

Controllable preparation of titanium peroxide and its adsorption on methylene blue and heavy metals

JI-GUO HUANG, HAI-TAO CHEN, SHUO PANG, HUAN-YU CUI, XUE-TING GUO, SHUANG-SHI DONG*, XING-JUAN LIU

Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun 130026, PR China

A series of titanium peroxide samples were prepared with the reaction of titanium sulfate solution and H₂O₂ solution on controllable preparation conditions and showed different adsorption properties on methylene blue. The optimum pH, highest temperature and volume of H₂O₂ is 9.0, 40 ± 2°C and 35 mL. The saturated adsorption capacities of the titanium peroxide for methylene blue, Cd (II), Cu (II), and Zn (II) were 263.25, 73.89, 73.54 and 41.83 mg/g at 25°C, respectively. The adsorption was rather fast. The controlling mechanism of adsorption processes could be electrostatic adsorption according to the characterization and adsorption results.

(Received July 25, 2015; accepted September 9, 2015)

Keywords: Titanium peroxide, Controllable preparation conditions, Adsorption; Methylene blue, Heavy metals

1. Introduction

The superoxide radical anion [O₂⁻] is an active oxygen species that possesses both anionic and free radical properties [1]. Ionic salts of superoxides, which generally are obtained by the reaction of dioxygen with metals such as potassium, rubidium, or cesium, are found to be paramagnetic with one unpaired electron per two oxygen atoms [2]. In 1970s, Schwarzenbach et al. [3] studied on the structure of peroxo titanium complexes in water solution. Peroxotitanate complex could be a good and effective precursor to prepare nano TiO₂. Bandga et al. [4] developed a simple, fast and cost-effective method for controllable synthesis of nano TiO₂ under mild chemical reaction conditions with aqueous peroxotitanate complex as a precursor. Titanium superoxide, a novel heterogeneous and readily accessible catalyst, was found to catalyze the selective oxidation of phenols to the corresponding 1,4-benzoquinones in preparative yields with aq. 30% H₂O₂ as oxidant under mild reaction conditions by Dewkar et al. [5]. Shaikh et al. [6] reported that titanium superoxide catalyzed aminobromination of olefins, which proceeded regioselectively in an anti-Markovnikov fashion and under truly heterogeneous conditions. Titanium superoxide was found to be very effective for the selective oxidation of anilines, aliphatic primary amines and phenols to the corresponding nitrobenzenes, oximes and quinones, respectively [1]. In our previous study, we researched the preparation of titanium peroxide and its selective adsorption property on cationic dyes [7].

Cationic dyes are extensively used in industry,

leading to the increase of the discharge of dye to the water [8]. The presence of dyes in water, even at very low concentrations, is highly visible and undesirable. In addition, the colored effluence also triggers an increasing toxicity and carcinogenicity, which threatens the water security for human and animals [9]. This results in a demand to remove the dyes from effluents. Therefore the treatment of cationic dyes has raised much attention and adsorption has been found to be superior to other techniques for dyeing water purification in terms of initial cost and flexibility [10].

Heavy metals are highly toxic and exist in the aqueous waste streams of many industries. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Cu (II), Ni (II), Fe (III), Cd (II), Zn (II), Pb (II), U (VI), Th (IV), and Co (II) are well-known heavy toxic metals that pose a serious threat to the fauna and flora of water bodies when discharged into industrial wastewater [11]. Much effort has been exerted in the last few years to find promising materials that can be utilized as good tools for extracting hazardous heavy elements. Adsorbent seems to be one of the several important tools in this application.

In this work, we studied controllable preparation conditions including pH, the highest temperature and the volume of H₂O₂ of titanium peroxide for the adsorption on methylene blue. According to the saturated adsorption capacities of samples, we can determine the preparation condition on which titanium peroxide shows the maximum adsorption capacity. In addition, we apply titanium peroxide as the adsorbent to adsorb heavy

metals, including Cd (II), Cu (II), and Zn (II). We hold the view that it is significant to both the research of titanium peroxide property and the removal of methylene blue and heavy metals.

