1. Introduction

In the past few decades semiconductor photocatalysis due to its great potential applications in energy and environment areas has been becoming more attractive. Among various semiconductors employed, titanium dioxide (TiO2) is well known to be an excellent photocatalyst because of its high transparency in visible light, good photocatalytic behavior and favorable chemical stability. Zinc oxide, as a direct wide-band-gap semiconductor with a band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, is discovered to be important semiconductor photocatalysis in recent years. And there have been several examples of ZnO displaying more impressive photocatalytic activity than widely studied titanium dioxide. In general, the photocatalytic activity is based on the generation of electron/hole pairs and limited by the recombinaction of electron/hole pairs. Many methods, such as doping, metal modification and coupling of composite semiconductors, have been investigated to suppress the recombinaction and increase the life time of separated electron and hole, hence to improve the photocatalyst properties. Among them the coupling of different semiconductor seems useful to achieve a more efficient electron/hole pair separation and prevent the recombinaction of electron/hole pairs efficiently. In this direction, different TiO2/ZnO composite materials were investigated in consideration of that both components have good photocatalytic activity. For example, ZnO/TiO2 composite was fabricated by site-specific deposition and the structure of the composite was analyzed. ZnO/TiO2 films were deposited on quartz substrate through E-beam evaporation and their photoluminescence properties were discussed. ZnO was also used as a buffer layer between the Si (111) substrate and the deposited rutile TiO2 film by magnetron sputtering. Nano-sized TiO2/ZnO composite film with different atomic ratio of Ti/(Ti + Zn) was prepared via sol–gel process and the photodegradation activity of methyl orange was detected and analyzed. Although these researches focused on the fabrication of TiO2/ZnO composite materials and their photocatalytic activity, there is still a need to study the structure and growth relation of the TiO2/ZnO composite and photocatalytic activity as well as the relevancy between photoluminescence and photocatalytic activity of the composite.

In the present work, TiO2/ZnO double-layer film was prepared on the quartz glass substrate by a simple pulsed laser deposition. The structure and composition of the as-deposited film was characterized with XRD, SEM, EDS and HRTEM. The optical properties were investigated with UV-Vis and photoluminescence (PL) spectra and their photocatalytic efficiency were evaluated by the photodegradation of methyl orange and methylene blue solution.

2. Experiment

TiO2/ZnO film was prepared on quartz substrate by pulse laser deposition and the pure TiO2 and ZnO films were also prepared for comparison. Pulsed Nd:YAG laser with a wavelength of 1064 nm was used. The distance between the target and the quartz substrate was kept at 2.5 cm. The chamber was evacuated first to a base pressure (below $5 \times 10^{-4}$ Pa) using a turbo molecular pump and then the gas pressure was kept at 10 Pa by feeding oxygen gases (99.99% purity) into the chamber. Table 1 shows the detail preparing condition of pure ZnO and TiO2 films. The TiO2/ZnO double layer film was obtained through the deposition of first ZnO film then TiO2 film following the procedure of Table 1.

![Table 1 Preparing condition of ZnO and TiO2 film.](image-url)
The crystal structure of the films was analyzed by XRD (Rigaku D/Max) with a Cu target and a monochromator at 50 kV and 300 mA. Field-emission Scanning Electron Microscopy (FESEM, JEOL-JSM-6700F) was used to observe the surface morphology of the films. The chemical stoichiometry of the film was analyzed by an Energy Dispersive X-ray Spectrometer (EDX, Oxford). Field-emission Transmission Electron Microscopy (FETEM, JEOL-JEM-2100F) was used to characterize the structure of TiO2/ZnO film and interface of them through the TEM and HRTEM images and selected area electron diffraction (SAED) patterns at working voltage of 200 kV. The optical properties of the TiO2 thin films were characterized by UV–vis spectrophotometer and photoluminescence with an Ar ion laser as a light source using an excitation wavelength of 325 nm.

The visible-light photocatalytic efficiency was estimated by the photo-degradations of aqueous methyl orange and methylene blue, respectively. The visual light was a 500 W high-pressure mercury lamp (100 mm long), which was surrounded by a circulating water jacket to cool the lamp. The films were put in the reaction vessel containing 30 mL of aqueous methyl orange (or methylene blue) of 20 mg/L, which were stirred through piping air into the beaker at a flux of 50 mL/min. The reaction vessel was exposed to the high-pressure mercury lamp perpendicularly. The distance between the lamp and the vessel was kept at 20 cm. Following the exposure to visible-light, the decolorizations of methyl orange at its maximum absorption wavelength (449 nm) or methylene blue at its maximum absorption wavelength (625 nm) was analyzed by using UV–Visible (UV–Vis) spectrophotometer and recorded as a function of time. The UV–Vis spectrophotometer was also used to measure the absorbance spectrum of the films. All operations were conducted at ambient temperature.

