*Applied Chemical Engineering (2021) Volume 4 Issue 2*
doi:10.24294/ace.v4i2.1352

## ORIGINAL RESEARCH ARTICLE

# Study on photocatalytic properties of $Cu_2O/TiO_2$ heterojunction composite films

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## ABSTRACT

$Cu_2O/TiO_2$ semiconductor heterostructure photocatalytic composite thin films were prepared by the sol-gel method and magnetron sputtering technology. Uniform and transparent $TiO_2$ thin films were prepared by sol dipping and pulling with butyl titanate as the raw material. P-type $Cu_2O$ thin films were reactive sputtered on the surface of $TiO_2$ thin films with metal Cu as target source. The catalysts were characterized by SEM, XRD and UV-Vis. The photocatalytic activity of heterojunction composite films under simulated sunlight was investigated by dye degradation experiments, and its mechanism is discussed. The results show that the heterojunction film formed by the composite of $TiO_2$ and $Cu_2O$ has good photocatalytic activity under simulated sunlight. The heterojunction composite expands the light response range and light response intensity of the catalyst and improves the quantum efficiency. It is a kind of photocatalytic composite film that makes full use of solar energy.

***Keywords:*** $Cu_2O/TiO_2$; Composite Film; Heterojunction; Photocatalysis; Solar Energy

**ARTICLE INFO**

Received: 13 July 2021
Accepted: 29 August 2021
Available online: 5 September 2021



## 1. Introduction

In recent years, in the research of photocatalysis, the research on improving the quantum yield and energy utilization efficiency of photocatalysis process is the most profound. Technologies such as semiconductor nanocrystallization[1], semiconductor crystal form control[2], semiconductor precious metal deposition[3], ion doping[4], semiconductor photosensitization[5] and surface treatment[6] have improved the photocatalysis efficiency to a certain extent. However, these methods are difficult to significantly broaden its response range to the spectrum, so they cannot effectively improve the utilization of visible light. The combination of n-type $TiO_2$ and p-type semiconductor (such as $Cu_2O$) is a new means to improve the photocatalytic performance[7]. Through the formation of interface heterojunction and the regulation of different band gaps, it can not only broaden the band absorption of sunlight, but also promote the separation of photogenerated carriers. In the research reported at present, the composite mode of n-type $TiO_2$ and p-type semiconductor is mainly particle composite[8]. When composite in the form of particles, the separated electrons and holes can play a photocatalytic role if they can timely contact the adsorbed molecules. However, the application of powdered photocatalyst is limited because it is easy

to inactivate and difficult to recover. In the particle composite mode, a large number of particles are buried inside and cannot fully contact with the surrounding receptors. Therefore, these active electrons and holes will gather locally, resulting in the capture of heterosexual charges and reducing the quantum efficiency of photocatalysis. In addition, $Cu_2O$ products prepared by chemical method usually contain a small amount of metal Cu and CuO impurities, which will also affect the quality and properties of the samples. Curing photocatalyst into thin film can overcome the above problems and has certain advantages. In this paper, $Cu_2O$ thin films are prepared by magnetron sputtering technology which is easy to control the structure and chemical composition of the thin films[9]. The $TiO_2$ thin films are prepared by the sol-gel method, and the obtained heterojunction composite films are better than single semiconductors.

## 2. Experiment

### 2.1 Experimental raw materials and preparation

Preparation of $TiO_2$ thin films by the dip pulling method: first inject 6.8 mL tetrabutyl titanate into a beaker containing 100 mL absolute ethanol, stir magnetically for several minutes, then 100 μL hydrochloric acid and 0.72 mL deionized water were added successively, continue the stirring reaction, and finally obtain a transparent $TiO_2$ sol. On the cleaned quartz glass substrate (35 mm × 15 mm × 1.5 mm), dry the $TiO_2$ film in air for a period of time, put it into muffle furnace, treat it at 450 ℃ for 2 h, and cool it naturally to room temperature to obtain $TiO_2$ bottom film[10].