2. Experimental

2.1 Materials

Titanium sulfate was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Sulfuric acid (95-98%) was obtained from Beijing Chemical Works. Hydrogen peroxide (30%) and ammonia were purchased from Xilong Chemical Co., Ltd. (China). Methylene blue was obtained from Tianjin Guangfu Fine Chemical Research Institute (China). Cadmium (II) sulfate octahydrate, Copper (II) sulfate pentahydrate and zinc (II) sulfate heptahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All reagents were of analytical grade.

2.2 Preparation of titanium peroxide

Titanium peroxide was prepared according to the methods introduced in our previous study [7]. Firstly, a certain volume of H₂O₂ (30%) was added to a solution of 100 mL 10% Ti(SO₄)₂ drop by drop and stirred constantly. In an instant, a dark red solution was obtained. Then, ammonia (10%) was added to change the pH of the solution and the color turned into yellow gradually. At the same time, the highest temperature was controlled. Finally, the precipitates were dried by water bath at 40°C after being washed for several times. The light yellow titanium peroxide powder was obtained after grinding the dried precipitates. Samples prepared on different conditions were listed in Table 1.

Table 1. Samples prepared on different condition

| Sample | pH | Highest temperature(°C) | Volume of H ₂ O ₂ (mL) |
|--------|------|-------------------------|--|
| P1 | 6.0 | 40 | 35 |
| P2 | 7.5 | 40 | 35 |
| P3 | 9.0 | 40 | 35 |
| P4 | 10.0 | 40 | 35 |
| T1 | 9.0 | 20 | 35 |
| T2 | 9.0 | 30 | 35 |
| T3 | 9.0 | 50 | 35 |
| V1 | 9.0 | 40 | 10 |
| V2 | 9.0 | 40 | 15 |
| V3 | 9.0 | 40 | 45 |

2.3 Characterization

XRD patterns were acquired on an X-ray diffraction spectrometer (BRUKER axs D8 ADVANCE, Cu K α , $\lambda=1.54056 \text{ \AA}$). The SEM images were recorded with a model XL 30 ESEM FEG from Micro FEI Philips at room temperature. TEM information was obtained with FEI-TECNAI F20 microscope operated at 200 kV. Before TEM analysis, the sample was sonicated in ethanol for 10 min and 2-3 drops of the sample were deposited onto a thin carbon film supported by a perforated copper grid. TG/DSC analyses were performed on a NETZSCH DSC 204 PC Instrument from 30 to 700°C at a heating rate of 10°C/min under N₂ (50 cm³/min at normal temperature and pressure). FT-IR curves were recorded on SHIMADZU 8400 s Fourier transform infrared spectrometer. XPS measurements were carried out with a Thermo ESCALAB 250 spectrometer using an Al K α (1486.6 eV) X-ray source. The zeta potential of all samples was measured by using a laser Doppler electrophoresis analyzer (Zetasizer Model ZEN 2600, Malvern Instrument Ltd., UK). All of the measurements were carried out at room temperature (25 ± 2°C).

2.4 Adsorption test

All the adsorption experiments were conducted under stirring at room temperature (25°C) in the dark. 0.2 g of prepared titanium peroxide was added into 200 mL of methylene blue solution (400 mg/L) and heavy metal compounds solution (200 mg/L). Samples of methylene blue solution were taken at appropriate time intervals and the adsorbents were separated from the suspension via centrifugation. The absorbance of supernatant was measured using UNICO 2100 visible spectrophotometer at the corresponding maximum absorption wavelength of 664 nm. The concentration of heavy metal compounds was measured by Atomic Absorption Spectrophotometer (Shimadzu AA-6000CF) after samples of heavy metal compounds solution were filtered through a 0.45 μ m cellulose acetate membrane filter.

