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Nanocrystalline TiO_2 composite films for enhanced photocatalytic activity

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***Abstract*— In order to decompose effectively organic pollutants in wastewater under visible light irradiation, we prepared successfully the Zr^{4+}/H_3BO_3 co-modified TiO_2 film through a simple sol-gel method. The as-prepared films were characterized by field emission scanning electron microscopy (FE-SEM) equipped with energy-dispersive spectroscopy (EDS), Brunauer-Emmett-Teller (BET) surface area, X-ray diffraction (XRD), differential thermal analysis-thermogravimetry (DTA-TG), UV-Vis absorption spectroscopy, and photoluminescence spectroscopy (PL). The FE-SEM images showed that the co-modified film without cracks was composed of smaller nanoparticles compared to pure TiO_2 film. The BET surface area results indicated that the specific surface area of the co-modified TiO_2 sample was 163.8 $m^2\ g^{-1}$, whereas that of pure TiO_2 was 47.9 $m^2\ g^{-1}$. The XRD and DTA-TG results showed that co-modification not only prevented effectively the transition of anatase to rutile but also improved the crystallinity of anatase. The photocatalytic activities were evaluated by degradation of an organic dye (acid naphthol red, ANR) in aqueous solutions. Compared with pure TiO_2 film and a singly-modified film, the co-modified TiO_2 film showed the best photocatalytic performances under both UV and visible light irradiations due to strong visible light adsorption and diminished electron-hole recombination.**

***Index Terms*— Zr^{4+}/H_3BO_3 co-modified, TiO_2 film, Photocatalytic activities**

I. INTRODUCTION

In the last few years, the environmental contamination caused by organic pollutants is becoming an urgent problem due to worldwide industrialization and population growth. Many traditional physical and biological treatment methods have been used to control aqueous organic contaminants.[1] However, these methods had not completely transformed the contaminants into non-hazardous compounds, particularly those with high toxicity but at very low concentration. Advanced semiconductor photocatalytic oxidation technology has received much attention of researchers around the world.[2] Among various semiconductors, titania (TiO_2) is considered as the most widely used photocatalyst owing to its nontoxicity, low cost, long-term stability, strong oxidizing power, and chemical and biological inertness.[3] TiO_2 is a semiconductor with a band gap of 3.2eV. Under UV light irradiation with photon energy $h\nu \geq 3.2$eV, the electrons in valence band will be excited to the conduction band of the semiconductor catalyst to generate electrons and holes. The holes can oxidize the water molecule on the TiO_2 surface to form hydroxide radicals and the electrons can react with oxygen molecule on the TiO_2 surface to form peroxide radicals. Then the peroxide radicals can oxidize electrons and protons to hydrogen peroxide. The hydroxide radicals and hydrogen peroxide can react with the contamination adsorbed on the TiO_2 surface to form carbon dioxide and water. Due to the wide band gap of TiO_2, ultraviolet light only covers 5% of solar energy is a prerequisite to facilitate the desirable electron-hole separation during the catalytic reaction. Furthermore, the main drawback related to its application is that most of the photo-generated electron-hole pairs will undergo recombination before reaching the surface of TiO_2.[4] To unravel these problems, many techniques were proposed to improve photocatalytic activity of TiO_2.[5,6] Metal doping is one of the most effective and simplest methods to modify TiO_2. TiO_2-ZrO_2 composite system or Zr^{4+}-doped TiO_2 used as photocatalyst has been reported recently, because the compositing or doping can potentially reduce the recombination rate of photogenerated carriers.[7] Moreover, acid treatment is another effective method to improve the photocatalytic activity of TiO_2 because the acidizing can increase the surface hydroxide radicals which is favorable to the photoreaction.[8]

Zr^{4+}/H_3BO_3 co-modified TiO_2 films have been developed in this paper. The photocatalytic activity was evaluated by photodegradation of an organic dye (Acid Naphthol Red, ANR) in solution. It is expected that the co-modified TiO_2 film may exhibit excellent photocatalytic activities due to the synergistic effect of two processes.

