

TiO₂ Film/Cu₂O Microgrid Heterojunction with Photocatalytic Activity under Solar Light Irradiation

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ABSTRACT Coupling a narrow-band-gap semiconductor with TiO₂ is an effective method to produce photocatalysts that work under UV–vis light irradiation. Usually photocatalytic coupled-semiconductors exist mainly as powders, and photocatalytic activity is only favored when a small loading amount of narrow-band-gap semiconductor is used. Here we propose a heavy-loading photocatalyst configuration in which 51 % of the surface of the TiO₂ film is covered by a Cu₂O microgrid. The coupled system shows higher photocatalytic activity under solar light irradiation than TiO₂ and Cu₂O films. This improved performance is due to the efficient charge transfer between the two phases and the similar opportunity each has to be exposed to irradiation and adsorbates.

KEYWORDS: photocatalysis • heterojunction • microgrid

INTRODUCTION

Photocatalysis has been widely used in environmental protection and energy conversion because organic pollutants can be decomposed completely and water can be split into oxygen and hydrogen by photocatalytically active semiconductors under light irradiation (1, 2). Currently, TiO₂ is the most popular semiconductor used in the heterogeneous photocatalysis processes. In general, researchers concentrate on two aspects to improve the performance of the photocatalysts: improving the photocatalytic efficiency and extending the absorption edge of the semiconductors from UV to visible light, i.e., increasing the absorption of solar light (3, 4).

Modifying the TiO₂ catalyst is an effective way to capture a greater portion of the solar spectrum. A promising method is to couple wide-band-gap TiO₂ with a narrow-band-gap semiconductor possessing a less anodic conduction band than that of TiO₂ (5). If the narrow-band-gap semiconductor is irradiated by visible light, electrons will be injected from the activated semiconductor into the inactivated one, while holes remain on the activated semiconductor. If both semiconductors are simultaneously activated using UV–vis irradiation, a vectorial transfer of electrons and holes from one semiconductor to another will occur: electrons will accumulate at the lower-lying conduction band of one semiconductor, while the holes will accumulate at the valence band of the other (5, 6).

The reported photocatalytic coupled-semiconductors exist mainly as a powder system, in which narrow-band-gap semiconductor particles were deposited on the surface of wide-band-gap semiconductor particles (7–10). Some wide-band-gap semiconductor particles cannot contact the narrow-band-gap semiconductor particles, causing photogenerated charges to accumulate if charges cannot be transferred to adsorbates in time. These accumulated electrons (or holes) will attract holes (or electrons) and become recombination centers, thus lowering the activity of the photocatalysts. Furthermore, the accumulated holes have a tendency to induce photocorrosion of the unstable semiconductors (11). As a result, the maximum loading amount of the second semiconductors, such as CdS (12), Bi₂S₃ (9), and Cu₂O (13), on TiO₂ is only about 10 % down to less than 1 %. Too large a loading amount will result in deteriorated photocatalytic activity. Because the narrow-band-gap semiconductor acts as the main absorber of visible light, the coupled system with a small loading amount cannot achieve high photocatalytic activity under solar light irradiation.

If TiO₂ and Cu₂O are coated on the substrate layer by layer to form a TiO₂ film/Cu₂O film heterostructure, charge transfer will happen among tens of particles because the depletion width in the films reaches more than 100 nm (14, 15). However, in the layer-by-layer films, photoinduced molecular transformations or reactions will take place mainly on the sample surface so that the underlying film loses the opportunity to contact the adsorbed molecules, thus resulting in the accumulation of excited or trapped electrons (or holes).

In order to enhance the activity of coupling photocatalysts, we have designed a configuration for the immobilized composite photocatalysts as shown in Figure 1d. A layer of a wide-band-gap TiO₂ film was first coated on a quartz substrate, followed by a layer of a narrow-band-gap Cu₂O

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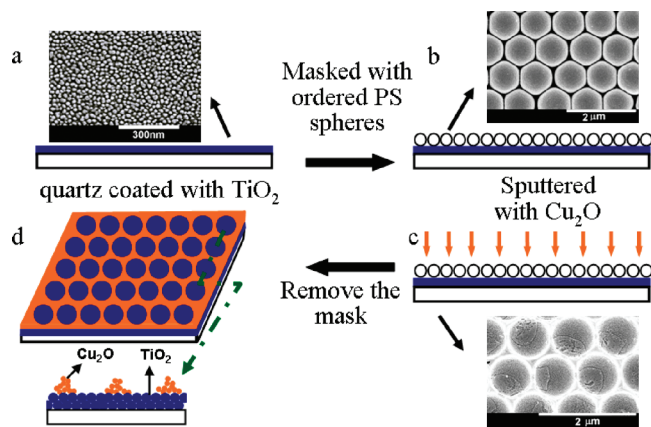


