

# Preparation of the strong reductive TiO<sub>2</sub> photocatalyst modified by Silicon-citric acid-Vanadium

QIANLIN CHEN, XINJIE YU

*Department of Chemical Engineering, Guizhou University, Gui Yang, China*

Vanadium doped titania (TiO<sub>2</sub>) nanoparticles was synthesized by sol-gel method. On this basis of using ultrasonic impregnation method by use of ethyl silicate and citric acid on the catalysts surface for further modification to prepare ether compound wrapped strong reducible photocatalyst. By using of 100 mg/L potassium dichromate and 30 mg/L methyl orange as degradation model, studied Si-citric acid-V co-modified TiO<sub>2</sub> catalyst redox property. Experimental results indicate that Si-citric acid-V co-modified TiO<sub>2</sub> catalyst particle size is the smallest nanometer sphere and have reunion phenomenon. On the surface of catalyst is introduced into the hole scavengers is helpful to improve the reduction of the catalyst while it is harmful to improve the oxidation ability. Si-citric acid-V co-modified TiO<sub>2</sub> photocatalytic performance relatively stable.

(Received April 25, 2012; accepted June 6, 2012)

*Keywords:* Sol-gel, Photocatalyst, Nanomaterial, Hole scavengers

## 1. Introduction

TiO<sub>2</sub> have stable chemical properties and high photocatalytic activity, which can make the chemical reaction in optical radiation surface can be realized and acceleration, while the TiO<sub>2</sub> light catalysis under normal temperature and pressure. It has not produced secondary pollution, and low cost, which have been widely used in sewage treatment, recovery of precious metal, nanometer antibacterial etc [1-3]. When nanometer TiO<sub>2</sub> absorbed the photon which wavelength of less than 385 nm, the electronic would be stimulated and transition to the conduction band to form the negatively charged highly active electrons. At the same time form a positively charged hole in the valence band, so the semiconductor surface form electron-hole pairs, photogenerated electrons with strong reducing power, there are holes in the valence band strong oxidation ability [4-5].

But the disadvantages of the rate of recombination between the photogenerated electronics-holes compound is high, the quantum efficiency is low and the adsorption of degradants performance is poor, so lower the electronic hole recombination rate, speed up the interface electronic transfer rate and improve the adsorption performance of catalyst is the focus of this research field [6]. Metal ions doping in semiconductor lattice can be introduced into defect position or change the crystallinity of TiO<sub>2</sub> to improve the TiO<sub>2</sub> photocatalytic activity and the light absorption ability [7]. Klosek S considered that V ion is mixed can improve the photocatalytic activity of TiO<sub>2</sub> and the utilization ratio of visible light [8]. Wu [9] found that increase of the V doping quantity will cause the TiO<sub>2</sub>

particle size increased and absorption peak redshift, and the V<sup>4+</sup> rather than V<sup>5+</sup> replace the Ti<sup>4+</sup> lattice position or into the TiO<sub>2</sub> lattice. Because of the electronic life in relative to the hole is short, the electronic transfer to oxygen is considered the photocatalytic reaction limiting step, so with the aid of auxiliary material to increase the carriers transport/capture rate is also a way of reduce the carriers recombination [10]. To the solution with the addition of hole scavengers, can extend the life of photogenerated electrons, which can effectively improve the photocatalytic reduction efficiency [11]. This paper using sol-gel method prepared V modified TiO<sub>2</sub> catalyst and introduced hole scavengers into catalyst surface. Studied Si-citric acid-V co-modified TiO<sub>2</sub> photocatalyst of Cr<sup>6+</sup> on photocatalytic reduction activity and analyzed the modified catalyst on reduction activity influence mechanism.