Preparation of $Cu_2O$ thin films by DC magnetron sputtering: JGP-350C multi-target sputtering system (produced by Sky Technology Development Co., Ltd.) is adopted, the target is metal Cu (purity >99.99%), and the background vacuum in the vacuum sputtering chamber can reach $6 \times 10^{-4}$ Pa, using $O_2$ (purity >99.999%) as the reaction gas. The target substrate distance is adjusted to 70 mm, the flow rates of $O_2$ and Ar are adjusted to 1:10, the sputtering pressure is 1 Pa and the sputtering power is 70 W. Before each sputtering, discharge in pure Ar gas for several minutes to remove the oxide on the surface of the target. In the process of sputtering coating, the deposition rate of $Cu_2O$ thin film can be kept constant under stable working pressure and constant sputtering power. It is about 2 nm/s measured by thin film step meter. The sputtering time is adjusted to obtain thin film samples with different $Cu_2O$ loading[11].

### 2.2 Characterization

The phase structure of the samples was analyzed by D/max-2200 X-ray diffractometer of Rigaku company, Japan. The scanning step was 0.02°/s; Hitachi S4200 scanning electron microscope (equipped with energy dispersive spectrometer) was used to characterize the surface morphology and EDS element analysis of the film; the thickness of the film was measured by Dektak 6M step meter; Hitachi UV-Vis spectrophotometer (U-3010) was used to measure the transmission spectrum of the film in the UV-Vis region.

### 2.3 Photocatalytic performance test

Put the sample into 5 mL methylene blue (MB) solution with a concentration of 5 mg/L, use 20 W sterilization lamp and 35 W xenon lamp as light sources, measure the absorbance of the remaining solution, convert it into concentration, and calculate the photocatalytic degradation amount, so as to compare the photocatalytic performance of the sample[10].

## 3. Results and analysis

### 3.1 Photocatalytic activity of $TiO_2$ films

$TiO_2$ films with different layers were prepared by the impregnation pull method. The photocatalytic comparative experiment was carried out by irradiating 254 sterilization lamp for 1 h. **Figure 1** shows the photocatalytic activity of $TiO_2$ films with different thickness obtained by impregnation pull method for photocatalytic degradation of MB. The results show that when the film is thin, the residual concentration of MB is low and the photocatalytic activity

of the sample is high; with the increase of film thickness, the photocatalytic properties of the samples decreased to the lowest value; when the film thickness continues to increase, the photocatalytic activity of the sample begins to increase, and tends to be stable with the increase of thickness.

