Desalination and Water Treatment
www.deswater.com
doi:10.5004/dwt.2019.23410

142 (2019) 179–184
February

Photocatalysis study of TiO_2 composite film containing nanocrystals and conductive layer

Zhenquan Li[a,b,*], Xuewen Yi[c]

[a]*Laboratory of new antitumor drug molecular design & synthesis, School of Basic Medicine, Jining Medical University, Jining 272067, China, Tel. +86-17321061769; email: lizhq18@sina.com*
[b]*School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China*
[c]*College of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China, email: 13818103668@163.com*

Received 14 April 208; Accepted 31 October 2018

ABSTRACT

TiO_2 thin film was deposited by magnetron sputtering at room temperature, and the uniformly distributed TiO_2 nanocrystals were obtained with controlled annealing conditions. Three kinds of multilayer composite samples, Ti/TiO_2, Ti/Au/TiO_2, and TiO_2/Au/TiO_2, were prepared. The impacts of metal conductive layers on photocatalytic performance were studied. It was found that the photocatalytic ability of the multilayer samples with conductive layer was better than that of monolayer TiO_2 sample without conductive layer. The conductive layer could inhibit the recombination of photocarriers and enhance the photocatalytic decomposition efficiency of TiO_2 thin film. Furthermore, Au conductive layer showed a more significant impact on the photocatalytic ability than that of Ti. It was also found that the photocatalytic abilities of Ti/Au/TiO_2 and TiO_2/Au/TiO_2 were almost the same. Experimental results indicated that the improved photocatalysis was mainly due to the contribution of both TiO_2 nanocrystals and conductive layer.

Keywords: Photocatalysis; Nanocrystals; Conductive layer; Magnetron sputtering

1. Introduction

Since Fujishima and Honda found that TiO_2 could decompose water into hydrogen and oxygen through photocatalytic effect in 1972, TiO_2, as a photocatalyst with advantages of high chemical stability, low cost, and nontoxic, has been widely studied [1]. TiO_2 photocatalytic technology has been applied in various fields, such as air purification, wastewater treatment, self-cleaning material, dye-sensitized solar cell, and sterilization [2–4]. TiO_2 mainly has three kinds of crystal structures: brookite, anatase, and rutile. As brookite is not stable, TiO_2 mainly exists in the form of anatase and rutile phases. The early studies mainly focused on TiO_2 powder because nano powder was featured as having large specific surface area and good photocatalytic effect. However, TiO_2 powder also has disadvantages of easy agglomeration, difficult separation, and recovery. In recent years, TiO_2 film has been widely studied due to its advantages of easy recovery and reuse. There are many methods to prepare TiO_2 film, including chemical methods and some physical methods, such as sol-gel method, hydrothermal method, electrochemical deposition, sputtering, evaporation, and pulsed laser deposition [5–7]. The chemical preparation method, such as sol-gel method, has characteristic of low cost, but the film adhesion is poor and prone to cracking during drying, and the film thickness is not easy to be controlled. Among the physical preparation methods, magnetron sputtering method has advantages of simple and controllable process, good repeatability, and can produce the film with good adhesion; tens of nanometer TiO_2 films with high quality can be obtained

* Corresponding author.

under room temperature, which is suitable for large scale of controllable production and application.

However, the broad bandgap of TiO_2 makes it only to absorb the ultraviolet light with wavelength less than 387 nm; so its utilization rate of solar energy is low. Moreover, electrons and holes generated by TiO_2 film under irradiation are easy to recombine. The above factors can lead to low photocatalytic efficiency of TiO_2. The researchers have targeted on how to improve the absorptive capacity of light catalyst, effectively control the generation, separation, transfer, and acquisition of photocarrier, and inhibit the recombination of photocarriers, so as to improve the catalytic efficiency of TiO_2 over many years [8–16]. In order to solve the problems above, the researchers have modified the material and structure of TiO_2 photocatalyst, except for developing new catalysts with higher photocatalytic efficiency. Most of the researches on TiO_2 photocatalyst are mainly focused on the following aspects: (1) adjusting the energy band structure of TiO_2 by means of doping, so that the absorption spectrum of TiO_2 can be extended from UV region to visible region; (2) inhibiting the recombination of photogenerated electrons and photogenerated holes by means of metal modification; and (3) increasing the specific surface area of TiO_2 by nanostructure loading and then improving the photocatalytic efficiency of TiO_2 and so on [9–12].

