Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2012, Article ID 758539, 8 pages
doi:10.1155/2012/758539

Research Article

Doped Titanium Dioxide Films Prepared by Pulsed Laser Deposition Method

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Received 28 January 2012; Accepted 2 April 2012

Academic Editor: Baibiao Huang

TiO_2 was intensively researched especially for photocatalystic applications. The nitrogen-doped TiO_2 films prepared by pulsed laser deposition (PLD) method were reviewed, and some recent new experimental results were also presented in this paper. A new optical transmission method for evaluating the photocatalystic activity was presented. The main results are (1) PLD method is versatile for preparing oxide material or complex component films with excellent controllability and high reproducibility. (2) Anatase nitrogen-doped TiO_2 films were prepared at room temperature, 200°C, and 400°C by PLD method using novel ceramic target of mixture of TiN and TiO_2. UV/Vis spectra, AFM, Raman spectra, and photocatalystic activity for decomposition of methyl orange (MO) tests showed that visible light response was improved at higher temperature. (3) The automatic, continuous optical transmission autorecorder method is suitable for detecting the photodecomposition dynamic process of organic compound.

1. Introduction

1.1. General Description of Preparation of TiO_2 Films. In recent years, the field of photocatalysis has became an extremely well-researched field due to wide application interest in self-cleaning surfaces, water or air purification, self-sterilizing surfaces, antifogging surfaces, optical or gas sensor [1–4], and so forth. TiO_2 is a fascinating material that has been intensively researched by worldwide researchers. For photocatalystic applications, much attention has been paid to prepare and use TiO_2 powder, for it has large specific area [5, 6], but it has shortcoming of difficulty to recycle in aqueous fluid. TiO_2 films have been prepared by many technologies, including chemical bath deposition (CBD) method [7, 8], electron-beam evaporation [9], reactive electron beam evaporation [10], magnetron sputtering [11, 12], sol-gel [6, 9, 13–17], and thermal oxidation [18, 19].

Much effort has been given to understanding and altering the optical properties of titanium dioxide, especially for enhancing visible light absorption mainly by narrowing the band gap (3.2 eV) for using the economical and ecological sunlight. Theoretical calculations have been performed to clarify the effect of anion doping of TiO_2 on band gap modifications [20–22].

Nitrogen-doped TiO_2 materials were intensively researched since Asahi et al. proposed that it has narrow band gap and little recombination of electrons and holes [23]. However, Batzill et al. reported that no band gap narrowing is observed for N-doped TiO_2 single crystals, but N-doping induces localized N 2p states within the band gap just above the valence band (VB). N is present in an N(III) valence state, which facilitates the formation of oxygen vacancies and Ti 3d band gap states at elevated temperatures. This thermal instability may degrade the catalyst during applications [24]. Socol et al. proposed that both substitutional N and O vacancies contribute to the visible light absorption [25]. The width of the TiO_2 band gap was not affected by the presence of fluorine either, as reported by Todorova et al. [5]. The red shift of the absorption edge was attributed to the increased rutile content in the fluorine-doped TiO_2 powers. The codoping effect between nitrogen and hydrogen is responsible for the

enhanced photoactivity of N-doped TiO_2 in the range of visible light [26].

Balek et al. prepared nitrogen and fluorine codoped titania photocatalyst samples for air purification by spray pyrolysis method [27]. A high photocatalytic activity in a visible light region of spectrum depended on the spray pyrolysis temperature and can be ascribed to a synergetic effect of nitrogen and fluorine doping. Synergetic effect also happened in Nd_2O_3 modified TiO_2 nanoparticles, formation of the surface anatase/rutile phase junction favors photoinduced charge separation and further improves its photocatalytic activity [28].