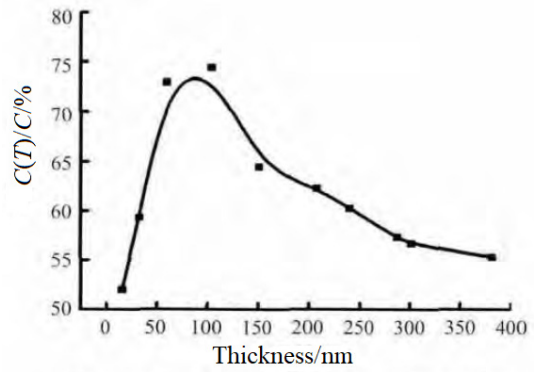


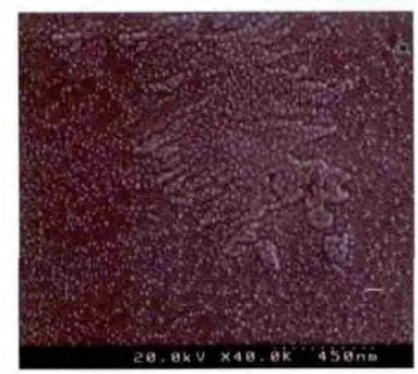

**Figure 1.** Photocatalytic activity of $TiO_2$ films with different thickness.

The change of photocatalytic performance is closely related to the microstructure of the films. The $TiO_2$ thin films prepared by the sol-gel method are granular stacking structures. Under UV irradiation, the surface particle excitation and deep particle excitation and their interaction process exist. For thin granular films, the excitation of surface particles will be dominant and the photocatalytic activity will be high; with the increase of the thickness of the film, the interaction between the surface and inner particles cannot be ignored. Because the inner $TiO_2$ particles cannot contact with the reactants, the electron hole pairs generated by photoexcitation can only be consumed through recombination, which will directly affect the photocatalytic performance of the film, i.e., resonance loss effect, resulting in the reduction of the photocatalytic performance of the sample; in addition, the contact between semiconductor film and electrolyte solution will cause the energy band bending in the film, which will lead to the directional diffusion of photogenerated carriers from the body to the surface. The thicker is the film thickness, the more total photons can be absorbed, the more total number of photogenerated carriers is diffused to the film surface, and the stronger is the photocatalytic performance of the sample[12]. Therefore, the photocatalytic performance of the film will increase with the increase of the thickness of the film; however, because the total light intensity is fixed, when the film thickness increases to a certain extent, the total number of carriers diffused to the film surface tends to be stable, and the photocatalytic activity of the sample also tends to remain unchanged.

Because the contact area between the bottom $TiO_2$ film and the upper $Cu_2O$ is certain, the thickness of the bottom layer will only increase the recombination probability of photogenerated carriers and reduce the photocatalytic activity. Therefore, the bottom layer of the composite film is a $TiO_2$ film with a thickness of about 33 nm with good UV catalytic activity.

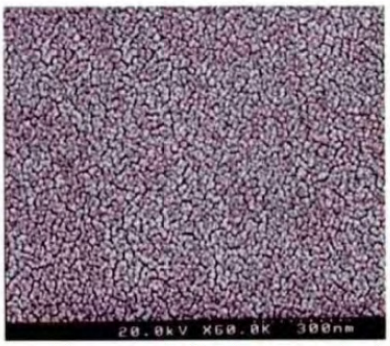
## 3.2 Characterization of $Cu_2O/TiO_2$ heterojunction composite films

The surface morphology of the bottom $TiO_2$ film and $Cu_2O/TiO_2$ composite film were characterized by SEM. **Figure 2a** shows the surface morphology of the underlying $TiO_2$ film, which is composed of $TiO_2$ nanoparticles. The film thickness is 33 nm, the particles are about 10–20 nm, and the particle arrangement is relatively loose and flat. **Figure 2b** is the SEM diagram of the composite film after DC reactive sputtering of $Cu_2O$ particles on the surface of $TiO_2$ film (sputtering time is 30 s). $Cu_2O$ particles are uniformly deposited on the surface of loose bottom layer, the density of particles is relatively improved, and the porosity between particles is conducive to the adsorption of degradation products; it can also be seen from the figure that $Cu_2O$ and $TiO_2$ particles are closely combined, the particle size is uniform, and the particle size is nanometer. **Figure 2c** shows the surface morphology of the sample after sputtering $Cu_2O$ (sputtering time is 90 s). Compared with **Figure 2b**, the particles grow obviously, agglomerate and agglomerate, and the surface tends to be flat, which is not conducive to the adsorption of degradation products. Therefore, the sputtering time of 30 s is the best load of $Cu_2O$. At this time, according to the deposition rate of $Cu_2O$, when the thickness of the upper film is about 60 nm, the composite film can have the best photocatalytic activity.



a. $TiO_2$ film

b. $Cu_2O/TiO_2$ composite film ($Cu_2O$ sputtering time is 30s)



c. $Cu_2O/TiO_2$ composite film ($Cu_2O$ sputtering time is 90s)

**Figure 2.** Surface morphology of thin films.

**Figure 3** shows the EDS element analysis of $Cu_2O/TiO_2$ composite films prepared after sputtering $Cu_2O$ (sputtering time is 30 s), and different positions are selected for scanning analysis. It can be seen from **Figure 3** that except the constituent elements of the substrate glass substrate, only Ti, Cu and O elements exist, which proves that the film is composed of oxides of Ti and Cu. The results of element analysis at three different positions correspond to three groups of tables. The percentage difference of Ti and Cu in each group of tables is small, within the range of 0.1%; at the same time, the results of the three groups are similar, indicating that the element distribution of the bilayer composite film is relatively uniform, and there are no excessive local single-type elements. In this way, the uniformity of the recombination of the two semiconductor particles is conducive to the formation of heterojunction.