For TiO_2 films, if the substrate is conductive, electrons and holes generated by light can be separated through the conductive substrate, which can effectively avoid the recombination of photoelectrons and holes, thus improve the photocatalytic efficiency of TiO_2 film. In this paper, the effects of noble metal Au and conventional Ti conductive layer on photocatalytic performance of TiO_2 thin film were studied. We prepared monolayer TiO_2 sample and three multilayer composite samples on the quartz substrate with the magnetron sputtering method, namely, Ti/TiO_2, $Ti/Au/TiO_2$, and $TiO_2/Au/TiO_2$, respectively. The morphology and microstructure of the samples were analyzed before and after annealing by atomic force microscope (AFM), X-ray diffraction (XRD), transmission electron microscope (TEM), and energy dispersive spectrometer (EDS). It was shown from decomposition of methyl orange that the photocatalytic ability of multilayer samples was obviously better than that of monolayer sample, and multilayer sample with conductive Au film had the highest photocatalytic ability. It was also found that the photocatalytic abilities of $Ti/Au/TiO_2$ and $TiO_2/Au/TiO_2$ were almost the same, which implied that their catalytic abilities mainly originated from the synergistic effect of the top TiO_2 nanocrystals and Au conductive layer, while the lower TiO_2 had no obvious effect on the photocatalysis.

2. Experiment

2.1. Sample preparation

TiO_2 thin film was prepared by radio frequency (RF) magnetron sputtering of TiO_2 target, Si and quartz were used as the substrates for this experiment, and all substrates were cleaned with acetone, ethanol, and deionized water. The purity of TiO_2 ceramic target is 99.99%, the sputtering gas is Ar, the substrate temperature is room temperature, and the sputtering power is 100 W. The samples were annealed at different conditions so as to obtain TiO_2 nanocrystals. In order to study the impact of metal layer on the photocatalytic performance, three kinds of multilayer samples with composite structure on quartz substrates, namely, Ti/TiO_2, $Ti/Au/TiO_2$, and $TiO_2/Au/TiO_2$, were prepared; as a comparison, monolayer quartz/TiO_2 sample was also prepared with TiO_2 film of 70 nm thickness.

2.2. Characterization and photocatalysis

The morphology and microstructure of samples were analyzed by means of AFM, XRD, TEM, and EDS. In order to study photocatalytic performances of Ti/TiO_2, $Ti/Au/TiO_2$, and $TiO_2/Au/TiO_2$ in the different metal layers and different structure of the sample, the photocatalytic abilities of three samples and monolayer quartz/TiO_2 sample were studied with methyl orange as target pollutants. A 50 mL methyl orange solution with concentration of 10 mg/L was preliminarily prepared for the photocatalytic experiment and put into a culture dish, and then the sample was also put in it. The culture dish was placed under UV lamp of 15 W for 5–7 h, a methyl orange solution was taken once with a certain interval, and the ultraviolet spectrophotometer was used to measure its absorbance, so as to determine the photocatalytic effect on methyl orange.

3. Results and discussions

The surface morphology of TiO_2 film was observed by AFM. Fig. 1(a) and (b) shows AFM images for as-deposited quartz/TiO_2 sample and the sample annealed at 500°C. It is shown from Fig. 1(a) that the sample is very smooth with a root mean square (RMS) of 0.3896 nm. While for the annealed sample, the RMS is increased to 0.5118 nm. Fig. 1(c) and (d) shows AFM images of the quartz/$Ti/Au/TiO_2$ sample before and after annealing. It is seen from Fig. 1(c) that the as-deposited quartz/$Ti/Au/TiO_2$ sample is also smooth and the RMS is 0.5335 nm, which is a little larger than the quartz/TiO_2 sample. For the annealed sample, the RMS becomes 0.5569 nm; no obvious change existed in film roughness before and after annealing.