Qu et al. prepared Fe(3+) and Ce(3+) codoped nanostructure titanium dioxide films via the improved sol-gel process. The samples had smaller crystal size, larger surface area, and larger pore volume. They also found that codoped ions could obviously not only suppress the formation of brookite phase but also inhibit the transformation of anatase to rutile at high temperature. Fe(3+)/Ce(3+) codoped TiO_2 film showed excellent photocatalytic activity compared with pure TiO_2 film, Fe(3+) or Ce(3+) single doped TiO_2 film. They concluded that the surface microstructure of the films and improved sol-gel process ions doping methods are responsible for improving the photocatalytic activity [29].

Our group has reported works about hydrophilicity between titanium oxide coatings with and without addition of silica. Through the investigation of change of water contact angle on the surface after UV exposure and sunlight radiation, it can be concluded that hydrophilicity of mixed coatings with low-temperature heat treatment of titanium oxide and silica is much better than a pure titanium oxide coating. This effect makes for an improved self-cleaning coating under natural sunlight. The mechanism is that particles of titanium oxide separated by silica reduce the contact chance of recombination of electrons and holes, thereby increasing the photocatalytic action on organic compounds. The addition of silica increases water absorption in the coating. Water molecules absorbed by silica will be photocatalyzed to free hydroxyl groups under the illumination of UV light. These groups benefit the hydrophilicity of coating [30].

As for photo-induced hydrophilic effect, Fujishima et al. have reached the conclusion that there is an aspect of this effect that does not involve simply the cleaning of the surface. The precise nature of the effect has not been elucidated even now, but researchers proposed that the surface species are basically the same ones involved with conventional photocatalysis [2]. Hendersonpresented recent research highlights of the significant insights obtained from molecular-level studies of TiO_2 photocatalysis. This comprehensive review has illustrated how a surface science perspective on TiO_2 photocatalysis can provide unique insights and motivate more fundamental research in photocatalysis [3].

1.2. TiO_2 Films Prepared by PLD Method. PLD technique is a versatile tool for preparing thin-films, because it is capable of preparing films with various properties by simply adjusting the deposition conditions, like the type of target, type of substrate and its temperature, distance between the target and substrate, type and pressure of ambient air, and laser wavelength, and so forth. Its advantages for the film growth of oxides and other multicomponent materials include stoichiometric transfer, growth from an energetic plasma plume, reactive deposition, good adherence to the substrate surface, excellent controllability, and high reproducibility. PLD has played a significant role in advancing our understanding of the physics of the thin-film structures, the material science of a new system, and so forth [31].

With the use of PLD, TiO_2 films doped with metal, transition metal, or nonmetallic elements have been prepared, and their properties were controlled by varying the preparing parameters [25]. Socol et al. have grown crystalline anatase phase TiO_2 thin films by PLD technique in oxygen, nitrogen, and methane and nitrogen with oxygen mixture. Their studies proved the positive influence of anion doping on the photoreduction activity under visible light exposure. The best photoactivity under visible light exposure was obtained for films deposited in pure nitrogen, which was correlated with the highest red-shift (480 nm) of the absorption edge and the larger nitrogen incorporation characteristic to these films. Quite different evolutions were observed in case of UV light irradiation. Significant results were obtained in this case for the films deposited in pure oxygen or methane, while the photoactivity (quantum yield) of the films deposited in nitrogen was lower as compared with the blank.

Sato et al. prepared N-doped TiO_2 films by the atmospheric controlled PLD (AC-PLD) method to generate visible light active photocatalytic films [32]. For nitrogen doping, the use of CH(3)CN gas was found to be more effective than the use of NH(3). The visible light absorption properties of the films were very sensitive to the CH(3)CN partial pressure during ablation. When using CH(3)CN, nitrogen and an equal quantity of carbon was uniformly doped into the TiO_2 films. The resultant films showed better catalytic performance than those which were either undoped or doped using NH(3). It is also suggested that stronger reducing agents such as carbon are required for doping nitrogen into TiO_2 films.