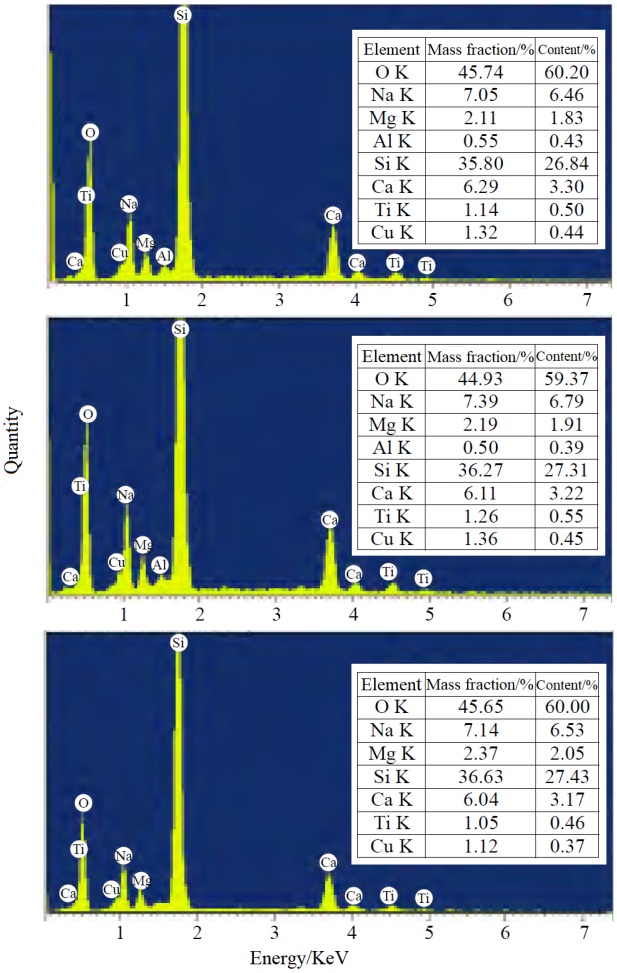



**Figure 3.** EDS elemental analysis of $Cu_2O/TiO_2$ composite films ($Cu_2O$ sputtering time 30 s).

**Figure 4** is the XRD diagram of $Cu_2O/TiO_2$ nanocomposite film. $TiO_2$ in the composite film mainly has (101) diffraction peak, while $Cu_2O$ mainly has (111) diffraction peak. The peak intensity shows that the crystallinity of the two semiconductor particles in the composite film is good. In order to ensure the stability of nano $Cu_2O/TiO_2$ composite film in air, the XRD lines were re-measured after several months, and there were no diffraction peaks of Cu and CuO, indicating that $Cu_2O$ in the composite film has stable chemical properties and is not easy

to be oxidized to CuO or reduced to elemental Cu.

