reaction, the solution was magnetically stirred in dark for 2 h to achieve an adsorption-desorption equilibrium among the photocatalyst, MB, and water. The photocatalytic reactions were carried out at room temperature, using a 300 W tungsten lamp (Philips Halogen) to simulate visible light. The degradation of MB was monitored from the intensity of

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