Metal nanoparticles can act as electron traps due to the formation of a Schottky barrier at the metal-semiconductor contact. Holes can decompose organic substances more efficiently, because it has strong oxidative power. Sauthier et al. used PLD technique to prepare Ag-TiO_2 nanocomposites to improve photocatalytic activity and compared with that of bare TiO_2 [33]. It was proposed that two distinct mechanisms can contribute to the enhanced photoreactivity under near-UV irradiation. The first is Ag NPs retard electron-hole recombination by photogenerated electron transfer from TiO_2. And the second one is localized surface plasma resonance absorption of Ag NPs, which can have positive effect on the photocatalytic activity.

The films with more clusters exhibited higher photocatalytic performances than the films with less clusters [34]. The author pointed out that the specific surface area of the films was increased by the deposition of clusters. The larger contact area induces high decomposition rate [35]. It is interesting that the clusters formed in PLD method are not desirable in other semiconductor industrial fields, like

solar cell and so forth, where smooth and uniform surface is desirable [36]. Suda et al. found that the particle size is changed with the substrate temperature, and larger particle size was obtained at higher temperature [37]. Table 1 lists part of the publications about the preparation of TiO_2 films by PLD method in recent years.

Chen et al. obtained heavily nitrogen doped of about 15% anatase TiO_2 films by using TiN target. Different from using N_2 gas as N source, TiN target as solid source might provide reactive molecular or cluster species with Ti-N bonds [43]. Suda et al. measured depth profiles of the prepared films by XPS and found that the film prepared using TiO_2 target has little nitrogen, while the film prepared using TiN target has almost 8% atomic ratio of nitrogen [37]. Somekawa et al. proposed that the N-doping occurred when N species and TiO_2 particles collide on the substrate [46]. We consider that when the laser pulse irradiate onto the solid N source, N ion with high energy is produced and ejects to the substrate. It is quite easier to migrate and incorporate into the film lattice than using the N_2 or NH_3 gas as N source.

One advantage of PLD technique is that there is stoichiometric transfer of material from target to film [31]. For preparing N-doped TiO_2 films, we used a novel type of target, ceramic target mixture of TiN and TiO_2 (molar ratio 1 : 3), different from pure TiN or TiO_2 targets used by other researchers [37, 43]. Energetic N ion, O ion, and Ti ion, produced at the same time with high-intensity pulsed laser irradiation may promote the growth of doped TiO_2 films.

2. Experiments

The N-doped TiO_2 thin films were prepared inside a stainless steel reaction chamber. A KrF excimer laser (wavelength: 248 nm, pulse frequency: 10 Hz, pulse duration: 25 ns) was used for the irradiation of N : TiO_2 targets. The target was prepared from TiN and TiO_2 powders (molar ratio 1 : 3) by pressing at 5 MPa and sintered at 1100°C for 4 h. The laser beam incidence angle onto the target was chosen of about 35°. The incident laser fluence on the target surface was set at about 2.5 J/cm^2.

To avoid piercing, the target was rotated at 10 rpm. And laser spot was scanned on the target surface to prepare large area film of 50 mm in diameter. The substrate is a round normal glass slip with 50 mm in diameter, its temperature was controlled from room temperature (RT) to 400°C. The dynamic ambient gas pressure during the irradiations was kept at 1 Pa by feeding pure oxygen and nitrogen gas (99.9%, ratio: $O_2 : N_2 = 1 : 1$) into the chamber for reduction the desorption loss in vacuum. After the preparation was completed, the sample was cooled down to RT with the same oxygen gas pressure.

The sample surface morphology was investigated by domestic CSPM5000 atomic force microscopy (AFM) test. Optical transmission spectra in the near UV and visible spectral regions were studied by PerkinElmer Lamda 950 UV/VIS spectrometer. The Raman spectra test was performed at room temperature with a Renishaw Invia Reflex confocal micro-Raman apparatus with He-Cd laser emitting at 325 nm.

The photocatalytic activity of the N-doped TiO_2 films with surface area of about 18 cm^2 was studied by decompositing organic methyl orange (MO) dye in aqueous solution. The initial concentration of MO solution is 2 mg/L, and the total solution is about 80 mL. A tungsten halogen lamp was used as visible light source with 180 mW/cm^2 power density on the surface of the MO solution. During the photodegradation experiments, the absorbance of the solution was measured at 460 nm wavelength, which corresponds to the peak absorbance of MO. The intensity of the transmitted detecting light was recorded by a data recorder, whose data sampling interval was set as 2 minutes. This photocatalystic activity evaluating experimental method has not been used before to our knowledge.

