Rare Metal Materials and Engineering
Volume 44, Issue 8, August 2015
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2015, 44(8): 1888-1893.

ARTICLE

Optical and Photocatalytic Properties of Cu-Cu_2O/TiO_2 Two-Layer Nanocomposite Films on Si Substrates

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Abstract: This paper introduced a process to prepare novel Cu-Cu_2O/TiO_2 two-layer nanocomposite films with Cu-Cu_2O mixture layers grown on TiO_2 films prepared by a magnetron sputtering method. The structure, the morphology and optical properties of the films were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), fluorescence spectroscopy (PL), X-ray photoelectron spectroscopy (XPS) and UV-vis diffuse reflectance spectroscopy (DRS). XRD patterns indicate that the Cu-Cu_2O mixture layer does not change the crystalline phase of TiO_2. XPS results show that the presence of Cu restrains the oxidation of Cu_2O surface for Cu-Cu_2O/TiO_2 layer. SEM analysis reveals that the well crystallized Cu-Cu_2O mixture nanoparticles are dispersed uniformly on the surface of TiO_2. Owing to UV-vis diffuse reflectance spectroscopy, an red shift of the extended absorption edge of Cu-Cu_2O/TiO_2 takes place. PL spectra confirm the presence of Cu which reduces the recombination rate of exited electron-hole. Photocatalytic experiments demonstrate that compared with pure Cu_2O/TiO_2, the as-prepared Cu-Cu_2O/TiO_2-8 shows greater efficiency in photogenerated carriers and a significantly improved photocatalytic performance. In addition the reason for improvement in photocatalytic activity of the Cu-Cu_2O/TiO_2-8 films was also discussed.

Key words: Cu-Cu_2O/TiO_2; Si; nanocomposite films; photocatalytic properties

TiO_2-based nanocomposites have received great attention because of their chemical stability, high refractive index, high dielectric constant, enhanced nonlinear optical property, and potential application in photocatalysis for the degradation of organic pollutants in air and water [1-4]. However, the photocatalytic efficiency of TiO_2 is limited by the high recombination rate of electron-hole pairs and by the weak absorption capability in visible range. Some approaches have been used to reduce the recombination of photogenerated electrons-holes and to extend the light absorption to the visible region [5]. In photocatalytic systems, coupled TiO_2 with other semiconductors was designed to extend the absorption wavelength range to the visible light region and to alleviate the charge carrier recombination. When the wide band gap of TiO_2 is coupled with a small band gap semiconductor having more negative conduction band level, the electron can be injected from the small band gap semiconductor to TiO_2. Combining Cu_2O with TiO_2 represents a promising way because the absorption of visible light is enhanced and the separation of the electrons-holes is ensured[6, 7].

Cuprous oxide (Cu_2O) is a p-type semiconductor with a direct band gap of 2.0 eV, which offers it the important applications in hydrogen production, superconductor, solar cell, and negative electrode materials[8,9]. Owing to the quantum size effects, Cu_2O nanoparticles show many particular optical, electrical and photo-electrochemical properties. It is demonstrated to be a promising photocatalyst in direct water splitting and organic contamination degradation under visible-light irradiation.

Received date: August 12, 2014
Foundation item: The Science and Technology Project of Shanxi Province (20130313003-2)

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Nevertheless, the application of Cu_2O as a photocatalyst is very limited due to its fast recombination of charge carriers and easiness to be oxidized. In order to solve this problem, the construction of Cu_2O complex with noble metal, other semiconductors or conductive materials would be a good way [10]. It has been proved that metal/semiconductor is an effective way to improve the separation of photo-generated electron-hole pairs and promote interfacial charge-transfer processes, which can enhance the photocatalytic efficiency[11, 12]. For the metal nanoparticles can capture the transferred electrons onto the surface of the semiconductor, and will be scavenged by the electron accepter, commonly the oxygen is absorbed on the surface [13]. Therefore, more photo-induced holes will get the opportunity to escape from the geminate recombination of electron-hole pairs and to participate in the following oxidation reactions which will result in the enhanced catalytic efficiencies. Copper is a potential substitute for noble metals due to its high activity towards pollutant-destroying reactions [14]. Lately, Cu_2O/Cu nanocomposites systems have also been reported to exhibit higher photocatalytic activity compared to the pure-phase Cu_2O in the visible range of the spectrum, with the interfaces between Cu and Cu_2O acting as the sites where rapid separation of photogenerated electrons and holes occurs [15].