3. Results and discussions

3.1 X-ray diffraction, SEM and TEM analysis

The sample was amorphous in nature according to the XRD pattern of P3, for the reason that there were no sharp peaks in the X-ray diffraction pattern. This was in accord with the result in the literature [1]. SEM and TEM images of P3 that magnified different times were shown in Fig. 1, which could also show the physical structure. The sample was relatively dispersed and seemed to be homogenous in morphology. These particles were not well crystallized and no obvious lattice

fringe was observed in Fig. 1, which was in agreement with the XRD results.

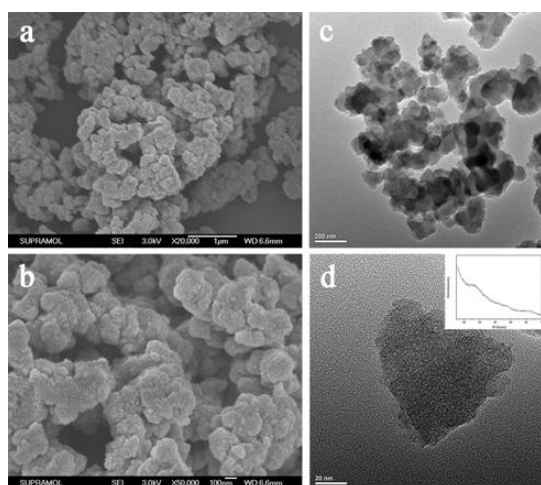


Fig. 1. (a, b) SEM images of P3 and (c, d) TEM images of P3. The inset of (d) shows the XRD pattern of P3.

3.2 TG/DSC analysis

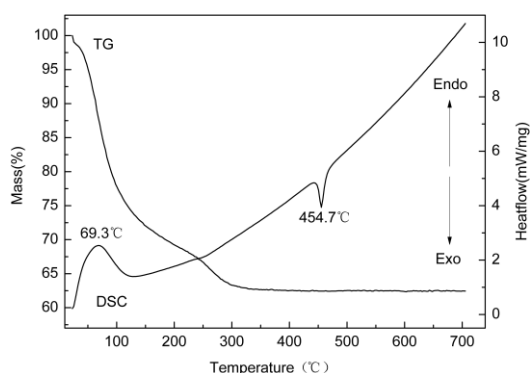


Fig. 2. The TG/DSC curves of P3.

Thermal analysis was adopted to evaluate the surface hydroxyl amount and the thermal stability of the sample. Fig. 2 showed the TG/DSC curves of P3. It could be found that the curve of the DSC exhibited a strong endothermic peak around 70°C, which was caused by the release of adsorbed water and part of constitution water in the titanium peroxide. The exothermic peak at about 450°C was considered to be caused by anatase-to-rutile transformation of TiO_2 , which was produced by the decomposition of the sample. The TG curve in Fig. 2 could be divided into three stages. In the first stage from room temperature to 100°C, a little mass loss was caused by the release of some residual adsorbed water and hydroxyl groups on the sample surface after drying the sample under 50°C in a vacuum condition. With the temperature increasing from 100°C to 350°C,

the mass loss was about 15% with constitution water and oxygen releasing, which came from the decomposition of peroxide root. There was no significant weight loss after 350°C, and it could be explained that water in the sample had almost released completely and most titanium peroxide had decomposed to TiO_2 and crystallized.

3.3 FT-IR spectra

The FT-IR spectra of P3 and P3 adsorbed methylene blue was shown in Fig. 3. The detected absorption peak at 878 cm^{-1} in the spectra of titanium peroxide was attributed to the peroxy groups [12]. The peak at 1401 cm^{-1} was attributed to the stretching vibration of the N-H bonds in NH_4^+ , which indicated that there were still residual NH_4^+ after washing the precipitation for several times [13,14]. The Ti-OH bending mode assigned to the band around 1632 cm^{-1} . The band at 3164 cm^{-1} and 3410 cm^{-1} in the spectra of titanium peroxide could be assigned to adsorbed water and hydroxyl groups on the material surface [15,16]. The stretching vibration of the band at 3164 cm^{-1} and 3410 cm^{-1} disappeared after adsorbing methylene blue, which could be ascribed to the adsorption happening between hydroxyl groups on the surface of the titanium peroxide and methylene blue.