FIGURE 1. Procedure to prepare the TiO₂ film/Cu₂O microgrid heterojunction: (a) cross-sectional schematic diagram and surface SEM micrograph of the quartz coated with the TiO₂ film; (b) cross-sectional schematic diagram and surface SEM micrograph of the TiO₂ film coated with a layer of PS array; (c) cross-sectional schematic diagram and surface SEM micrograph of the samples after Cu₂O was deposited on the surface of the sample; (d) three-dimensional and cross-sectional schematic structure of the TiO₂ film/Cu₂O microgrid heterojunction.

microgrid. An attractive characteristic of the TiO₂ film/Cu₂O microgrid heterojunction is that TiO₂ and Cu₂O each has the opportunity to be excited by UV–vis light and absorb molecules in the solution.

EXPERIMENTAL SECTION

The TiO₂ film/Cu₂O microgrid heterojunction was manufactured by the microsphere lithography method, as illustrated in Figure 1.

The TiO₂ film was deposited on the quartz substrate by dip-coating the TiO₂ sol and then annealing in air for 2 h at 723 K. The TiO₂ sol was prepared as follows: 55 mL of Ti(OC₄H₉)₄ and 200 mL of C₂H₅OH were mixed using a magnetic stirring apparatus in a 1000 mL beaker. Then 1 mL of HCl was added to the solution as an inhibiting agent, followed by the addition of 200 mL of C₂H₅OH. Later, 5 mL of CH₃COCH₂COCH₃ was added to the mixture as a stabilizer. Finally, 11 mL of deionized water was added to the above solution dropwise with agitated stirring for 1 h to get a stable TiO₂ sol. The sol was aged at room temperature for about 2 months before using it to prepare the TiO₂ film on the substrate.

Polystyrene (PS) spheres with a diameter of 1.0 μm were first assembled to a closed-packed monolayer on the TiO₂ film surface by dip-coating a well-ordered PS particle array suspended on a water surface (16). Cu₂O was then sputtered on the template by a direct-current (dc) reactive magnetron sputtering system in a mixture of oxygen and argon at room temperature. The total pressure was 1 Pa, the argon flow rate was 40 sccm, the ratio of oxygen to argon was 1:10, and the sputtering power was 70 W. The sputtered composite film immersed in a tetrahydrofuran (THF) solution was supersonically vibrated for about 1 min to remove the PS spheres from the sample surface, followed by washing in C₂H₅OH and deionized water in sequence. Finally, the samples were dried at 80 °C in air to obtain the expected TiO₂ film/Cu₂O microgrid heterojunction.

The photocatalytic activities of the Cu₂O film, TiO₂ film, and TiO₂ film/Cu₂O microgrid heterojunction attached on the same-sized quartz substrate were evaluated by measuring the degradation rates of the methylene blue (MB) molecule in an aqueous solution under irradiation of UV–vis, visible, or UV light. A single-side-coated sample (35 × 15 × 1.5 mm) was immersed

in 6 mL of an aqueous MB solution (5 mg L⁻¹) in a quartz cell (40 × 20 × 20 mm) and irradiated in the perpendicular direction by the irradiation source. UV–vis light was generated using a 35 W xenon lamp that can simulate the solar spectrum. The visible light can be obtained by removing the UV radiation using a 420 nm cut filter. A 30 W mercury lamp with the main emission wavelength at 253.7 nm was used as a UV light source. When UV–vis light was used, the distance between the light source and the sample was 40 cm, and when a UV light source was employed, the distance was 6.5 cm.

A control experiment was conducted by directly irradiating the MB solution to account for any photolysis, the result of which was denoted as MB control.

The morphologies of the samples were investigated by scanning electron microscopy (SEM; Hitachi S4200) and atomic force microscopy (AFM; Nanoscope III_a SPM). A UV–vis spectrophotometer (Hitachi UV-3010) was employed to characterize the transmittance spectra of the samples and measure the concentration of the MB solution during the photocatalytic degradation process.