## 2. Experimental section

### 2.1. Materials

Tetra-n-butyl Titanate and Vanadium pentoxide were used for prepare V doping photocatalyst. Anhydrous alcohol as solvent for preparing photocatalyst. Branched agent (ethyl silicate) and hole scavengers (citric acid) as the secondary treatment photocatalyst materials. Potassium dichromate as the detection of photocatalyst catalytic reduction reaction efficiency model. Deionized water is used for the preparation of all solutions.

## 2.2. Catalyst preparation

The typical sol-gel synthesis of V doped TiO<sub>2</sub> nanoparticles is as detailed below. The tetrabutyl titanate and alcohol mixed liquid dripped into the corresponding proportion of alcohol and deionized water and V<sub>2</sub>O<sub>5</sub> solution

(Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>:C<sub>2</sub>H<sub>5</sub>OH:H<sub>2</sub>O=50:250:1;V:Ti=0.2%), and the solution was kept undisturbed for 1 hour to get a homogeneous mixture, then put the mixture ultrasonic dispersion 30min. When the resulting mixture turned to be a sol, it was stirred for 10 hours and aged for 6 hours to form a gel. The gel was dried at 80°C for 4 h and finally ground. The resulting powder was calcined at 600 °C for 2 h. Grinded it, made of V modified TiO<sub>2</sub> catalysts. Took 6g modified catalyst into 4.5 ml ethyl silicate, 100 ml anhydrous alcohol and 24 ml 0.1 M citric acid mixture solution. Scattered in ultrasonic instruments, and heated to a 50 °C, when ethyl silicate and citric acid reaction completely. Then put it to dry and grind, made of Si-citric acid-V Co-modified TiO<sub>2</sub> optical catalyst.

## 2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were collected with a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu K $\alpha$  radiation,  $\lambda$  1.54056 Å), operated at 40 KV and 40 mA. The sample light absorption performance (UV-Vis DRS) characterization at 722 type ultraviolet-visible spectrometer. The particle morphology (SEM) of the catalyst was observed by means of JSM-6490 LV scanning electron microscopy with dispersive X-ray spectrometer. Transmission electron microscopic (TEM) images were recorded using a JEOL TEM-2000FX electron microscope operating at an accelerating voltage of 180 keV. FT-IR spectra were recorded using a FT-IR spectrometer (MAGNA-IRA750).

## 2.4. Photocatalytic degradation studies and analysis

The experiment device was operated in the camera obscura. Using low pressure mercury lamp as the experimental UV irradiation light source (125 W, 365nm, 12.4×100 $\mu$ W/cm<sup>2</sup>). All the photocatalysis experiments were not pump oxygen into the solution, also did not addition other degradation material. Reaction liquid level height was 2cm, by use of the magnetic stir to maintain the reaction solution suspended. Using the concentrations of chromium (VI) and methyl orange as a catalyst for reductive analysis index. The catalyst concentration was 4g/L. Before the reaction, put the reaction solution to ultrasonic oscillations 20 min, stirred 20 min to adsorption balance. Every time took 10 ml reaction liquid, filtered and tested the absorbance.

Took filtrate into quartz colorimetric plate and then put in 722 type UV-visible spectrophotometer to determine the filtrate absorption, the degradation rate is

$$X=[(A_0-A_t)/A_0]\times 100\%.$$

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1 are pure TiO<sub>2</sub>, V-TiO<sub>2</sub> and Si-citric acid-V co-modified TiO<sub>2</sub> samples of XRD spectra. As Fig. 1 shows all the samples exhibit anatase crystal structure. According to the strongest diffraction peak, anatase (101), by scherrer formula calculate all the samples average particle size (TiO<sub>2</sub>: 73.19nm; V-TiO<sub>2</sub>: 39.08 nm; Si-citric acid-V co-modified TiO<sub>2</sub>: 25.80nm). Due to the low V dopant and highly dispersed in TiO<sub>2</sub> surface, so did not found V diffraction peak. In Si-citric acid-V co-modified TiO<sub>2</sub> catalyst surface didn't found silicon crystal either. It is because most ethyl silicate and citric acid has reaction and generated ether compound or combined with TiO<sub>2</sub> surface hydroxyl and generated -Si-O-Ti-O, which exist as amorphous form [12]. It can be observed clearly that the anatase (211) diffraction peak of V doped catalyst is more sharply compared to pure TiO<sub>2</sub>, and anatase (101) diffraction peak is more sharp. Therefore in the same calcination temperature and time (600 °C, 2h), the V modified catalyst of anatase crystal phase is more complete and mature.