II. EXPERIMENTAL

2.1. Film preparation

TiO_2 sol was prepared by the sol-gel method. Tetrabutyl titanate ($Ti(OC_4H_9)_4$) is used as raw material, while nitrite acid (HNO_3) is used as catalyst. A total volume of 1 mL $Ti(OC_4H_9)_4$ was dissolved in 20 mL absolute ethanol under vigorous stirring in a clean and dry vessel at room temperature. After 5 min, 20 mL nitric acid solution (0.2 mol L^{-1}) was added dropwise and kept on stirring until the colloidal suspension could be obtained. All sol-films were coated on the surface of glass substrate (25 mm×25 mm×1 mm) by the controllable dip-coating device in the atmosphere. The speed was controlled at 1 mm s^{-1}. After dip coating for different times, the TiO_2 sol film of different thickness was obtained. The thickness of the film was 0.3~0.5 μm in our preparations. $Zr(NO_3)_4{\cdot}5H_2O$ and H_3BO_3 were chosen as zirconium source and acidizing reagent, respectively. The film was treated by 0.08 mL boric acid solution (0.1 mol L^{-1}),

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then 0.02 mL Zr^{4+} ions (1×10^{-3} mol L^{-1}) were doped onto the surface layer via coating a thin Zr^{4+}-doped TiO_2 sol onto as-dried TiO_2 film. Finally, the films were calcined in air at a rate of 5 ℃/ min up to 450 ℃ and left to stay in the furnace for 1 h for organics removal and crystalline TiO_2.

2.2. Catalyst test

The photocatalytic properties of the films were evaluated by degradation of ANR (4×10^{-4} mol L^{-1}) in aqueous solution under both UV and visible light irradiation. The pure TiO_2 and the modified films were settled in 5 mL aqueous target pollutant in a weighing bottle. Prior to irradiation, samples were placed in the dark for 30 min to ensure the establishment of adsorption-desorption equilibrium of target pollutants on the catalyst surface. In our experimentation, a lamp equipped with UV cut-off filters ($\lambda > 400$ nm) was used as a visible light source whose average light intensity was 40 $mW\cdot cm^{-2}$. The wavelength of 365 nm was used as a UV light source whose average intensity of irradiation was 6.5 $mW\cdot cm^{-2}$. UV-Vis spectrophotometer (TU-1901) was adopted to assess the photodegradation activity of the film photocatalysts. Their photocatalytic degradation rate can be calculated by formula: $D = (A_0 - A) / A_0 \times 100\%$, in which A_0 is the absorbency of the target pollutant solution before illumination while A after it. The measurements were repeated for each catalytic system, and the experimental error was found to be within the acceptable limit (±5 %).

2.3. Catalyst Characterization

The surface morphology of the pure TiO_2 and the modified TiO_2 films were characterized by high-resolution field emission scanning electron microscope (FE-SEM). The Brunauer-Emmett-Teller (BET) surface area of the pure TiO_2 and the modified TiO_2 powders were analyzed by nitrogen adsorption/desorption apparatus (ASAP 2020). The identity of crystalline phase and size were identified by D8 Focus X-ray diffraction (XRD) with a diffractometer employing Cu Kα radiation at a scan rate of 0.03° s^{-1}. The accelerating voltage and the applied current were 40 kV and 25 mA, respectively. The crystallization behavior of the pure TiO_2 and the co-modified TiO_2 were monitored using a differential thermal analysis-thermogravimetry (DTA-TG) machine. The UV-Vis diffuse reflectance spectra (DRS) of various films were recorded on a UV-Vis spectrophotometer with an integrating sphere accessory (IS 19-1) using blank glass plate as a reference. The photoluminescence (PL) emission spectra were recorded at room temperature by a FLS 920 spectrometer with a 300 nm line of 450 W xenon lamps as excitation source.

III. Results and Discussion

3.1. Photocatalytic activity

Fig. 1 shows UV–Vis absorption spectra (a) and degradation percentage (b) of ANR solutions using pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films on glass substrates under UV-lamb irradiation with wavelength of 365 nm for 45 min. From Fig. 1b, it can be seen that the average degradation rates of aqueous ANR solution using Zr^{4+}/H_3BO_3 co-modified TiO_2 is 84.2%, compared with Zr^{4+} doped TiO_2 51.1%, H_3BO_3 acidized TiO_2 66.8%, and TiO_2 film18.2%.