In order to analyze the crystallization characteristics of TiO_2, XRD spectra were measured for quartz/TiO_2 and quartz/$Ti/Au/TiO_2$ samples annealed at different conditions. For comparison, the as-deposited quartz/TiO_2 and quartz/$Ti/Au/TiO_2$ samples were also tested. The results are shown in Fig. 2. Fig. 2(a) is the XRD spectrum of pure TiO_2 sample, and Fig. 2(b) is the XRD spectrum of $Ti/Au/TiO_2$ sample. It was explicitly indicated from Fig. 2(a) that no crystallization peaks appeared for as-deposited pure TiO_2, while a number of crystallization peaks appeared after annealing at 50°C. In contrast with the standard powder diffraction file card, the diffraction peaks correspond to the (101), (200), and (211) crystal of anatase TiO_2. It was implied from XRD results that TiO_2 film prepared by means of magnetron sputtering could be transformed into anatase phase structure after annealing at 500°C. For the $Ti/Au/TiO_2$ sample, as shown in Fig. 2(b), obvious Au signal was observed for both as-deposited and annealed $Ti/Au/TiO_2$ samples. Besides Au diffraction peaks, (101), (200), and (211) diffraction peaks were also observed. Because Au signal is too strong, the diffraction peaks of TiO_2 look very weak.

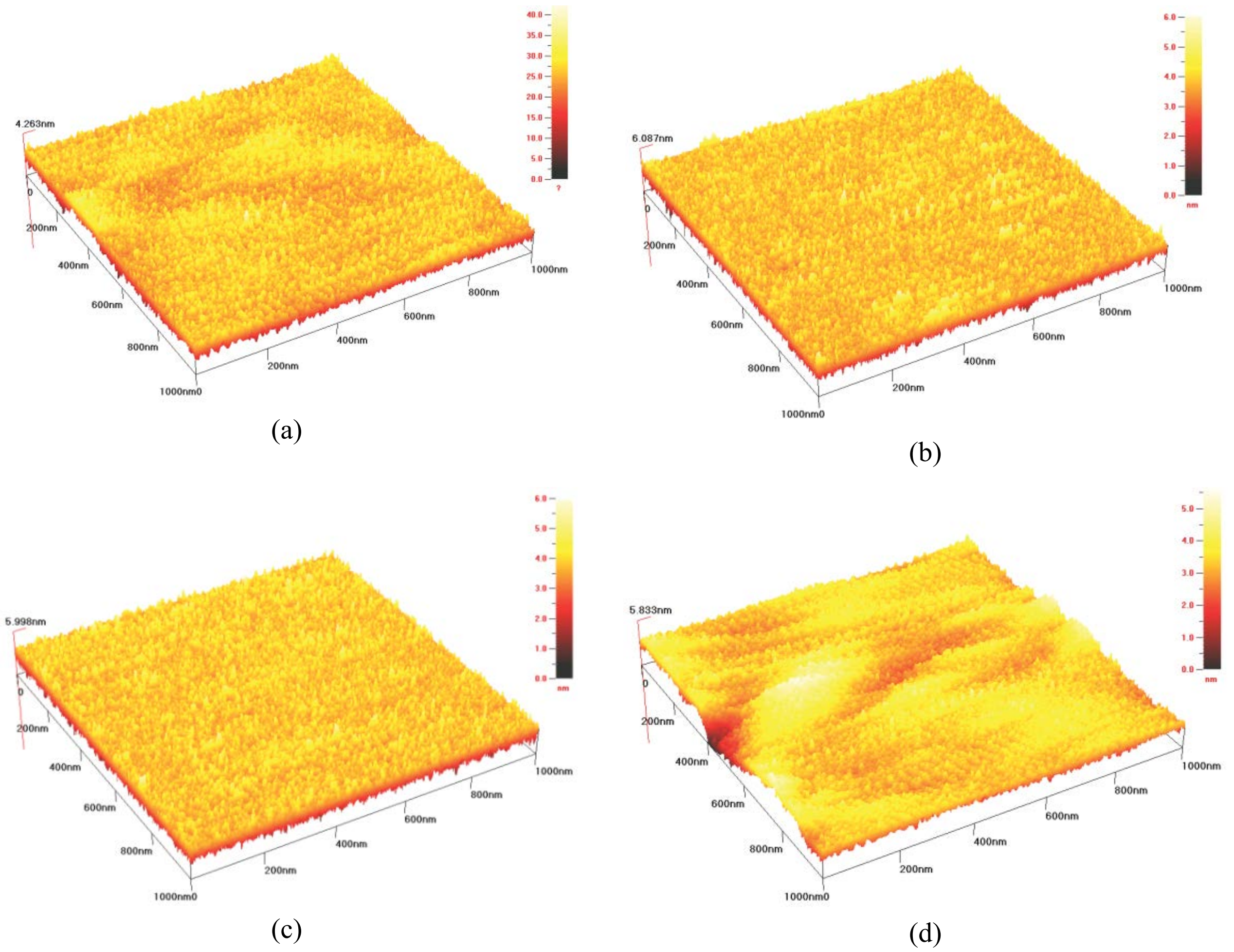


Fig. 1. AFM images before (a) and after (b) the quartz/TiO_2 sample was annealed; AFM images before (c) and after (d) the quartz/Ti/Au/TiO_2 sample was annealed.