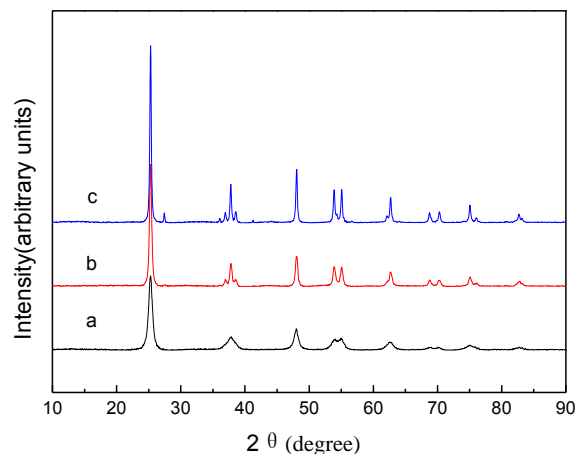


Fig. 1. XRD patterns of (a) pure TiO<sub>2</sub>, (b) V-TiO<sub>2</sub>, (c) Si-citric acid-V co-modified TiO<sub>2</sub>.

Fig. 2 are Si-citric acid-V co-modified TiO<sub>2</sub> photocatalyst sample's SEM photo. There is uneven distribution of agglomerated particles. The Fig. 2 shows Si-citric acid-V co-modified TiO<sub>2</sub> pristine TiO<sub>2</sub> nanoparticles synthesized by the same sol-gel process exhibit a uniform spherical shape and sphere boundary is clear. However, defective terrace as a result of agglomeration of tiny grains is not seen in these SEM images. Fig. 3 is the energy spectrum of Si-citric acid-V co-modified TiO<sub>2</sub> photocatalyst. It shows that the Ti, Si, C

elements in TiO<sub>2</sub> is clearly identified from the energy spectrum. Because of the V doping quantity is less, so the V peak did not appear in the energy spectrum.

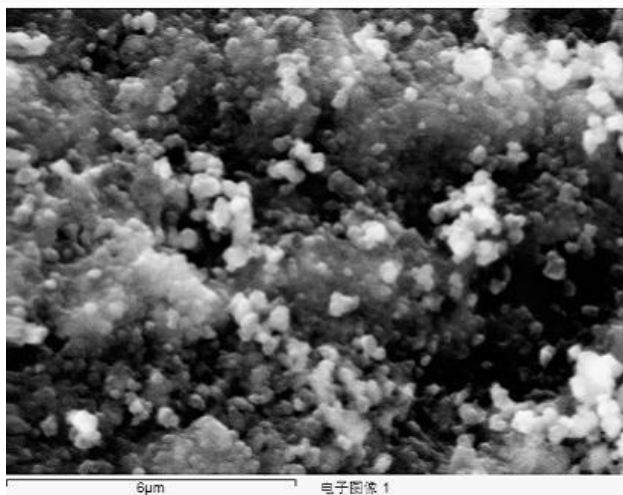


Fig. 2. SEM micrograph of Si-citric acid-V co-modified TiO<sub>2</sub>.