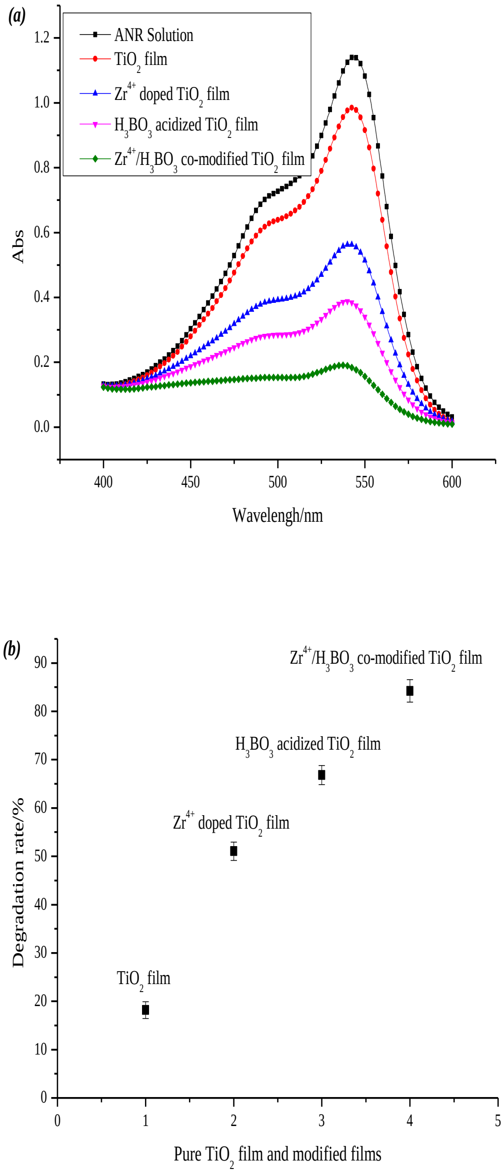


Figure 1

Fig. 1- UV–Vis absorption spectra (a) and degradation percentage (b) of ANR solutions using pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films on glass substrates under UV-lamb irradiation with wavelength of 365 nm for 45 min.

Fig. 2 shows decomposition kinetics of ANR solution using pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films under visible light irradiation for 2 hours. It can be observed that the degradation rate of ANR solution using the Zr^{4+}/H_3BO_3 co-modified TiO_2 film is 90.4%, compared with Zr^{4+} doped TiO_2 film 45.4%, and H_3BO_3 acidized TiO_2 film 57.9%. It also should be noted that the degradation percentage of ANR using pure TiO_2 film is about 30.6%. This is due to the fact that the adsorbed dyes can absorb visible light to be excited and electrons can be injected into the conduction band of TiO_2 to realize the charge separation and extend the photo-response of TiO_2 from UV to visible region.

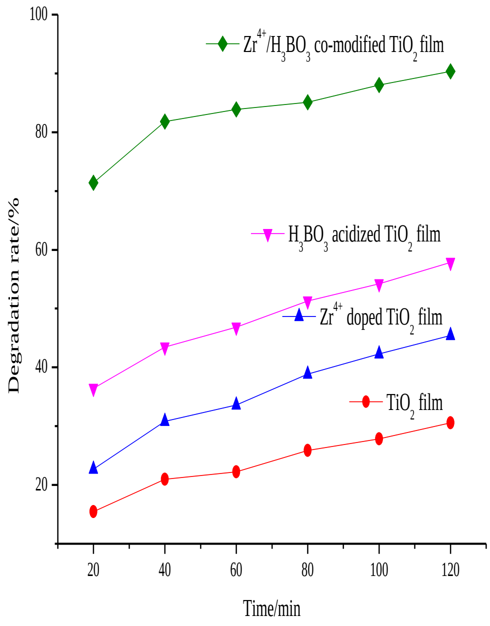
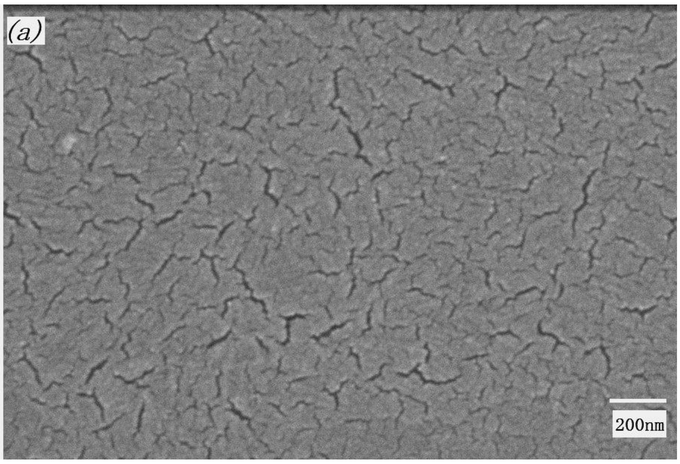


Figure 2

Fig. 2- Decomposition kinetics of ANR solution using pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films under visible light irradiation for 2 hours.