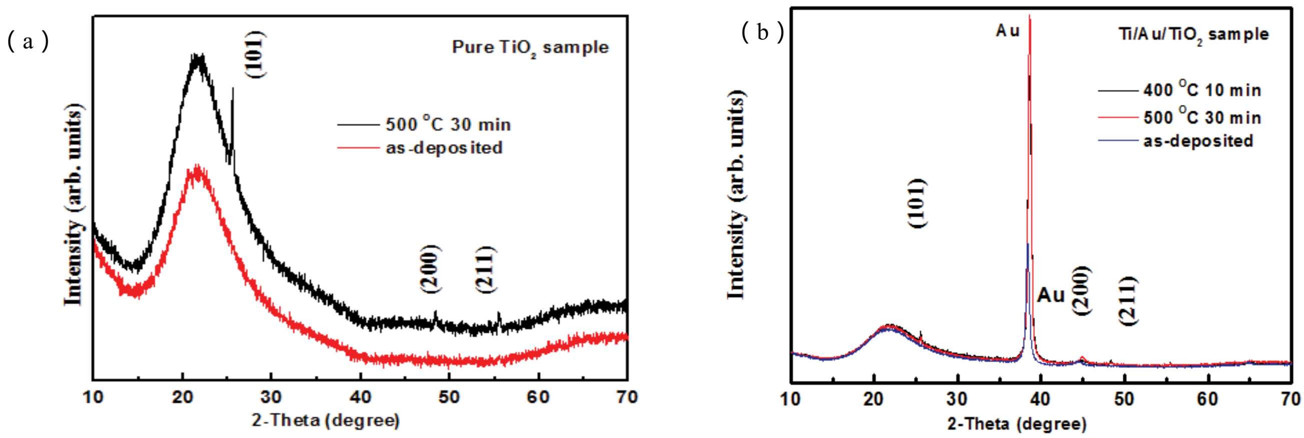
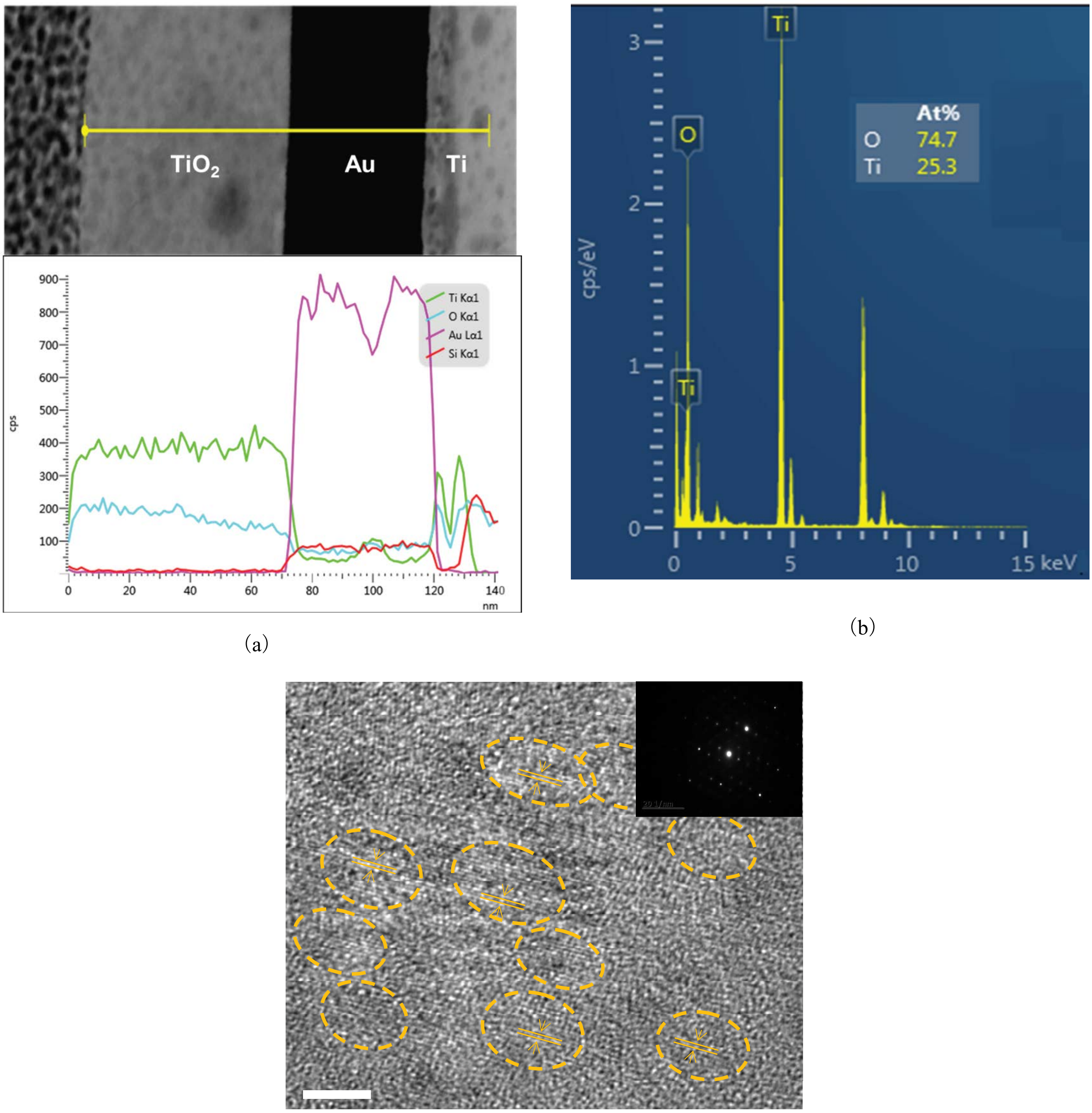