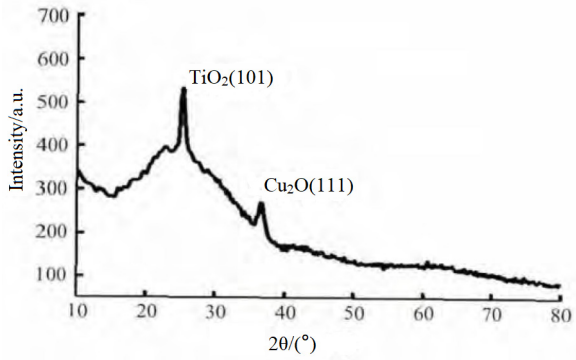



**Figure 4.** XRD diagram of $Cu_2O/TiO_2$ composite films.

The two semiconductors of heterojunction composite are combined into nano films, which can absorb ultraviolet and visible light respectively under light. Therefore, the light absorption characteristics of composite films are different from those of single films. The transmission spectrum line in **Figure 5** shows that $TiO_2$ film has low transmittance in the ultraviolet region and good UV absorption performance, while it has high transmittance in the visible region and is difficult to use visible light. In addition, $Cu_2O$ thin films have a wide range of optical response, which is due to the spatial confinement of electrons and holes when the semiconductor particle size is small to the nano scale, and the quantum size effect will lead to the phenomenon of energy level change and energy gap widening, resulting in low transmittance of $Cu_2O$ in the whole spectral range[13]. The light response ability of the composite film in the UV and visible range is significantly better than that of $TiO_2$ and $Cu_2O$ films. The matching of the two semiconductors expands the light absorption range and improves the light absorption intensity of the whole light region. The optical properties of materials are important performance indicators of photocatalytic reaction. The light absorption ability of composite films in the whole UV-Vis region will stimulate the generation of more photogenerated carriers and provide more active sites for photocatalytic oxidation-reduction. The catalytic performance of the catalyst under sunlight must be better than that of a single semiconductor film.

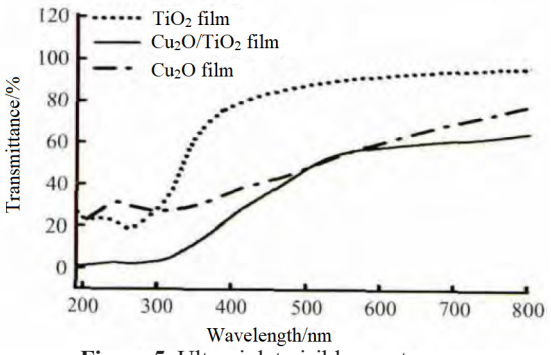



**Figure 5.** Ultraviolet visible spectrum.

## 3.3 Photocatalytic properties of $Cu_2O/TiO_2$ heterojunction composite films

From the above characterization results, the $Cu_2O/TiO_2$ bilayer composite semiconductor film has the characteristics of uniform particle size, good crystallinity, stable physicochemical properties and excellent optical properties. Due to the matching of the energy band structures of the two semiconductors, the $Cu_2O/TiO_2$ type bilayer composite film can be regarded as a heterojunction structure. Both semiconductor films are thin and composed of nanoparticles. The semiconductor particles in the film are in direct contact and effectively separate the photogenerated carriers through heterojunction. The semiconductor particles have grain boundary connection and do not exist in isolation, because the space charge region width of heterojunction can reach hundreds of nanometers or even microns, the two semiconductors can transfer electrons and holes in a wide range. Even if the $TiO_2$ particles are not in direct contact with $Cu_2O$, the photogenerated electrons and holes can be transferred with $Cu_2O$ through adjacent $TiO_2$ particles under the action of built-in electric field; similarly, $Cu_2O$ not in direct contact with $TiO_2$ can also transfer photogenerated electrons and holes with $TiO_2$through adjacent $Cu_2O$ particles. That means that no external electric field can effectively inhibit the recombination of photogenerated electrons and photogenerated holes and enhance the quantum efficiency of catalytic reaction[14,15].

It can be seen from **Figure 6** that the photocatalytic activity of composite films with different $Cu_2O$ loading is different. The photocatalytic activity first increases and then decreases with the increase of

$Cu_2O$ loading, meaning that there is an optimal $Cu_2O$ loading, and the catalyst activity with sputtering time of 30 s is the highest, which is consistent with the conclusion obtained in surface morphology characterization. Moreover, only when the sputtering time is 10 s and 30 s, the photocatalytic activity of the composite film is better than that of $TiO_2$ film. Due to the short deposition time, less $Cu_2O$ is compounded with $TiO_2$, meaning that there are few particles in contact between the two semiconductors, and the coupling effect of heterogeneous binding is not obvious, which does not promote the photocatalytic activity of the composite films; when the deposition time of $Cu_2O$ is 30 s, the $Cu_2O$ particles on the $TiO_2$ surface increase, and the particle size in the composite film (**Figure 2b**) is relatively uniform. The two particles are closely combined to form a coupling effect of heterogeneous binding, which helps to improve the photocatalytic activity of the composite film and has good UV-Vis photocatalytic activity. When the $Cu_2O$ load continues to increase, even if the initial photogenerated electrons and holes can be separated, the photogenerated electrons and holes are enriched on $TiO_2$ and $Cu_2O$ respectively. If they cannot be consumed in time, they are easy to become the recombination center of heterosexual charges. In addition, with the increase of surface $Cu_2O$ loading, the shielding effect on the bottom $TiO_2$ film is also gradually enhanced, so that the bottom $TiO_2$ is not only less likely to be excited by light, but also cannot transfer electrons to the receptor in time. A large number of accumulated carriers will become internal recombination centers, resulting in the reduction of photocatalytic efficiency.