3.2. Surface morphology

Fig. 3 shows the FE-SEM images for (a) pure TiO_2 film and (b) Zr^{4+}/H_3BO_3 co-modified TiO_2 film calcined at 450℃ in air for 1h. It is clear that the Zr^{4+}/H_3BO_3 co-modified TiO_2 film is composed of smaller nanoparticles or aggregates, and its surface is more uniform and smooth without cracks compared to pure TiO_2 film, indicating that the Zr^{4+}/H_3BO_3 co-modification can effectively suppress the growth of TiO_2 crystals. A good dispersion and reduced aggregation among particles are favorable to photodegradation of organic compounds. Composition analysis by EDS indicates that the atomic concentrations of Ti, O, B and Zr in the co-modified TiO_2 sample are 32.6%, 64.1%, 2.8% and 0.5%, respectively.



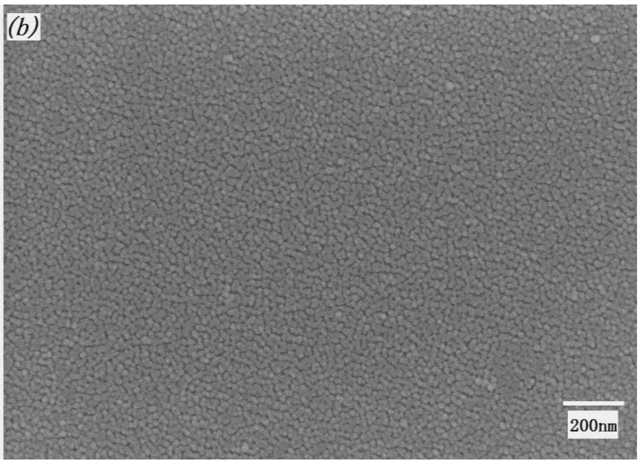
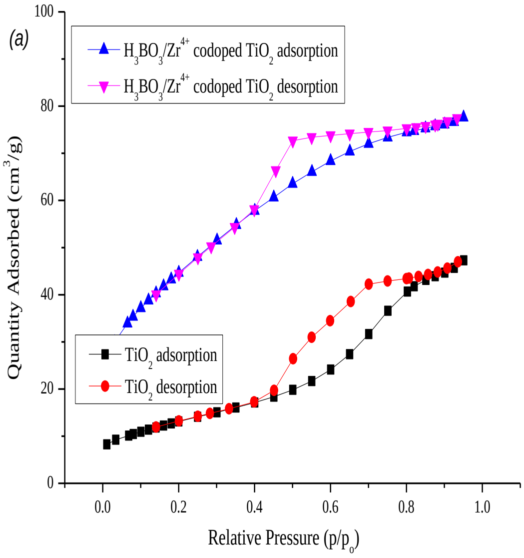


Figure 3

Fig. 3- FE-SEM images for (a) pure TiO_2 film and (b) Zr^{4+}/H_3BO_3 co-modified TiO_2 film calcined at 450℃ in air for 1h.

3.3. Surface areas

N_2 adsorption/ desorption isotherms (a) and pore size distribution (b) of pure TiO_2 and Zr^{4+}/H_3BO_3 co-modified TiO_2 powders are shown in Fig 4. From Fig. 4a, it can be seen that the two samples exhibit hysteresis loops at high relative pressure from 0.4 to 0.8. The two samples show the type Ⅳ isotherms according to IUPAC classification, indicating the presence of mesoporous structure. The surface areas of pure TiO_2 and Zr^{4+}/H_3BO_3 co-modified TiO_2 were 47.9 m^2g^{-1} and 163.8 m^2g^{-1}, respectively. The incorporation of Zr^{4+} and H_3BO_3 into the TiO_2 catalysts may reduce particles size thus increase the surface area of TiO_2. The pore volume of the pure TiO_2 sample is 0.08 cm^3g^{-1}, whereas that of the Zr^{4+}/H_3BO_3 co-modified TiO_2 sample is 0.12 cm^3g^{-1} as shown in Fig. 4b. The large surface area and pore volume can effectively adsorb more H_2O, O_2, and pollutants. The excellent adsorption ability facilitates the diffusion of pollutant molecule from solution to the surface of catalysts, and thus improves its photocatalytic performance.