3. Results and Discussion

3.1. Optical Spectra. The sample color is transparent prepared at RT or 200°C, and light yellow at 400°C. Figure 1 shows the transmission spectra of N-doped TiO_2 films prepared under different temperature. The absorption edges shift toward longer wavelengths from 300 nm to 350 nm with the increase of the substrate temperature, indicating a decrease in the band gap of the films, which may due to the N composition increase with the increasing temperature. This is different from the results suggested by Farkas et al. [47]. Another reason is the grain size increases with increasing temperature, resulting to weak quantum size effects causing the red-shift of the absorption edge [48]. X-ray photoelectron spectra measurement should be performed to detect the state and component of N element in the films. The N element is usually formed as $TiO_{2-x}N_x$ in films prepared by PLD method [42, 43, 47].

3.2. AFM Measurements. Figure 2 shows the AFM images of N-doped TiO_2 films prepared at room temperature, 200°C, and 400°C. The grain sizes are 18.5, 19.2, and 28.1 nm, and their root mean square (rms) of roughness is 3.32, 3.96, and 6.73 nm, respectively. This is in agreement with results obtained by Suda et al. [37]. With the temperature increasing, the grain size and roughness increase, which suggests an increase of crystallinity of the films, and inducing red-shift in absorption spectrum because of quantum size effect.

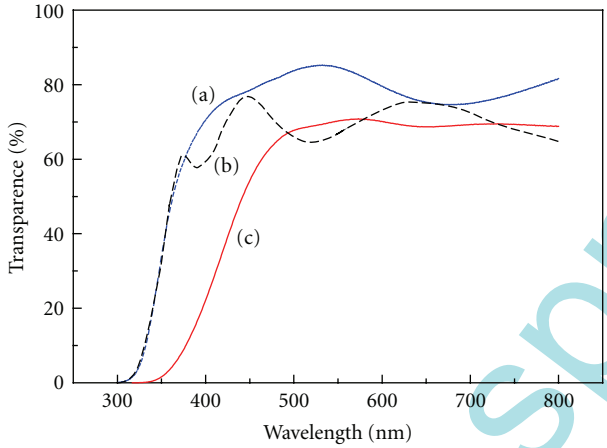
3.3. Raman Spectra. The micro-Raman spectra of TiO_2 films are shown in Figure 3. It can be seen that intense Raman peak does not occur until temperature reaches 400°C, indicating the crystallization realized at that point. This is in accord with that in [48]. In our experiments, only anatase structures appearing as the typical Raman modes at 145, 198, 396, 517, and 640 cm^{-1} are assigned to the E_g, E_g, B_{1g}, A_{1g}, and E_g modes, respectively. The strongest mode at 145 cm^{-1} indicates that the anatase phase with a long-range order has been obtained [49].

3.4. Photocatalystic Activity. Shinguu et al. proposed a reflectance method to evaluate the photodecomposition rate of TiO_2 films [41]. We have used the conductivity

Table 1: Preparation of TiO_2 thin films by PLD method.