RESULTS AND DISCUSSION

The TiO₂ film is composed of spherical particles with a uniform size of about 20 nm, as shown in Figure 1a. The thickness of the film is about 50 nm. X-ray diffraction (XRD) patterns of the TiO₂ film indicate that the film consists of a single anatase phase. PS forms a well-ordered, monolayered template of latex spheres, as indicated in Figure 1b. XRD patterns of the copper oxide film synthesized using dc reactive magnetron sputtering show that the film consists of a single Cu₂O phase (17, 18). The thickness of the Cu₂O film is about 70 nm. The sputtered sample was finally immersed in THF to remove the PS spheres, yielding the expected TiO₂ film/Cu₂O microgrid heterojunction.

The morphology of the TiO₂ film/Cu₂O microgrid heterojunction is displayed in Figure 2. The underlying TiO₂ film is composed of nanosized particles covered by microgrids of Cu₂O, which are composed of particles smaller than 20 nm (Figure 2a). Using the micrograph, we can calculate that about 51 % of the surface of the TiO₂ film is covered by the Cu₂O microgrid, which indicates that the two semiconductors have similar surface areas exposed to the irradiation source as well as to substances in the solution. Figure 2b displays the AFM micrograph of the TiO₂ film/Cu₂O microgrid. The vertical thickness of the Cu₂O microgrid is about 20 nm after the superfluous Cu₂O deposited on the PS spheres fell, along with the PS debris, into the THF solution.

The transmittance spectra of the samples coated on the quartz substrate are illustrated in Figure 2c. The absorption edge of the Cu₂O film is at about 520 nm, corresponding to a band gap of 2.4 eV, while the band-gap of the TiO₂ film is about 3.2 eV. Cu₂O can absorb visible light; thus, depositing the Cu₂O microgrid on the TiO₂ film will enable the coupled semiconductors to absorb both UV and visible light, as is illustrated using the schematic energy diagram in Figure 2d.

The TiO₂ film/Cu₂O microgrid heterojunction possesses higher photocatalytic activity than the TiO₂ and Cu₂O films under UV–vis light irradiation, as shown in Figure 3a. Several causes result in the high photocatalytic activity of the TiO₂ film/Cu₂O microgrid heterojunction. First, TiO₂ and Cu₂O absorb UV or visible light directly to generate holes and

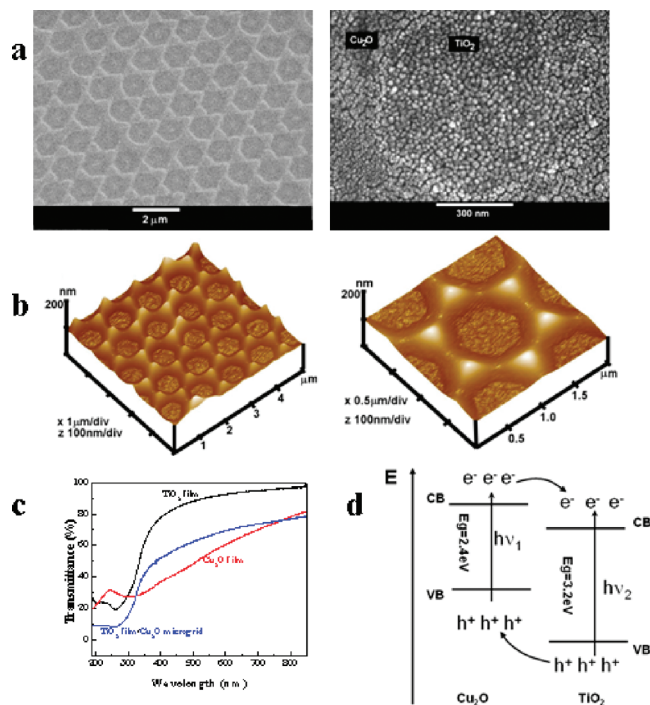


FIGURE 2. (a) SEM micrographs of the TiO₂ film/Cu₂O microgrid heterojunction. (b) AFM micrographs of the TiO₂ film/Cu₂O microgrid heterojunction. (c) Transmittance spectra of the TiO₂ film, Cu₂O film, and TiO₂ film/Cu₂O microgrid heterojunction. (d) Schematic energy diagram of Cu₂O and TiO₂.

electrons, which will migrate to the surface of the particles and accomplish the photocatalysis procedure. The similar opportunity that each has to be exposed to the adsorbates reduces the recombination of electrons and holes. Meanwhile, the excited electrons on Cu₂O can also transfer to TiO₂ because the conduction band of Cu₂O is less anodic than that of TiO₂, favoring the charge separation and efficiency of the photocatalysis process (5, 11). Furthermore, the electron–hole separations are also driven by the built-in electric fields in the heterojunction because Cu₂O is a p-type semiconductor and TiO₂ is an n-type semiconductor. In addition, Cu₂O can accelerate the rate of electron transfer to oxygen (7). Another unignorable cause is the enlarged surface area of the microgrid compared to the film (19). Therefore, the TiO₂ film/Cu₂O microgrid system exhibits much higher photocatalytic activity than the TiO₂ and Cu₂O films.