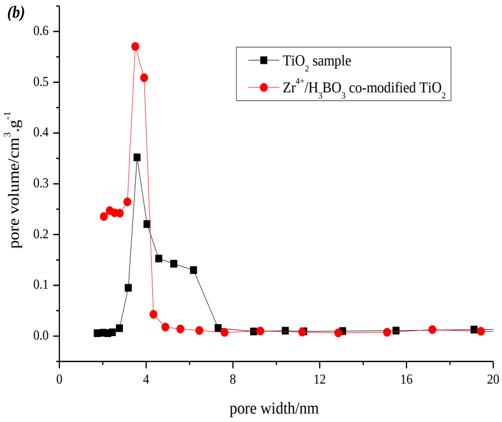


Figure 4

Fig. 4- N_2 adsorption/ desorption isotherms (a) and pore size distribution (b) of pure TiO_2 and Zr^{4+}/H_3BO_3 co-modified TiO_2 powders.

3.4. Crystal structure

TiO_2 occurs in nature in three crystallographic phases: rutile, anatase and brookite. It is well known that the efficiency of TiO_2 as a photocatalyst strongly related to its crystal structure. Fig. 5 shows the XRD patterns of pure TiO_2 and Zr^{4+}/H_3BO_3 co-modified TiO_2 samples calcined at 450 ℃ in air for 1 h. It can be seen that pure TiO_2 exhibits a mixture of anatase (25.6°, 37.8°, and 48.3°), rutile (27.6° and 36.1°), and brookite (30.87°), but the anatase phase is predominant in the samples. After co-modification, it can be seen clearly that the rutile peaks have almost disappeared thus forming an anatase-brookite heterojunction titania photocatalyst. Normally, anatase is the most commonly employed in photocatalytic applications due to its inherent superior photocatalytic properties. Nevertheless, as the latest report, the heterojunction of anatase/brookite biphase TiO_2 can achieve higher photocatalytic activity than single phase TiO_2 due to the synergistic effect between the two phases.[9] Furthermore, the ion radius of B^{3+} (0.023 nm) from H_3BO_3 is smaller than that of Ti^{4+} (0.064 nm), so boron ions may be present in the interstitial site of titania, which can balance the residual charge of the TiO_2 nanoparticles thus reduce the surface energy and hindering the growth of the nanoparticles.

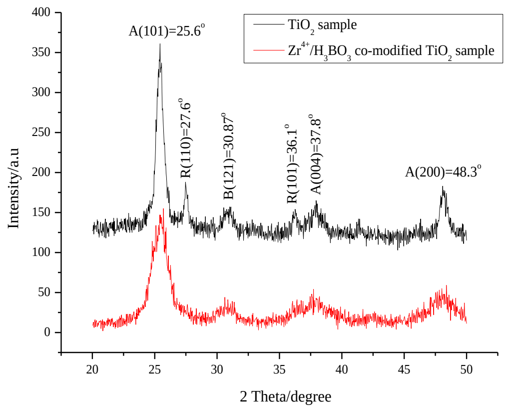


Figure 5

Fig. 5- XRD patterns of pure TiO_2 and Zr^{4+}/H_3BO_3 co-modified TiO_2 samples.