Laser	Substrate	Target	Dopant	Crystalline phase	Ambient air	Photocatalytic activity *	Year	Ref.
Nd:YAG,532 nm	glass	TiO_2	—	rutile	O_2	—	1999	[38]
ArF 193 nm	Mica, quartz, Si	TiO_2	—	Rutile, anatase	Ar	—	2002	[39]
ArF 193 nm	α-Al_2O_3	Ti	—	Rutile, anatase	O_2	—	2004	[40]
Nd:YAG,266 nm	Si	TiO_2	—	Rutile, anatase	O_2	MB, anatase with clusters	2005	[34]
Nd:YAG,532 nm	SiO_2(corning 7059)	Ti,TiO,TiO_2,TiN	N	anatase	O_2, N_2	MB, TiN target	2005	[37]
Nd:YAG,532 nm	Glass	Ti	N	anatase	$NH_3/N_2/O_2$	—	2006	[26]
KrF 248 nm	Si or quartz glass	Ti, TiO_2, WO_3	multilayer	—	O_2	MB, WO_3, 5%	2006	[41]
Nd:YAG,1064 nm	quartz glass	TiO_2	N	anatase	O_2, N_2	MB, MO, Eg = 1.0 eV, 2.5 eV	2008	[42]
KrF 248 nm	LSAT	TiO_2,TiN	N	anatase	O_2	—	2008	[43]
Nd:YAG,266 nm	quartz	TiO_2, La_2O_3	La	Rutile	N_2	MB, 900°C postannealing	2009	[44]
KrF 248 nm	glass	TiO_2	C, N	anatase	O_2, N_2,CH_4	Cr(II), N doped	2010	[25]
KrF 248 nm	SiO_2 quartz	TiO_2	N	anatase	O_2, N_2	—	2010	[45]
KrF 248 nm	SiO_2 quartz	Ag, TiO_2	—	anatase	O_2	MB	2011	[33]

* Organic compound for decomposition and optimal conditions obtained. MO: methyl orange, MB: methylene blue, Cr(II): toxic Chromium ion, it can be photoreducted to Cr(III) state.



(a) RT
(b) 200°C
(c) 400°C

Figure 1: Transmission spectra of N-doped TiO_2 films prepared at different temperature, (a) RT, (b) 200°C, (c) 400°C.

method to check the rate [35, 50]. Recently, we developed a transmittance method to detect the concentration of the MO to evaluate the photocatalystic activity of the N-doped TiO_2 films. The setup is shown in Figure 4. The light source can be visible or UV light as demand. The LED light is 460 nm or 650 nm wavelength, which corresponds to the peak absorbance of MO or MB. The relationship between the transmittance and concentration was calibrated. This method has the advantages of continuous, automatic check without disturbing the reaction process, and avoiding danger to operator when use UV light source, and so forth.

Figure 5 shows the decomposition rate with time of MO using N-doped TiO_2 films prepared at different temperatures under visible light irradiation. It is clearly shown that photocatalystic activity of N-doped TiO_2 films strongly depends on the preparation temperature. MO was almost decomposed completely after 4 hours for sample prepared at 400°C. This is due to band gap narrowing by nitrogen atom, larger surface area, and better crystallization at higher temperature.

3.5. Discussions. TiO_2 film is a versatile material for use in many fields. For photocatalysis applications, the main problems are to narrow the band gap for visible light and to retard the recombination of electrons and holes. Anion or cation doping, or codoping, noble mental, and multilayer structure modification methods, and so forth have been proposed to improve TiO_2 photocatalystic activity till now. PLD technique is a widely used method to prepare oxide materials; it is easy to change the growth parameters to get various properties of doped films. Its controllability and reproducibility provide much convenience for base research of films materials with high melting point or multicomponent.

In our N-doped TiO_2 preparation experiments, laser pulses with intensity density about 1.0×10^{12} W/m^2 was irradiated onto the surface of N : TiO_2 ceramic target. Plasma plumes were produced. Energetic N ion, Ti ion, and O ion, as well as N containing TiO_2 micrograins are ejected from the target surface to the glass substrate. The TiO_2 crystal nucleus formed and became larger with the subsequent plasma plume until they combined with each other to form thin film. During this process, N element was easier to incorporate into the lattice of TiO_2 as oxygen substitutor or interstitial atoms than that using N_2 air as N source, due to it got energy from the laser irradiation directly [37, 43]. Higher substrate temperature, 400°C in our procedure, is beneficial to form crystallization, and larger grains as shown in the AFM image. Large grains and high rms of roughness provide large surface area resulting to big contact chance of organic compound. Mole ratio of TiN and TiO_2 in target is 1 : 3, but we can speculate that the corresponding ratio inside the film is smaller due to relative easier desorption of small mass atom