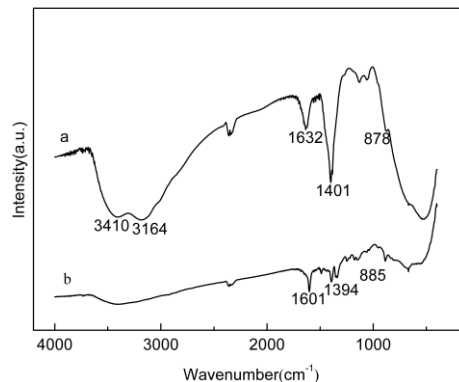


Fig. 3. FT-IR spectra of (a) P3 and (b) P3 adsorbed methylene blue.

3.4 XPS spectrum

XPS is a surface probe detecting electrons that are generated from a depth of a few nanometers on the surface of the sample. The XPS spectra of P3 for the Ti2p, O1s, and N1s region was shown in Fig. 4. The Ti2p region shown in Fig. 4 (a) could be fitted into two peaks, located at 458.7 eV and 464.5 eV, respectively. It could be seen that Ti2p peak shifted positively comparing with the standard TiO_2 sample [17,18]. The shifting of Ti2p binding energy might be ascribed to the fact that the TiO_2 nanostructure had partly changed from the feature of Ti^{4+} into Ti^{2+} . Fig. 4 (b) showed the XPS spectra for the O1s region of the sample. The

corresponding values were 530.7 eV and 532.5 eV for the sample. The peak at 530.7 eV was mainly attributed to the contribution of Ti-O, and the peak at 532.5 eV was closely related to the hydroxyl groups (-OH) [19]. This result was consistent with FT-IR spectra. The peak of N1s for the sample was shown in Fig. 4 (c). The N1s spectra showed a main peak at 401.2 eV with a shoulder at 407.1 eV. The 401.2 eV was assigned to the N-H in the sample which was caused by adding ammonia, while the shoulder at 407.1 eV could be attributed to the N-O. The formation of N-O might be assigned to the N atom replacing the O atom in the O-O and free oxygen reacted with H₂ produced by the decomposition of H₂O₂. The abundant O-H increased the saturated adsorption capacity of the sample.

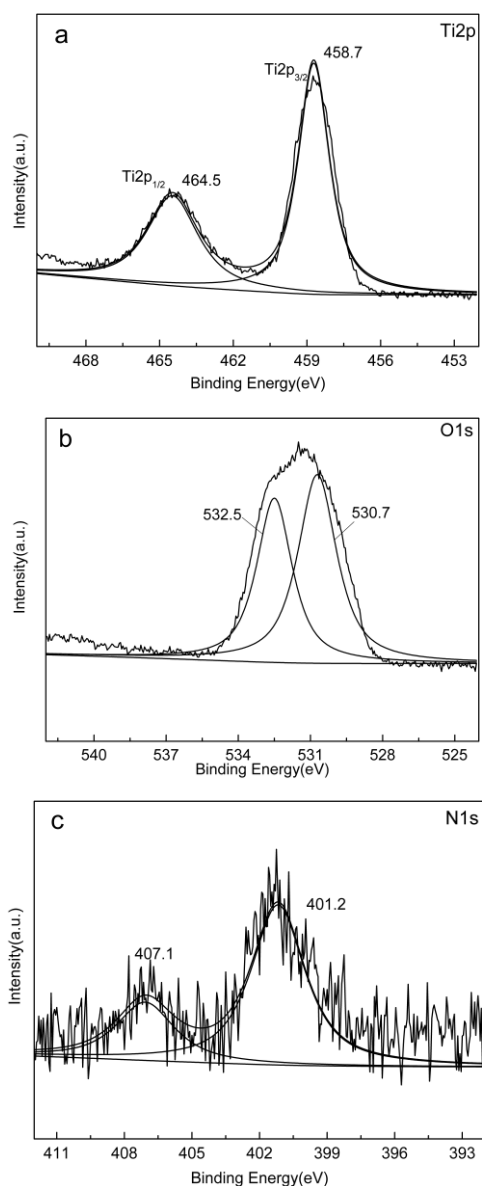


Fig. 4. XPS spectra of P3: (a) Ti2p spectra, (b) O1s spectra, (c) N1s spectra.