3.5. Thermal analysis

Fig. 6 shows the typical DTA-TG curves of (a) pure TiO_2 and (b) Zr^{4+}/H_3BO_3 co-modified TiO_2 powders. On the DTA curve, a broad endothermic peak at 103.6 ℃ is due to dehydration, and a relatively small exothermic peak at 201.2 ℃ is due to combustion of organic substances contained in the gel.[10] It is observed that an endothermic peak appears at 224.8 ℃, which is due to the dehydration of chemical bonding water. After 300 ℃, an exothermic peak appears due to the transformation of TiO_2 form amorphous to crystalline which exists in the form of brookite, and at about 361.6 ℃ the anatase phase appears. At 425 ℃ an exothermic peak observed may be due to the transformation from brookite phase to anatase. The DTA curve also shows a small exothermic peak at 591.5 ℃ due to the phase transformation from anatase to rutile. From Fig. 6b, the DTA curve of Zr^{4+}/H_3BO_3 co-modified TiO_2 sample is quite different from that of pure TiO_2. It can be seen clearly that the DTA curve becomes smooth, showing that the phase transformations of brookite to anatase and anatase to rutile are suppressed by Zr^{4+} doping and H_3BO_3 acidizing. The phenomenon is in a good agreement with the result obtained from XRD spectra. Moreover, according to the TG curve, the curve becomes to be a straight line at about 450 ℃, indicating that organic substances have been completely burned.

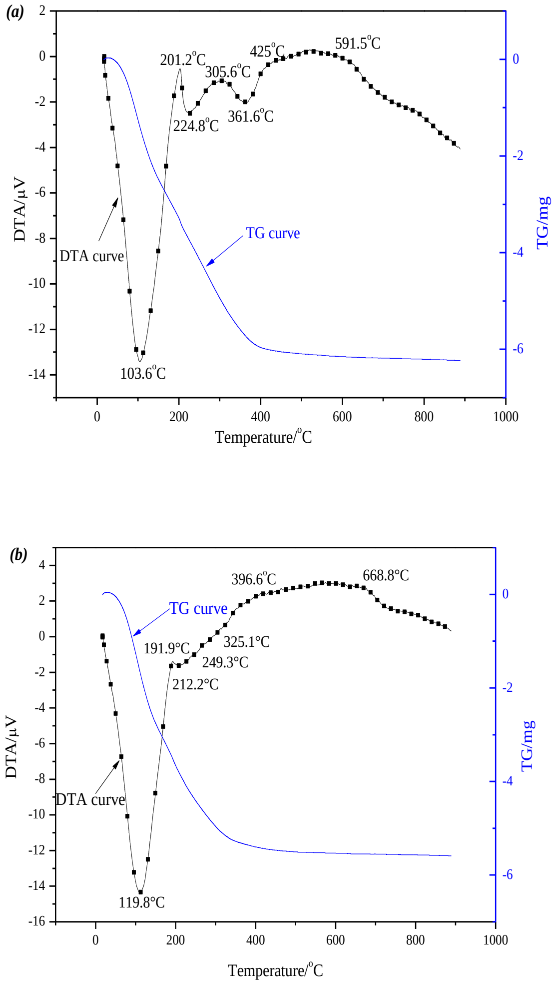
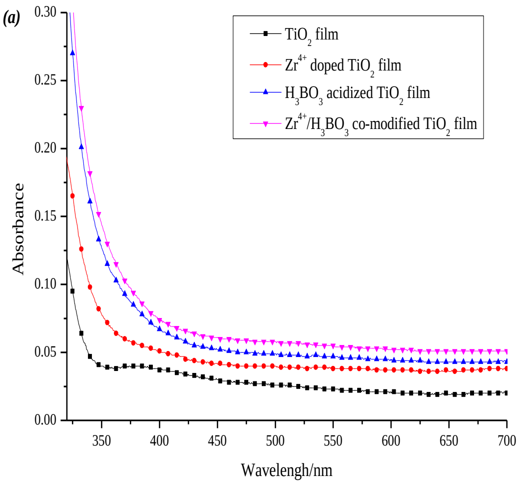


Figure 6

Fig. 6- Typical DTA-TG curves of (a) pure TiO_2 and (b) Zr^{4+}/H_3BO_3 co-modified TiO_2 powders.

3.6. Optical absorption

Fig. 7 shows UV-Vis absorption spectra (a) and Plots of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$) (b) for pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films. Compared with pure TiO_2 and a singly modified film, the Zr^{4+}/H_3BO_3 co-modified TiO_2 film has an obviously red shift to visible region. The optical band gap can be inferred by the formula for a crystalline semiconductor: $\alpha h\nu=A(h\nu-E_g)^{n/2}$, so the band gap energy of TiO_2 can be determined from a plot of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$).[11] Form Fig. 7b, it can be seen that the band gap of the Zr^{4+}/H_3BO_3 co-modified TiO_2 film is 2.8 eV, while that of the H_3BO_3 acidized TiO_2, Zr^{4+} doped TiO_2, and the pure TiO_2 are 3.0 eV, 3.1 eV, and 3.3 eV, respectively. The lower band gap has a positive effect on the photocatalytic activity of TiO_2 because photocatalytic reactions can be activated by photons with lower energy.