Fig. 2. XRD spectra of as-deposited and annealed samples: (a) quartz/TiO_2 sample, (b) quartz/Ti/Au/TiO_2 sample.

The microstructure of annealed Ti/Au/TiO_2 sample was further analyzed by means of TEM, EDS, high resolution transmission electronmicroscopy (HRTEM), and selected area electron diffraction (SAED). In order to facilitate preparation of sample for electron microscope, the thickness of Au layer was increased. Fig. 3(a) is the cross-sectional structure of the Ti/Au/TiO_2 sample and EDS line-scanning diagram. It was indicated from the picture that three-layer structure of sample can be explicitly observed, and the Ti, Au, and TiO_2 layers were displayed from the quartz substrate to the



(a)

(b)

(c)

Fig. 3. Profile structure of Ti/Au/TiO_2 sample and EDS line scanning (a), spot scanning (b), and HRTEM image and the SAED pattern (c).

left, of which thickness are about 10, 50, and 70 nm, respectively. Fig. 3(b) is the EDS spot-scanning diagram of the Ti/Au/TiO_2 sample, which further confirms the formation of TiO_2. Fig. 3(c) is the HRTEM and SAED results for Ti/Au/TiO_2 samples. It could be observed from HRTEM images that a lot of nanocrystals with relatively uniform distribution were generated in the film after annealing and the size of the nanocrystals was 10 nm or less. By analyzing the lattice fringes, these nanocrystals are mainly anatase structure TiO_2 with (200) orientation, which was consistent with the XRD results.

The crystalline TiO_2 exists in three crystal structures, namely, anatase, rutile, and brookite; among them, anatase structure has significant photocatalytic properties, which can decompose the insoluble organic pollutants. A comparative study on photocatalytic performance was conducted on TiO_2, Ti/TiO_2, Ti/Au/TiO_2, and TiO_2/Au/TiO_2 samples with methyl orange taken as a target pollutant. The photocatalytic