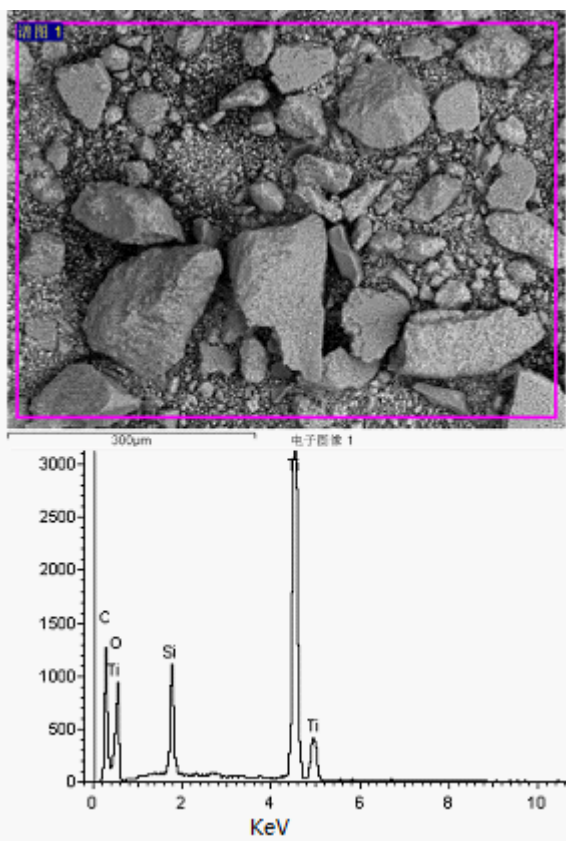


Fig. 3. Energy spectrum of Si-citric acid-V co-modified TiO<sub>2</sub>.

Fig. 4 are the Si-citric acid-V co-modified TiO<sub>2</sub> photocatalyst sample's TEM photo. The photocatalyst have reunion phenomenon, dispersivity is poor. This is because

the nano catalysts particle size is smaller and had a higher surface energy.

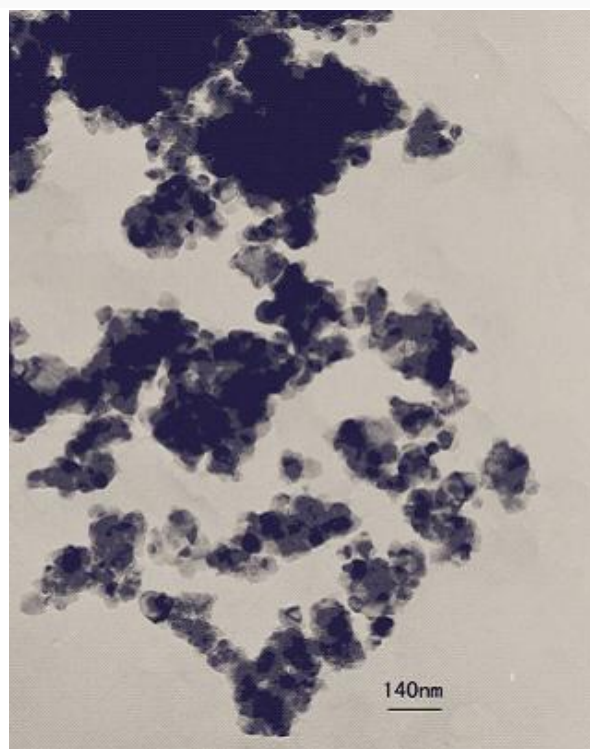


Fig. 4. TEM micrograph of Si-citric acid-V co-modified TiO<sub>2</sub>.