Metal and oxide recombination semiconductor has rarely been reported up to now. In this paper, the Cu-Cu_2O/TiO_2 two-layer film were firstly prepared by a magnetron sputtering method. Here, the surface of TiO_2 thin films was modified by Cu-Cu_2O nanoparticles. The structure, the surface morphology, the optical and photocatalytic properties of the Cu-Cu_2O/TiO_2 nanostructured two-layer films were investigated. Our experimental results clearly gave the evidence that Cu plays an important role in tuning the photocatalytic activity of the Cu-Cu_2O/TiO_2 thin films. The Cu metal nanoparticles can act as electron sinks allowing a more efficient separation of the charges, assisting the electron to transfer to oxygen or other electron acceptors and thus preventing electron–hole recombination to a higher degree.

1 Experiment

The Cu-Cu_2O/TiO_2 films were prepared by magnetron sputtering technique. Prior to deposition, the glass substrates (2 cm×6 cm) were ultrasonically cleaned with acetone, absolute ethyl alcohol, and de-ionized water for 10 min. TiO_2 films were deposited on the Si substrates of 300 °C by a high vacuum multifunctional magnetron sputtering equipment (JGP560I) using Ti metallic targets. During the sputtering, reactive gases and sputtering gases were Ar and O_2, and they were kept constant values of 6 and 24 mL/min, respectively. The chamber pressure was maintained at 4 Pa and the sputtering power was 100 W. And then, Cu_2O and Cu-Cu_2O films were deposited on TiO_2 films to form Cu_2O/TiO_2 and Cu-Cu_2O/TiO_2 two-layer films. During the deposition, the reactive DC power for Cu target was 100 W and the flow rate of Ar was 16 mL/min. Pure argon was used as sputter gas and oxygen as reactive gas. The flow rates of both argon and oxygen gases were controlled individually. Cu_2O films were deposited at 12 mL/min flow rate of oxygen gases. The film samples were denoted by Cu-Cu_2O/TiO_2-x, where x (x=5, 8) represents flow rate of oxygen gases (in unit of mL/min) in the Cu deposition. The thickness of the films was measured by scanning electron microscope, and the corresponding deposition rate of TiO_2, Cu-Cu_2O and Cu_2O films were then calculated at about 16, 22 and 22 nm/min. In Cu-Cu_2O/TiO_2 two-layer films, the thicknesses of TiO_2 and Cu-Cu_2O layers were 100 nm and 100 nm. For comparison, TiO_2 (100 nm) thin films and Cu_2O (100 nm)/TiO_2 (100 nm) thin films were also investigated.

The crystal structures of the films were analyzed with Cu Kα line from a Rigaku D /max 2500 X-ray diffractometer (XRD) with patterns recorded in a range of 20°~80° (2θ). Scanning electron microscope (SEM) (JSM-6700F) operating at 10 kV was employed to investigate the morphologies of the films. Optical absorption of the thin films in the wavelength ranging from 300~800 nm was measured by a UV/Vis spectrophotometer (Perkin Elmer Lambda 750). The binding energy was identified by X-ray photoelectron spectroscope (XPS) (Escalab250). The photoluminescence emission spectra of the samples were measured at room temperature by Cary Eclipse Fluorescence Spectrophotometer (VARIAN).

The photocatalytic activities of samples were evaluated by measuring the degradation rates of the methyl orange (MO) molecule in aqueous solution under visible light irradiation. The samples were settled into a 10 mL MO aqueous solution with a concentration of 8 mg/L in a cylindrical glass reactor. Before the photocatalytic reaction, the solution was magnetically stirred in the dark for 2 h to achieve the adsorption-desorption equilibrium among the photocatalyst, MO, and water. The photocatalytic reactions were carried out at room temperature, using a 300 W tungsten lamp (Philips Halogen) to simulate the visible light source. The degradation of MO was monitored from the intensity of absorption peak of MO (460 nm) relative to its initial intensity using a Perkin Elmer Lambda 750 UV/Vis Spectrometer under various illumination time.

2 Results and Discussion

Fig.1 shows XRD patterns of TiO_2, Cu_2O/TiO_2, Cu-Cu_2O/TiO_2-8, and Cu-Cu_2O/TiO_2-5 films. It is observed that TiO_2 thin films exhibit diffraction peaks (101), (004), (200), (105), and (211) of the anatase-TiO_2 (JCPDS 78-2846) which demonstrates that the anatase-TiO_2