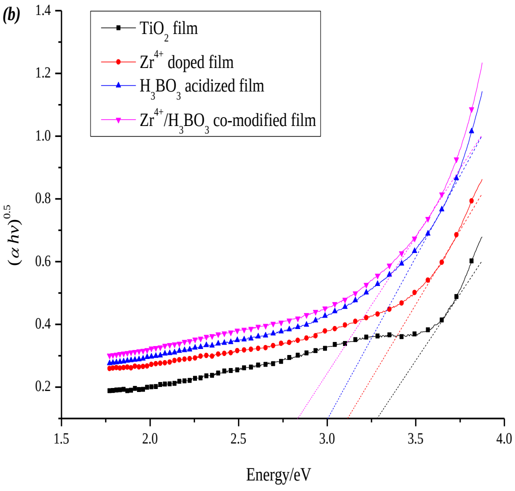


Figure 7

Fig. 7- UV-Vis absorption spectra (a) and Plots of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$) (b) for pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films.

3.7. PL analysis

Fig. 8 is the PL spectra of pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films. It can be observed that the PL intensity of Zr^{4+}/H_3BO_3 co-modified TiO_2 film was the lowest among all samples, indicating that the recombination of electron and hole was effectively prohibited by co-modification. Zr^{4+} doping may enhance the concentration of oxygen vacancies that can trap electrons, which may positively influence the mobility of photogenerated charge carriers so that more holes can reach the surface trapping sites before recombination with electrons. Meanwhile, B^{3+} ion can also effectively trap photo-generated electrons for its positive charge and separate holes on the surface of the TiO_2 film, so it elongates the life of photo-excited electrons and holes.

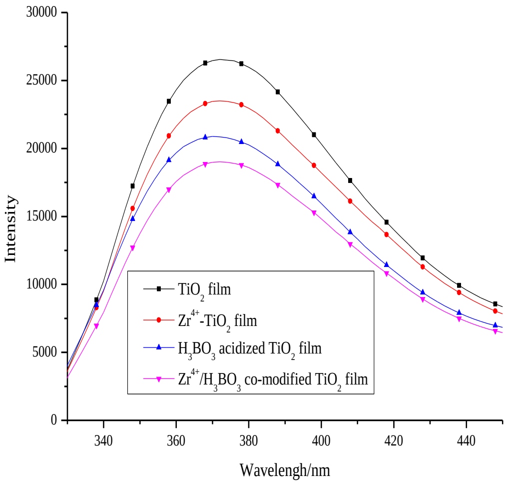


Figure 8

Fig. 8- PL spectra of pure TiO_2, Zr^{4+} doped TiO_2, H_3BO_3 acidized TiO_2, Zr^{4+}/H_3BO_3 co-modified TiO_2 films.

In a word, the Zr^{4+}/H_3BO_3 co-modified TiO_2 film exhibit excellent photocatalytic activity under both UV and visible light irradiations. According to the FE-SEM, XRD and BET analyses, Zr^{4+} doping and H_3BO_3 acidizing can effectively lessen the aggregation of the TiO_2 nanoparticles, increase specific surface area and pore volume of the TiO_2 sample, and inhibit the transformation of anatase to rutile. Moreover, the high activity of the co-modified TiO_2 film may be attributed to improving the visible light absorption and reducing the recombination of the photogenerated charges. These factors lead to effective photodegradation of organic pollutants.

IV. CONCLUSIONS

We have synthesized Zr^{4+}/H_3BO_3 co-modified TiO_2 nanocrystalline film on the surface of common glass substrates through a sol-gel method. Experimental results show that the co-modified TiO_2 film has the best photocatalytic activities compared to the pure TiO_2 film and a singly modified TiO_2 film under both UV and visible light irradiations. It is the synergistic effect of Zr^{4+} doping and H_3BO_3 acidizing that reduce the recombination of photogenerated carries and induce strong visible light absorption, herein enhancing the photoreaction activity of the TiO_2 film. The co-modified TiO_2 films may be a promising photocatalyst for the decontamination of many emerging anthropogenic organic pollutants, particularly those with high toxicity but at very low concentration.

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