Fig. 5 are Si-citric acid-V co-modified TiO<sub>2</sub> photocatalyst infrared spectrum. 3434 cm<sup>-1</sup> absorption peaks correspond to the catalyst physical adsorption water HO-H bond stretching vibration; 1625 cm<sup>-1</sup> absorption peaks belonging to TiO<sub>2</sub> surface water absorption peaks of a OH [13], 1385 cm<sup>-1</sup> is one COO group characteristic absorption peak. 1300 cm<sup>-1</sup>-1250 cm<sup>-1</sup> is ether characteristic absorption peak, which testify on the surface of catalyst happened esterification reaction. The characteristic bands for the Si-O-Si bonds (V<sub>as</sub> (Si-O-Si) at 1210 cm<sup>-1</sup>, V<sub>as</sub> (Si-O-Si) at 1080 cm<sup>-1</sup>, V<sub>as</sub> (Si-OH) at 980 cm<sup>-1</sup>, V<sub>as</sub> (Si-O-Si) at 790 cm<sup>-1</sup> and δ (Si-O-Si) at 450 cm<sup>-1</sup>) are clear present in the IR spectra [14-18]. The 1094cm<sup>-1</sup> near high intensity peaks corresponding to the SiO<sub>2</sub> tetrahedron in Si-O-Si of the symmetric stretching vibration, as well as the band of oxygen in the antisymmetric stretching vibration [19]. In 970 cm<sup>-1</sup> have Si-O-C band absorption peak, which shows that the TEOS and citric acid happened esterification reaction. In 946cm<sup>-1</sup> have absorption peak, while SiO<sub>2</sub> and TiO<sub>2</sub> in 900-1000cm<sup>-1</sup> are no absorption peak, which shows that the catalyst exists in the Ti-O-Si band [20]. It can testify that during the esterification reaction SiO<sub>2</sub> and TiO<sub>2</sub> happened binding reaction.

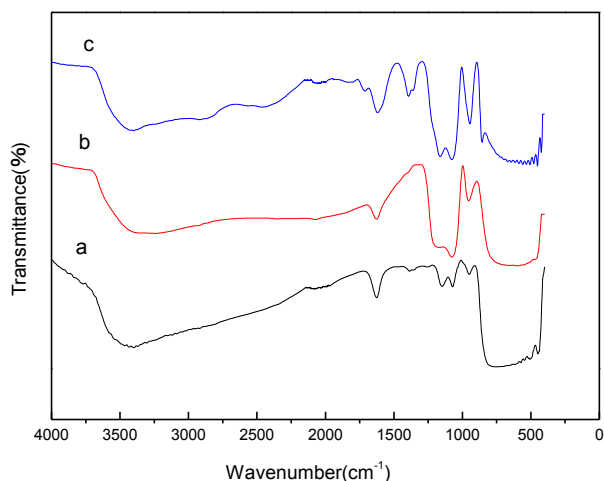


Fig. 5. FT-IR spectra of (a) V-TiO<sub>2</sub>, (b) Si-V-TiO<sub>2</sub>, (c) Si-citric acid-V co-modified TiO<sub>2</sub>.

### 3.2. Evaluation of photocatalytic activity of secondary processing V doped TiO<sub>2</sub> nanoplates

Fig. 6 is the rate of degradation of potassium dichromate using pure TiO<sub>2</sub>, V-TiO<sub>2</sub> and Si-citric acid-V co-modified TiO<sub>2</sub> samples. As the figure shows the V modified TiO<sub>2</sub> adsorption ability is stronger than pure TiO<sub>2</sub>, but Si-citric acid-V co-modified TiO<sub>2</sub> adsorption is decreased, this is due to part of the hydrolyzed silica blocked the TiO<sub>2</sub> microporous. The reduction of V modified catalyst decrease. This is because V can't be completely wrapped in the pure TiO<sub>2</sub>, part of V ion distributed on catalyst surface, which cannot form the bottom doping [16]. V ion trapping photogenerated electrons or holes, but at the same time it may become the electron-hole recombination center, so that the photocatalytic activity of TiO<sub>2</sub> reduced. Si-citric acid-V co-modified TiO<sub>2</sub> photocatalyst degradation of potassium dichromate rate increase greatly. It is due to catalyst the surface is introduced into the hole, which prolong electronic the life, thereby greatly improving the photocatalytic reduction activity. Fig. 7 shows that the rate of degradation of methyl orange using Si-citric acid-V co-modified TiO<sub>2</sub> is low. The hole scavengers inhibit the oxidation photocatalytic activity.