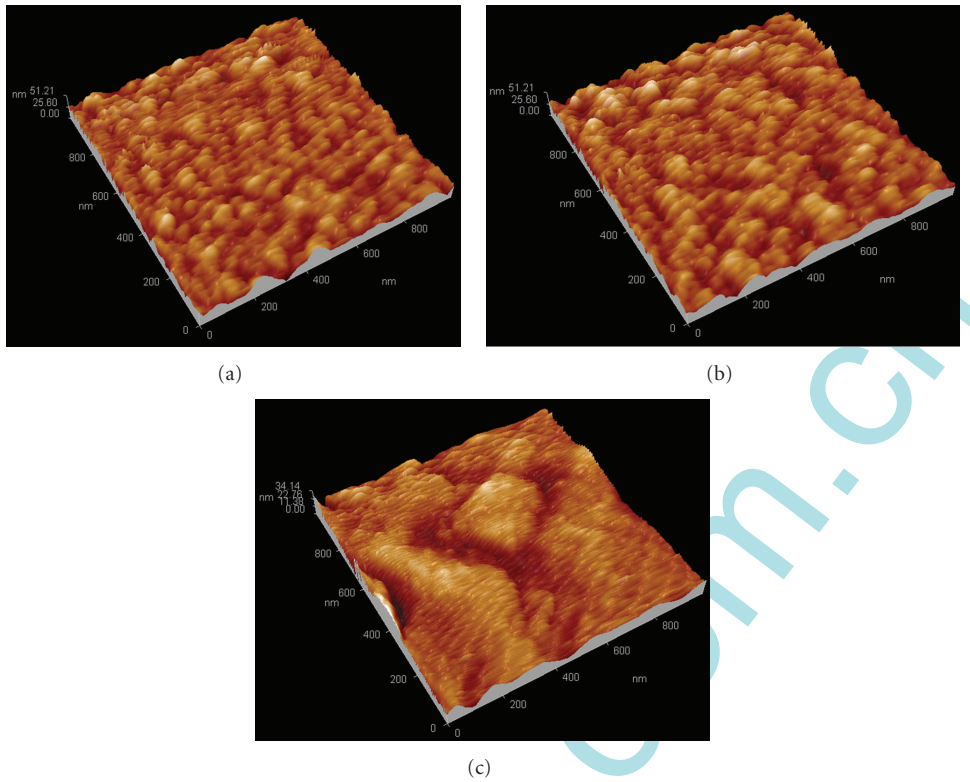
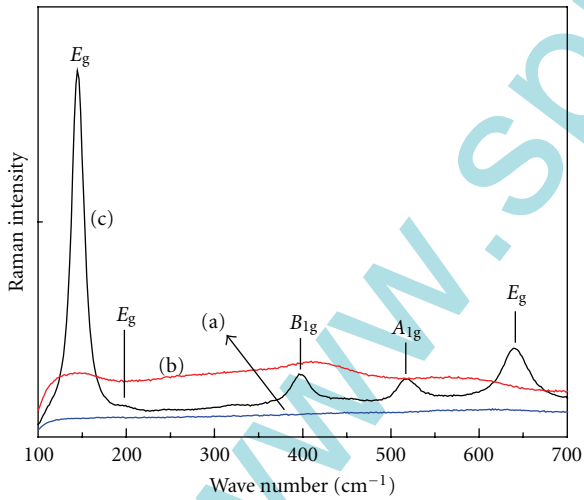


Figure 2: AFM images of the surface morphology of N-doped TiO_2 films under different temperature, (a) RT, (b) 200°C, and (c) 400°C.



(a) RT
(b) 200°C
(c) 400°C

Figure 3: Raman spectra of N-doped TiO_2 films prepared at different temperature, (a) RT, (b) 200°C, (c) 400°C.