3. Results and Discussions

3.1 Structure characterization of TiO2/ZnO films

Figure 1 shows the XRD patterns of ZnO, TiO2 and TiO2/ZnO films deposited on quartz substrate. From the pattern of the ZnO film only two peaks of (002) and (103) plane were detected. It shows typical hexagonal structure and strong c-axis orientation. The as-deposited TiO2 film shows typical anatase structure with two peaks of (101) and (004) planes. It is interesting that the TiO2 layer on TiO2/ZnO film shows anatase phase with high c-axis (004) orientation vertical to the bottom ZnO film. The degree of crystal-axis orientation can be estimated using the Lotgering orientation factor f23

\[ f = \frac{P_{hkl} - P_{0}^{0}}{1 - P_{0}^{0}} \]  

where \( P_{hkl} \) is peak intensity ratio of the oriented (hkl) direction to the sum of all diffraction directions for oriented sample and \( P_{0}^{0} \) is the corresponding value for the standard sample (from JSPDS card). The orientation factor \( f = 1 \) means the complete orientation growth of the (hkl) direction; on the other hand, complete random state is shown by \( f = 0 \).22

The values of \( f_{(004)} \) for as-deposited TiO2 film and the top TiO2 layer on the double-layer film are calculated to be 0.07 and 0.92, respectively. That is, the TiO2 film shows nearly random growth, while TiO2 layer of the double-layer film shows nearly complete (004) c-axis orientation growth. Meanwhile, only the (002) peak of the bottom ZnO can still be detected. That indicates that the bottom ZnO layer grew directionally in the process of TiO2 film deposition. Similar study has been reported before: the (001) oriented BaTiO3 thin films by using [0001] texture ZnO template were successfully fabricated.23

The crystal structure of anatase TiO2 is tetragonal crystal lattice with the standard constants: \( a = 0.37854 \text{ nm} \) and \( c = 0.95143 \text{ nm} \). ZnO has wurtzite structure with the standard lattice constant of \( a = 0.32498 \text{ nm} \) and \( c = 0.52066 \text{ nm} \). The experimental lattice constant \( c \) of TiO2 film deposited on ZnO film can be calculated by Bragg equation: 2d\( \sin \theta = n \lambda \) through the diffraction peak angle of (004) plane. The calculated result is \( c = 0.9561 \text{ nm} \), which is much bigger than the standard value. As the matching relationship between TiO2 and ZnO is \( (004)_{\text{TiO2}} // (002)_{\text{ZnO}} \), the value of the lattice mismatch \( \delta \) can be calculated by the equation below:24

\[ \delta = \frac{a_{t} - a_{s}}{a_{s}} \]  

where \( a_{t} \) and \( a_{s} \) denoted the lattice parameter of the film (TiO2, \( a_{t} = 0.37854 \text{ nm} \)) and the substrate (ZnO, is considered as the substrate for TiO2, \( a_{s} = 0.32498 \text{ nm} \)), respectively. Therefore, the calculated lattice mismatch value is \( \delta = 16.5\% \). As \( a_{t} > a_{s} \), this bigger lattice mismatch may cause a compressive internal stress on TiO2 lattice in horizontal direction and hence a lattice shrinkage of TiO2 in this direction. To balance this compressive internal stress, a lattice expansion in vertical direction or c-axis direction (0.9561 nm/0.95143 nm = 1.005) is reasonably expected.

Figure 2 shows the FESEM images of TiO2, ZnO and TiO2/ZnO thin films. It is seen from Figs. 2(a) and 2(b) that the TiO2 film shows wafer grains with average grain size of 24 nm and ZnO film shows column grains with average grain size of 22 nm. Figure 2(c) shows the 45° perspective view image of TiO2/ZnO film and the EDX spectra of point A and B. It can be confirmed that the bottom layer of the film (point A) is ZnO film and the top layer is TiO2 (point B). In order to observe the morphology and structure of the film...
clearly, a high resolution FESEM image was shown in Fig. 2(d). The thicknesses of the ZnO layer and TiO2 layer were measured to be about 100 and 450 nm, respectively. The ZnO film deposited on quartz substrate shows column grains with average diameter of about 40 nm, while the TiO2 deposited on ZnO film are nanorods of rectangular or polygon column with average diameter about 100 nm and length of about 450 nm, whose growth direction is [001] direction [see Figs. 2(d) and 2(e)].