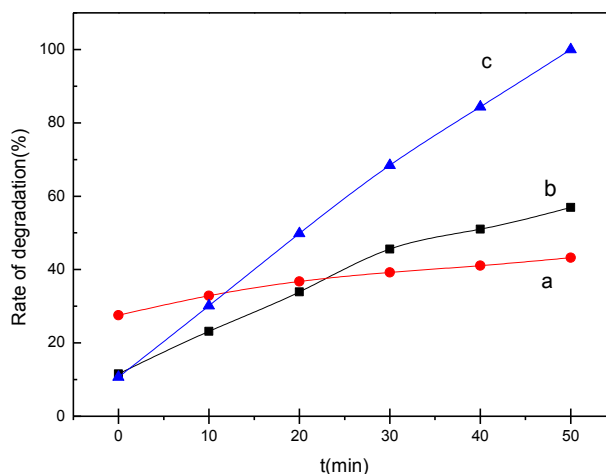


Fig. 6. The degradation rate of potassium dichromate (a) pure TiO<sub>2</sub>, (b) V-TiO<sub>2</sub>, (c) Si-citric acid-V co-modified TiO<sub>2</sub>.

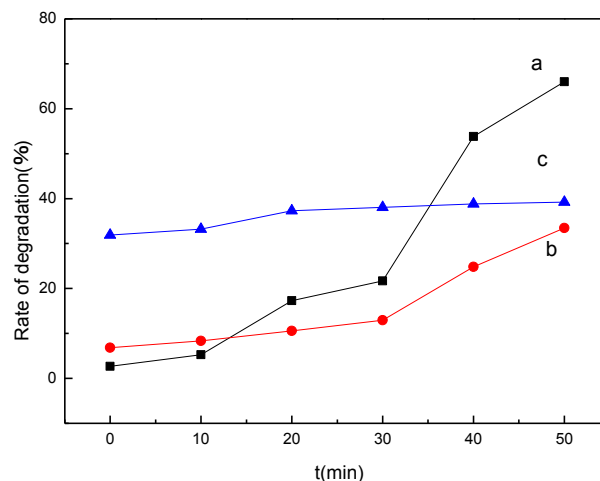


Fig. 7. The degradation rate of Methyl orange (a) pure TiO<sub>2</sub>, (b) V-TiO<sub>2</sub>, (c) Si-citric acid-V co-modified TiO<sub>2</sub>.

### 3.3. Stability of second processing V Doped TiO<sub>2</sub> photocatalyst

Fig. 8 is the degradation rate of potassium dichromate using Si-citric acid-V co-modified TiO<sub>2</sub> which has been ultrasonic washed 30 min. Seen by the graph, the photocatalyst is relatively stable, ultrasonic 30 min washed on its photocatalytic effect is very small. Because of the washed catalyst have agglomeration phenomenon, thus the washed catalyst adsorption performance is weaker than not washed.

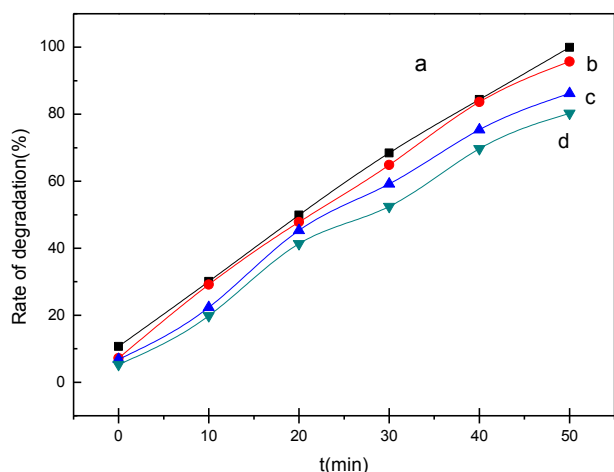


Fig. 8. The degradation rate of potassium dichromate of (a) Si-citric acid-V co-modified TiO<sub>2</sub>, (b) washed 30min catalyst, (c) washed 60min catalyst, (d) washed 90min catalyst.