3.5 Zeta potential

Combined with the TG and FI-IR characterization results, there were many hydroxyl groups on titanium peroxide surface, which were negatively charged. It could be hypothesized that electrostatic adsorption happened between titanium peroxide and the positively charged cationic dyes [7]. It could be concluded that the titanium peroxide with more hydroxyl groups had greater saturated adsorption capacity. However, Table 2 showed that the absolute zeta potentials decreased with the ability to adsorb methylene blue improving. In Low's studies [20], the charge density on the shear plane was calculated from the zeta potential; the surface charge density was calculated from the values of the total amount of surface charges and the values of specific surface areas [21]. Hydroxyl groups ought to be on the surface of the particles. This was in accord with the result that the absolute zeta potentials decreased with the ability to adsorb methylene blue improving. It could be concluded that the sample with higher absolute zeta potential had higher stability in reaction system [13], while it had poorer ability to adsorb methylene blue. As a result we could conclude that the adsorption had no contact with the stability of the samples. The adsorption was electrostatic adsorption not traditionally physical adsorption, which was in accord with the result in the literature [7].

Table 2. Zeta potential of samples and the saturated adsorption capacities for methylene blue.

| Sample | Zeta potential (mV) | The saturated adsorption capacities for methylene blue (mg/g) |
|--------|---------------------|---|
| P1 | -27.6 | 157.98 |
| P2 | -26.5 | 176.38 |
| P3 | -23.6 | 263.25 |
| P4 | -23.8 | 238.33 |
| T1 | -34.6 | 7.22 |
| T2 | -31.7 | 20.15 |
| T3 | -26.0 | 216.11 |
| V1 | -26.3 | 202.22 |
| V2 | -23.7 | 226.11 |
| V3 | -27.5 | 177.32 |

3.6 Adsorption experiment

The saturated adsorption capacities of prepared titanium peroxide samples were demonstrated with 400 mg/L methylene blue solution and 200 mg/L heavy metal compounds solution. As shown in Fig. 5, all adsorption curves exhibited the same regularity. The concentration of methylene blue or heavy metal ions decreased dramatically in the first 5 min. This was due to the strong electrostatic interaction between positively charged methylene blue or heavy metal ions and negatively charged titanium peroxide [7]. Subsequently, the

concentration of methylene blue or heavy metal ions slowed down, while the adsorption rate was slower than that at the beginning stage. It could be explained that the decreasing adsorption vacant surface sites became difficult to be occupied due to the repulsive forces between the adsorbed molecules [22].