Further structural characterization of the TiO2/ZnO film was revealed by using TEM. From the TEM image of a piece of the double layer film shown in Fig. 3(a) it can be seen that the film was very dense and uniform. The short bottom (left) part is ZnO and the long right part is TiO2. The SAED [Fig. 3(b)] diffracted on Fig. 3(a) reveals the coexistence of both TiO2 and ZnO. The TEM observation of one selected TiO2 nanorod is shown in Fig. 3(c). It is seen that the TiO2 nanorod presents obviously rectangular column. The attached
SAED shown in Fig. 3(d) indicates that the TiO$_2$ nanorod is a single crystalline throughout its length. Figure 3(e) shows the HRTEM image of the selected area of Fig. 3(c). In order to reveal it clearly, Fig. 3(f) shows the enlarged filtered image and the atomic arrangement simulation image of the zone framed in Fig. 3(e). By the filtered image the growth orientation of the nanorod is determined to be along [001] direction, which is the growth axis parallel to the substrate surface according to Fig. 2(d). Both the filtered image and the atomic simulation image (simulation state: indices of zone axis: [010]; JEM-2100F: 200 KV, Cs = 1.0 mm; thickness: 11 nm; defocus: 92 nm; no aperture) show that the TiO$_2$ nanorods grown on the ZnO film have high crystal quality.

### 3.2 Optical and photocatalytic properties

Figure 4 shows UV–vis absorption spectra of TiO$_2$, ZnO and TiO$_2$/ZnO films. Compared with that of the TiO$_2$ film, the absorption spectrum of TiO$_2$/ZnO film obviously shifts to visible light and displays an evident enhancement of photo-absorptions in visible region. The optical absorption coefficient $\alpha$ near the absorption edge obeys the following relation for high photon energies: $(a(hv - E_g)^n)$. 

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Fig. 3 The TEM and HRTEM images: (a) TEM image of the TiO$_2$/ZnO double-layer film; (b) the SAED of (a); (c) TEM image of the TiO$_2$ nanorods; (d) the SAED of (c); (e) the HRTEM image of the selected area of (c); (f) enlarged filtered image and the atomic arrangement simulation image of the zone framed in (e).
where $A$ is a constant, $\alpha$ (cm$^{-1}$) is the absorption coefficient and $h\nu$ (eV) is the energy of excitation, $n$ is 0.5 and 2.0 for a direct transition semiconductor and indirect transition semiconductor, respectively. Assuming the absorption coefficient $\alpha$ corresponding to the band gap energy, in the fundamental absorption region, better linearity was observed from the $(\alpha h\nu)^2$ vs. $(h\nu)$ plot, which was used to determine the band gap energy ($E_g$). The band gaps of TiO$_2$, ZnO and TiO$_2$/ZnO film were estimated to be 3.33, 3.26 and 3.03 eV, respectively. The significant red shift has also been reported by other studies. These differences in the surface state, which promote the separate absorption region, better linearity was observed from the $(\alpha h\nu)^2$ vs. $(h\nu)$ plot, which was used to determine the band gap energy ($E_g$). The band gaps of TiO$_2$, ZnO and TiO$_2$/ZnO film were estimated to be 3.33, 3.26 and 3.03 eV, respectively. The significant red shift has also been reported by other studies. It may be owing to insignificant differences in the surface state, which promote the separate efficiency of photogenerated charges and extend the range of excited spectrum.

Figure 5 shows the room temperature photoluminescence (PL) spectra of TiO$_2$, ZnO and TiO$_2$/ZnO thin films on quartz glass substrate. The TiO$_2$ film shows no UV emission and weak visible emission, while the ZnO film shows strong UV emission (around 376 nm) with a narrow full width at half maximum (FWHM) of 18 nm (or 0.15 eV) and a weak deep level emission around 558 nm (2.22 eV). The strong UV emission from ZnO film is attributed to the high quality ZnO film preferred grown on c-axis orientation. Compared to the spectra of single TiO$_2$ film and ZnO film, the PL spectrum of TiO$_2$/ZnO film shows a lower UV emission and a slightly higher deep level emission. Because TiO$_2$ shows no UV emission, the UV emission should come from the bottom ZnO film and was weakened by the top TiO$_2$ layer. The deep level emission may result from the cooperation of TiO$_2$ and ZnO films. That is, some excited UV photons from ZnO may have been absorbed by the coated TiO$_2$ nanorods, and the TiO$_2$ nanorods were excited by both the laser light and UV emission from the bottom ZnO. These two excitation channels enhance the intensity of deep level emission of the TiO$_2$/ZnO thin film to be higher than that of the as-deposited TiO$_2$ film.