#### 4. Conclusions

The Si-citric acid-V co-modified TiO<sub>2</sub> nanocomposites have been prepared by employing the alkoxide and aqueous routes of the sol-gel method and ultrasonic impregnation method, which can significantly improve the photocatalyst reduction activity. This is because the surface into the hole scavengers in the catalyst, the load in V-TiO<sub>2</sub> surface of citric acid and TEOS generated compounds can be very effective trap the photo-excited holes, which promote the electron-hole pairs separate and inhibit it recombinant, therefore the photocatalyst reduction activity increased significantly. The nanocomposite materials were characterized from structural and textural point of view. The FT-IR spectra indicated that the hole scavengers were successfully connected to the catalyst. The XRD spectra indicated that in the same calcination temperature and time (600 °C, 2h), the V modified catalyst of anatase crystal phase is more complete and mature. Due to high surface energy, we can see the photocatalyst have reunion phenomenon from the SEM and TEM micrograph of Si-citric acid-V co-modified TiO<sub>2</sub>. The Si-citric acid-V co-modified TiO<sub>2</sub> is stability and the ultrasonic washing have little influence on its photocatalytic activity.

#### References

- [1] G. Cui, B. Wang, L. Wang, G. Mai. *Industr Water Treat.* **1**, 10 (2000).
- [2] Rajeshwar K, Ibanez J. G. *Environ Electrochem.* **24**, 1070 (1994).
- [3] T. Ihara, M. Miyoshi, Y. Iriyama, et al. *Appl Catal B Environ.* **6**, 403 (2003).
- [4] Carraway, J. Hofmann. *Environ Sci Technol.* **28**, 786 (1994).
- [5] Li G, Ruth M. Qumt. *J Chem Soc Taraday Trans.* **87**, 1097 (1991).
- [6] X. Yu, C. Liang, J. Cheng. *Bull Chin Ceram Soc.* **1**, 53 (2000).
- [7] Y. Xie. *Rare Met.* **23**, 20 (2004).
- [8] Klosek S, Raffery D. *J Phys Chem B.* **105**, 2815(2001).
- [9] J. Wu, C. Chen. *J Photochem Photobiol.* **163**, 509 (2004).
- [10] X. Ding et al. *J Mater Sci lett.* **13**, 462 (1994).
- [11] S. Liu, C. Sun. *Acta Phys-chim Sin.* **20**, 355 (2004).
- [12] X. Fu, Clark L. A., Q. Yang. *Environ Sci Tech.* **30**, 647 (1996).
- [13] J. Yu, X. Zhao et al. *J Mater Sci lett.* **20**, 1745 (2001).
- [14] L. Wang, G. Jia, T. Xu. *Chinese J Inorg Chem.* **21**, 1505 (2005).
- [15] A. Jitianu, M. Raileanu, M. Crisan et al. *J Sol-gel Sci Techn.* **40**, 317 (2006).
- [16] D. Predoi, R. Clerac, A. Jitianu et al. *Dig J Nanomater Bios.* **1**, 93 (2006).
- [17] M. Raileanu, M. Crisan, A. ballo et al. *J. Optoelectron. Adv. Mater.* **9**, 1399 (2007).
- [18] A. Bertoluzza, C. Fagnano, M. A. Morelli et al. *J Non-Cryst Solids.* **48**, 117 (1982).
- [19] J. Qin, D. Yu, J. Chen. *J Mol Catal.* **18**, 472 (2004).
- [20] S. Liu, T. Xie, Z. Zhang, Y. Yan. *Nat Sci Edit.* **35**, 91 (2007).

\*Corresponding author: 594142590@qq.com; cq11018@163.com