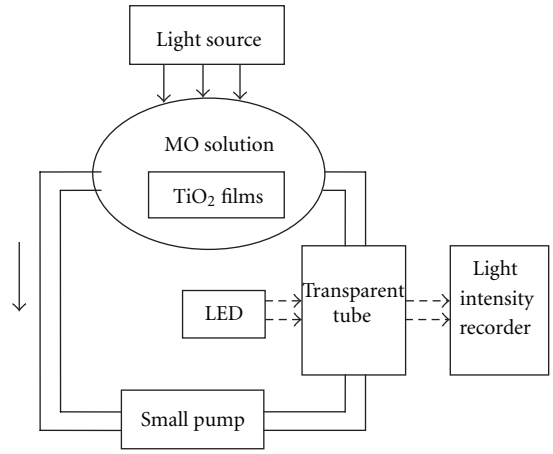
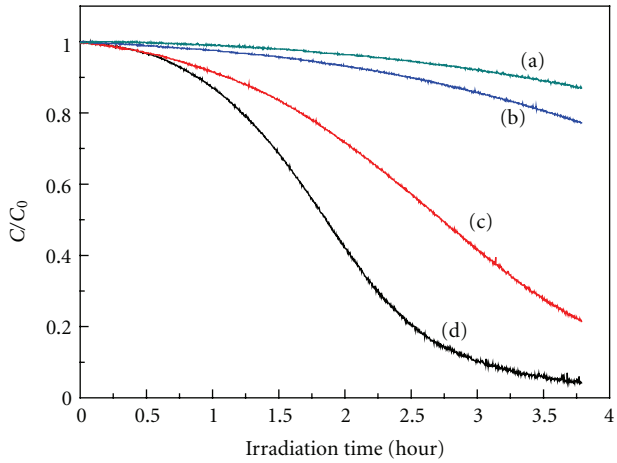


Figure 4: The schematic diagram of experimental setup for automatic detecting the photodecomposition rate. The whole setup is put in an aluminum box. The data record interval can be set from 1 minute to 1 hour. MO solution: methyl orange solution.

from the film surface [31]. MO was almost photodegraded completely using visible light after 4 hours.

Tachikawa et al. concluded that the adsorption dynamics of substrates and organic compound, the electronic interaction between TiO_2 and adsorbents, and the band structure and morphology of TiO_2 nanomaterials are crucial factors for establishing efficient photocatalytic reaction systems. The morphology of TiO_2 affects the charge recombination dynamics, and anisotropic adsorption was found in recent research [51].

Photocatalysis is a complex process involving chemical and physical reactions. The researchers should combine



(a) Blank
(b) RT
(c) 200°C
(d) 400°C

Figure 5: Decomposition rate with time of MO using N-doped TiO_2 films prepared at different temperature under visible light irradiation, (a) without TiO_2, (b) RT, (c) 200°C, (d) 400°C. C_0 is the initial concentration of Methyl orange about 2 mg/L, and C is the concentration changing with time.

chemical methods and physical methods to overcome problems from photocatalystic material modification to degrade organic compound. For example, Rimeh et al. prepared Ti/TiO_2 electrode by PLD technique and obtained a degradation rate of almost 75% of chlortetracycline within 2 hours [52].

4. Conclusions

Fascinating TiO_2 films were worldwide researched using various preparing method. PLD technique is a versatile method for preparing films of oxide materials. Its advantages of controllability and reproducibility are suitable for basis research for preparing various properties of TiO_2 films. Some recent experimental results obtained in our group were presented. N-doped TiO_2 anatase films were prepared at substrate temperature from RT to 400°C by PLD method using a novel ceramic target of mixture of TiN and TiO_2 and were characterized by UV/Vis optical spectra, AFM, Raman spectra, and photocatalystic activity for decomposition of methyl orange. It was found that the film crystallinity, the visible light response, and decomposition rate were significantly improved at higher temperature. New method of continuous autodetecting the solution optical transmission for evaluating the photodecomposition dynamic process was developed.

Acknowledgment

Financial support by Shenzhen basic research project of science and technology (JC201005280419A) is gratefully acknowledged.

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