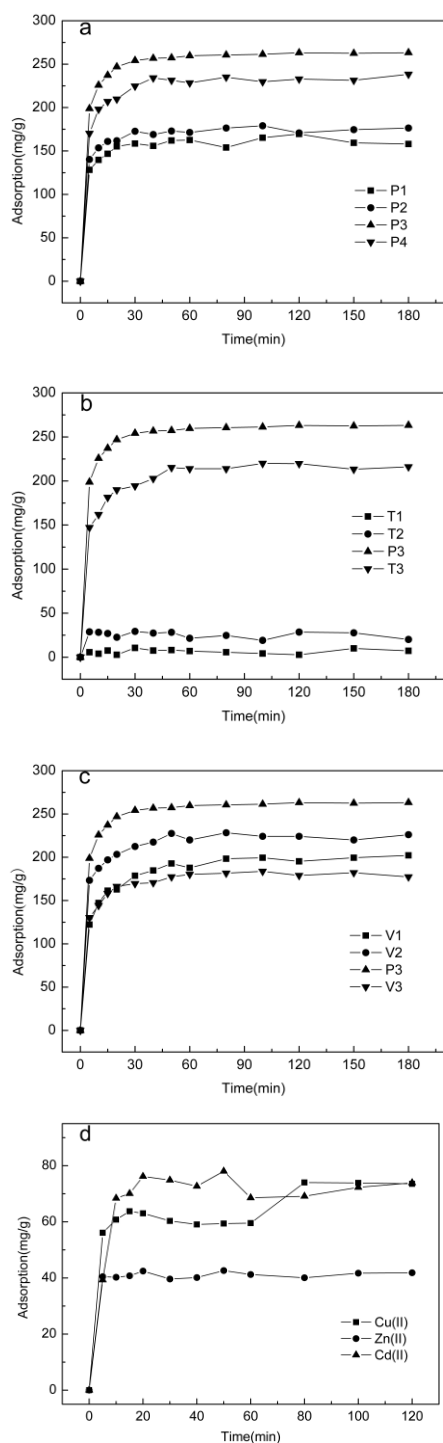


Fig. 5. Adsorption curves of samples: (a) samples with different pH on methylene blue, (b) samples with different temperature on methylene blue, (c) samples with different volume of H₂O₂ on methylene blue and (d) P3 on heavy metals.

The results of P1, P2, P3 and P4 adsorption on methylene blue were shown in Fig. 5 (a). As we could see, the adsorption rate of P3 was the maximum, then P4, P2 and P1. The results could be explained that in alkaline solution, the titanium peroxide was stable [3], while hydroxyl groups were excess in high pH solution (pH > 9.0) which interfered the procedure of methylene blue adsorbed by titanium peroxide. The saturated adsorption capacities of P1, P2, P3 and P4 for methylene blue were shown in table 2.

Fig. 5 (b) showed the adsorption curves of T1, T2, P3 and T3 adsorption on methylene blue. P3 adsorbed the most methylene blue, with T1 and T2 adsorbing a small amount of methylene blue. It could be concluded that temperatures prepared T1 and T2 were too low to form a large amount of hydroxyl groups on titanium peroxides, while hydroxyl groups on titanium peroxides would be damaged with too high temperature. Table 2 showed the saturated adsorption capacities of T1, T2, P3 and T3 for methylene blue.

As the adsorption curves of V1, V2, P3 and V3 adsorption on methylene blue shown in Fig. 5 (c), the result was that P3 also showed the maximum adsorption rate. At the beginning, the adsorption rate of the samples became larger with the volume of H₂O₂ (30%) added increasing, for the reason that more hydroxyl groups appeared on titanium peroxide. Then, to a certain degree, the volume of H₂O₂ (30%) was enough to form the most hydroxyl groups, while more H₂O₂ (30%) would have a negative effect on the saturated adsorption capacity of the sample. The saturated adsorption capacities of V1, V2, P3 and V3 for methylene blue were shown in table 2.

The adsorption curves of P3 adsorption on Cd (II), Cu (II), and Zn (II) were shown in Fig. 5 (d). The result was that the adsorption of Cd (II) was approximately 73.89 mg/g, that of Cu (II) was approximately 73.54 mg/g and that of Zn (II) was approximately 41.83 mg/g. The results showed that equilibrium could be reached quickly, and heavy metals could also be adsorbed by titanium peroxide.

4. Conclusion

A series of titanium peroxide samples were prepared with the reaction of titanium sulfate solution and H₂O₂ solution on controllable conditions and showed different adsorption properties on methylene blue. The optimum pH, highest temperature and volume of H₂O₂ is 9.0, 40 ± 2°C and 35 mL. The sample can not only adsorb methylene blue, but also has excellent adsorption property on heavy metals. The saturated adsorption capacities of the titanium peroxide for methylene blue, Cd (II), Cu (II), and Zn (II) were 263.25, 73.89, 73.54 and 41.83 mg/g at 25°C, respectively. The adsorption was rather fast and adsorption equilibrium was reached in a short period of time for methylene blue and all three heavy metals. Characterization results suggested the obtained mesoporous material was amorphous in nature,

existing peroxy groups and hydroxyl groups, and the controlling mechanism of adsorption processes could be electrostatic adsorption.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51308252), Jilin Province Science and Technology Development Plans (No.20130101091JC) and the analysis and testing foundation of Jilin University and Changchun Technology Innovation Fund (No. 2009086).