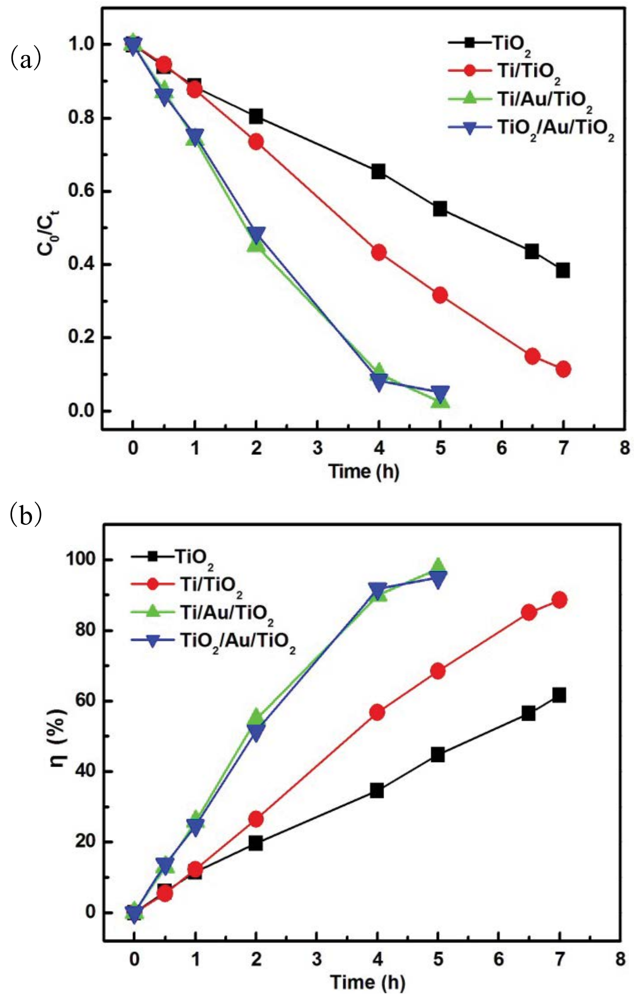


Fig. 4. Photocatalytic performances of TiO_2, Ti/TiO_2, Ti/Au/TiO_2, and TiO_2/Au/TiO_2 samples (a) and the corresponding catalytic efficiency (b).

experimental results are shown in Fig. 4. It could be seen that the photocatalytic decomposition was obvious for all samples, and the concentration of methyl orange decreased rapidly with increasing irradiation time. For monolayer TiO_2 sample, the decomposition rate of methyl orange accounts for about 40% under the UV irradiation for 5 h. While for Ti/TiO_2 sample, the decomposition rate of methyl orange was about 60% when it was irradiated for 5 h. Obviously, the decomposition rate of Ti/TiO_2 was significantly improved. While for Ti/Au/TiO_2 samples the concentration of methyl orange decreased more rapidly with UV irradiation time increasing, methyl orange could be decomposed about 50% for 2 h with UV irradiation. The decomposition rate of methyl orange was equivalent to the decomposition rate of TiO_2 samples after irradiating for 5 h or that of Ti/TiO_2 samples after irradiating for 4 h. The decomposition rate of methyl orange could reach up to 90% when Ti/Au/TiO_2 sample was irradiated for 4 h, and the rate was up to 100% when it is irradiated for 5 h. Furthermore, it was worth to point out that the photocatalytic ability was almost the same for TiO_2/Au/TiO_2 and Ti/Au/TiO_2 samples. So the catalytic ability of TiO_2/Au/TiO_2 sample was mainly attributed to synergism of top layers of TiO_2 and Au films, instead of the bottom TiO_2 film.

4. Conclusions

By using RF magnetron sputtering and thermal annealing, the nanocrystalline size of TiO_2 can be controlled below 10 nm with uniform distribution. The photocatalytic efficiency of TiO_2 thin film was significantly improved through the combination of TiO_2 nanocrystals and conductive layers. The photocatalytic activity of multilayer sample with metal conducting layer was obviously better than that of monolayer sample without metal conducting layer. Different metal conductive layers had different effects on the photocatalytic properties, and Au conductive layer had better photocatalytic activity than Ti conductive layer. Furthermore, it was indicated from the experimental results of Ti/Au/TiO_2 and TiO_2/Au/TiO_2 samples that the photocatalytic ability was mainly from the synergistic effect of top TiO_2 nanocrystals and Au conductive layer. The study provides a valuable reference for photocatalytic structure design.

Acknowledgement

This work was supported by the Supporting Fund for Teachers' research of Jining Medical University (No.JYFC2018KJ012), National Undergraduate Innovation Training Program of Ministry of Education (No. 201610443019) and Undergraduate Innovation Training Program of Jining Medical University (No. cx2016019).

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