If UV light is filtered off from the UV–vis irradiation source, the TiO₂ film shows almost no photocatalytic reactivity. The decrease of the MB concentration is due to photolysis (20), which is similar to the MB control, as shown in Figure 3b. The Cu₂O film presents an obvious ability to decompose the MB dye under visible irradiation, and the TiO₂/Cu₂O microgrid heterojunction shows higher photocatalytic activity than the Cu₂O film. Although the TiO₂ film cannot be excited by visible light, the photogenerated electron transfer from Cu₂O to TiO₂ causes charge separation in Cu₂O. The transferred electrons on the surface of TiO₂ can be trapped by absorbed oxygen to produce superoxide ion radical (O₂^{•-}). This superoxide ion radical can attack organics directly or lead to the formation of oxidative H₂O₂ and hydroxyl radicals ([•]OH) (4).

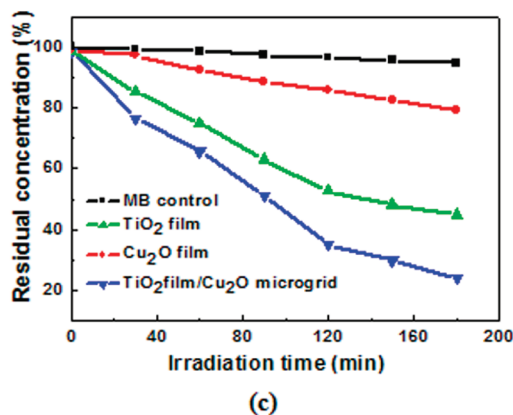
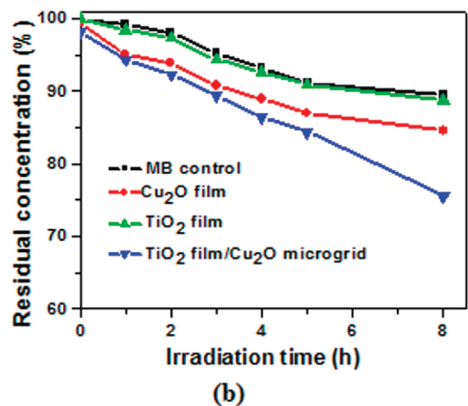
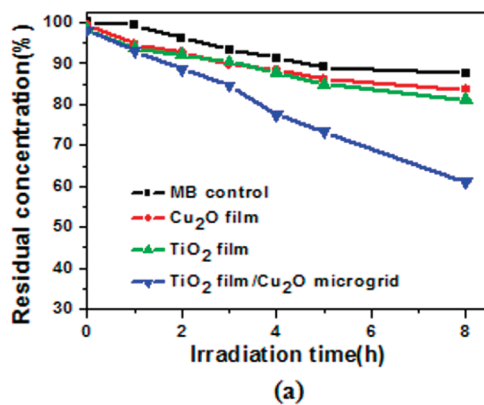


FIGURE 3. Photocatalytic decomposition of MB by the Cu₂O film, TiO₂ film, and TiO₂ film/Cu₂O microgrid heterojunction under irradiation of (a) UV–vis, (b) visible, and (c) UV light.

Similar results were achieved if the TiO₂ film/Cu₂O microgrid heterojunction was irradiated using UV light, as shown in Figure 3c. Though Cu₂O can be excited with UV light, the photocatalytic activity is much lower than that of TiO₂ because of the high recombination of charge carriers and the large difference between the band-gap energy and the UV-light energy. Even though half of the TiO₂ film has been covered by the Cu₂O microgrid, charge transfer between TiO₂ and Cu₂O leads to the higher photocatalytic activity of the TiO₂ film/Cu₂O microgrid compared to the intrinsic TiO₂ film.

CONCLUSION

In summary, the TiO₂ film/Cu₂O microgrid heterojunction was prepared by depositing a Cu₂O microgrid on the surface

of a TiO₂ film. Photocatalysts in this configuration showed higher photocatalytic activity for decomposing MB under irradiation of UV–vis, visible, and UV light than Cu₂O and TiO₂ films. This work provides a method to exploit highly efficient photocatalysts that can work under solar light irradiation.

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