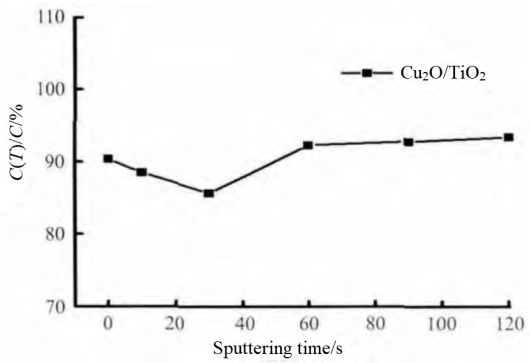



**Figure 6.** UV visible photocatalytic activity of composite films (changing $Cu_2O$ sputtering time).

The photocatalytic activity of $Cu_2O/TiO_2$ composite semiconductor film is mainly caused by the absorption of visible light by narrow band gap semiconductors and the synergistic effect with wide band gap semiconductors. The degradation performance of $Cu_2O/TiO_2$ composite film is much stronger than that of single semiconductor film, as shown in **Figure 7**. This shows that when irradiated by xenon lamp without filter, $TiO_2$ can absorb ultraviolet light and $Cu_2O$ can absorb visible light. At the same time, they form heterojunction to improve carrier utilization, have good solar photocatalytic activity, and their advantages become more and more obvious with the extension of time.

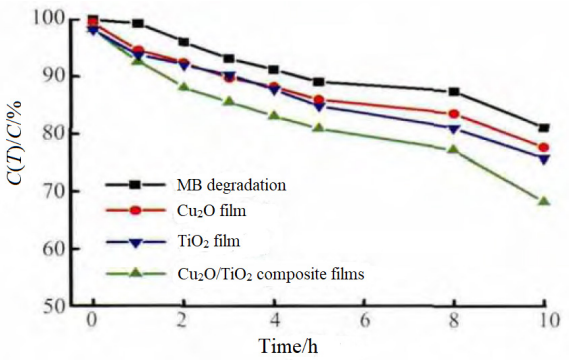



**Figure 7.** MB degradation curve of composite films with the sputtering time of 30 s (simulating sunlight).

## 4. Conclusion

Homogeneous $Cu_2O/TiO_2$ composite heterostructure photocatalyst thin films were prepared by the sol-gel method and magnetron sputtering technology. The structure of $Cu_2O/TiO_2$ bilayer composite film is controllable, and the crystal form of $Cu_2O$ is stable in the composite film; the nanoparticles in the composite films are uniform in size and closely combined; the response ability to light is obviously improved, and the light absorption range of photocatalyst is expanded. The photocatalytic activity of the composite films first increased and then decreased with the increase of $Cu_2O$ loading. In the composite films with the best photocatalytic activity, the thickness of $TiO_2$ is about 33 nm and that of $Cu_2O$ is about 60 nm. Under xenon lamp irradiation, the catalytic activity of composite films is better than that of the single film, and the longer it takes, the more obvious the advantages of photocatalytic degradation

of MB. Therefore, the catalyst is a heterojunction composite film that makes full use of solar energy.

## Conflict of interest

The authors declare that they have no conflict of interest.

## Acknowledgements

The paper was supported by the National Natural Science Foundation of China (61306152), the Natural Science Foundation of Shandong Province (ZR2010EQ001) and the Youth Scientific Research Fund of Weifang University (2012Z15).

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