Table 2 shows the degradation efficiency of the TiO$_2$ ZnO and TiO$_2$/ZnO films for methyl orange and methylene blue for 10 h. The TiO$_2$/ZnO film shows the highest degradation efficiency of methyl orange: 32.9%, which is 29% higher than that of TiO$_2$ film and 73% higher than that of ZnO film. All the films show low-rise degradation efficiency at high wavelength range of 665 nm. Comparing with the natural degradation efficiency of 5.9% of methylene blue without catalysts, ZnO film shows no evident increase of degradation efficiency (8.7%), and TiO$_2$ film shows a limited increase of 12.3%. TiO$_2$/ZnO double layer film still exhibits the highest degradation efficiency of 18.6%, which is 50% higher than that of TiO$_2$ film. So the TiO$_2$/ZnO double layer film exhibits improved photocatalytic activity in a relative wide visible light region and can be considered as a potential photocatalytic material for pollutant degradation in water environment, as the fabrication processing and cost are similar to those of TiO$_2$ and ZnO films. The improved photocatalytic property can be explained by the following three reasons:

1) The wavelength response range of TiO$_2$/ZnO film estimated by the optical band-gap is <409 nm (3.03 eV), which is larger than those of TiO$_2$ film and ZnO film (<372 nm (3.33 eV) and <380 nm (3.26 eV), respectively), as shown by Fig. 4. The double layer film also shows obviously enhanced absorption ability in wide visible-light region. So, more visible-light can be utilized in photocatalytic process.

2) Although the ZnO and TiO$_2$ have similar band gap, the composite of them may modify the electrons and holes migration process. Both the electrons transition between the conduction band of TiO$_2$ and conduction band of ZnO and the corresponding holes transition between the ZnO valence band and TiO$_2$ valence band increase the channels for

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A$ at 449 nm (a.u.)</th>
<th>$A$ at 665 nm (a.u.)</th>
<th>$D$ of methyl orange (10 h) (%)</th>
<th>$D$ of methylene blue (10 h) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No sample</td>
<td>0.00</td>
<td>0.00</td>
<td>6.8</td>
<td>5.9</td>
</tr>
<tr>
<td>TiO$_2$ film</td>
<td>0.054</td>
<td>0.006</td>
<td>25.5</td>
<td>12.3</td>
</tr>
<tr>
<td>ZnO film</td>
<td>0.097</td>
<td>0.033</td>
<td>19</td>
<td>8.7</td>
</tr>
<tr>
<td>TiO$_2$/ZnO film</td>
<td>0.38</td>
<td>0.101</td>
<td>32.9</td>
<td>18.6</td>
</tr>
</tbody>
</table>

$A$ is the absorption of the film.

$D$ (Degradation efficiency) = $A_i - A_f$/ $A_i$ ($A_i$ is the absorption of the indicator after degraded, $A_f$ is the absorption of the original indicator).

![Fig. 4 Optical absorption spectra of the TiO$_2$, ZnO and TiO$_2$/ZnO thin films.](image)

![Fig. 5 PL spectra obtained from TiO$_2$, ZnO and TiO$_2$/ZnO films.](image)
electrons and holes transition and hence can greatly reduce the recombination probability of electron–hole pairs.14) (3) When the double layer film irradiated by light not only the TiO2 nanorods involved in the photocatalytic process, but also the ZnO in the bottom joined in the photocatalytic reaction since the top TiO2 has high transmittance (>90%) in wave length region >370 nm. Since the PL process proceeds in the same time as the light irradiation, the top TiO2 nanorods were excited by both the exposure light and UV emission from the bottom ZnO film just as shown in Fig. 6. More effective use of irradiation light can obviously improve the photodegradation efficiency.

4. Conclusions

Nanocrystalline double layer thin films of TiO2/ZnO were prepared by pulsed laser deposition on quartz glass substrate. The microstructure and the optical property of the film were investigated. It was found that the TiO2 film on the ZnO film grow with nanorod mode and the growth matching relationship of TiO2 and ZnO is (004)TiO2 // (002)ZnO. TiO2/ZnO film showed enhanced absorption in visible light. The top TiO2 nanorods were excited by both the laser light and UV emission from the bottom ZnO, so its deep level emission was extended. The double layer TiO2/ZnO film showed improved photocatalytic activity in the degradation of methyl orange, which is attributed to its wide wavelength response range, more effective use of irradiation light and the retarded recombination of electron–hole pairs of the two phase film.

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