References

- [1] R. S. Reddy, T. M. Shaikh, V. Rawat, P. U. Karabal, G. Dewkar, G. Suryavanshi, A. Sudalai, *Catal Surv Asia*. **14**, 21 (2010).
- [2] D. T. Sawyer, J. S. Valentine, *Acc Chem Res*. **14**, 393 (1981).
- [3] J. Mühlebach, K. Müller, G. Schwarzenbach, *Inorg Chem*. **9**, 2381 (1970).
- [4] A. Bandgar, S. Sabale, S. Pawar, *Ceram Int*. **38**, 1905 (2012).
- [5] G. K. Dewkar, T. M. Shaikh, S. Pardhy, S. S. Kulkarni, A. Sudalai, *Indian J Chem*. **44**, 1530 (2005).
- [6] T. M. Shaikh, P. U. Karabal, G. Suryavanshi, A. Sudalai, *Tetrahedron Lett*. **50**, 2815 (2009).
- [7] X.-G. Zhao, J.-G. Huang, B. Wang, Q. Bi, L.-L. Dong, X.-J. Liu, *Appl Surf Sci*. **292**, 576 (2014).
- [8] A. Öztürk, E. Malkoc, *Appl Surf Sci*. **299**, 105 (2014).
- [9] P. Wang, M. Cao, C. Wang, Y. Ao, J. Hou, J. Qian, *Appl Surf Sci*. **290**, 116 (2014).
- [10] J.-G. Huang, M.-X. Zhao, H.-T. Chen, L.-L. Dong, X.-T. Guo, X.-J. Liu, *Optoelectron. Adv. Mater.-Rapid Comm*. **9**, 471 (2015).
- [11] K. A. Gschneidner, *Ame Chem Soc: Washington, DC*. 1981.
- [12] D. Klissurski, K. Hadjiivanov, M. Kantcheva, L. Gyurova, *J Chem Soc, Faraday Trans*. **86**, 385 (1990).
- [13] J. Liao, L. Shi, S. Yuan, Y. Zhao, J. Fang, *J Phys Chem C*. **113**, 18778 (2009).
- [14] C. Randorn, S. Wongnawa, P. Boonsin, *Sci Asi*. **30**, 149 (2004).
- [15] U. K. Nizar, J. Efendi, L. Yuliati, D. Gustiono, H. Nur, *Chem Eng J*. **222**, 23 (2013).
- [16] K. Bubacz, B. Tryba, A. W. Morawski, *Mater Res Bull*. **47**, 3697 (2012).
- [17] F. Dong, W. Zhao, Z. Wu, *Nanotechnology*. **19**, 365607 (2008).
- [18] J.-G. Huang, S. Pang, B. Wang, H.-Y. Ma, M.-Y. Zheng, L.-L. Dong, X.-J. Liu, *Optoelectron. Adv. Mater.-Rapid Comm*. **9**, 139 (2015).
- [19] V. Štengl, T. M. Grygar, J. Henych, M. Kormunda, *Chem Cent J*. **6**, 113 (2012).
- [20] P. F. Low, *Soil Sci Soc Am J*. **45**, 1074 (1981).
- [21] H. Li, S. Wei, C. Qing, J. Yang, *J Colloid Interf Sci*. **258**, 40 (2003).
- [22] J. Huang, Y. Cao, Z. Liu, Z. Deng, W. Wang, *Chem Eng J*. **191**, 38 (2012).

*Corresponding author: 2433317235@qq.com