The Photocatalytic Activity of Nano-TiO$_2$ (anatase) Gradient Coating on Tourmaline Beads

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Abstract. Gradient nano-TiO$_2$ (anatase) /tourmaline beads were prepared by sol impregnated method, and the phase composition and microstructure of gradient coating were characterized by XRD and SEM, and the photocatalytic activity were evaluated by degradation of methyl orange (MO), compared with that of pure nano-TiO$_2$ (anatase), tourmaline beads. The result indicated that the MO degradation ratio by tourmaline beads is 5.8%; that by pure nano-TiO$_2$ (anatase) is 38.2%; while the MO degradation ratio approached 70.4% by gradient nano-TiO$_2$ (anatase) /tourmaline beads, much better than the other two types of catalysts. When the gradient nano-TiO$_2$ (anatase) /tourmaline beads are illuminated by UV irradiation, the electron–hole pairs are generated and the photogenerated carrier will be adsorbed tightly on the anode of tourmaline, owing to its strong electrostatic field, which suppresses the recombination of the electron–hole pairs, and enhances photocatalytic efficiency.

1. Introduction

With the rapid development of the global economy, the global environment is becoming increasingly serious, all kinds of poisonous and harmful material seriously pollutes people's living environment, and has attracted extensive attention all over the world. Tourmaline mineral material has natural electrical polarity, thermoelectricity, piezoelectricity, radiation wavelength 4-14 μm infrared performance, release negative ions performance[1]. The use of natural environmental mineral tourmaline material management air or water heavy metal ions pollution has begun to research reports[2].TiO$_2$ by researchers' attention is due to its higher oxidation activity, good chemical stability, non-toxic to the human body, low cos, pollution-free and wide range of applications[3]. However, Titania can only operate under UV light irradiation because of its wide bandgap (Eg=3.2ev, λg < 384 nm) [4], and the fast recombination of the photogenerated electron-hole pairs restrict its technological utility for limited applications [5]. The method by doping and modified has been proven to be an efficient route to improve the photo-catalytic activity of TiO$_2$[6-10].

In this paper, Gradient nano-TiO$_2$ (anatase) /tourmaline beads prepared enhance titanium dioxide light response range. And the phase composition and microstructure of gradient coating were characterized by XRD and SEM, and the photocatalytic activity were evaluated by degradation of methyl orange.

2. Experimental procedure
At room temperature, 15ml of Ti (OC\textsubscript{4}H\textsubscript{9})\textsubscript{4} and diethanol amine was mixed with 60 ml of anhydrous ethanol (solution A). Solution B consisted of 0.9mL deionized water, 12mL anhydrous ethanol in the required stoichiometry. Then solution B was added dropwise into solution A under vigorous stirring at room temperature for 0.5 h until the transparent sol was obtained. The above sol was allowed to stand for 20 h to form a viscous sol. The change in viscosity with time was monitored using Brookfield viscometer.

The tourmaline beads were degreased, cleaned thoroughly and dried in an oven at 70°C before deposited on it. Afterwards, the tourmaline beads were impregnated into the viscous sol. The viscous TiO\textsubscript{2} sol adhered to the tourmaline beads was dried in open atmosphere at room temperature. A very thin and uniform film of TiO\textsubscript{2} was further dried in an oven at 70°C for 3 h. Following this method the more coatings were prepared. Gradient nano-TiO\textsubscript{2} (anatase) /tourmaline beads were prepared.

The crystalline phase of the samples was analyzed by XRD (Shimadzu D/Max – 2200 /PC). The particle morphology and microstructure of the samples were performed on SEM (Hitachi S4800).

The photocatalytic activity of each simple was evaluated by the degradation of MO in TiO\textsubscript{2} aqueous solution under UV irradiation. The different Gradient nano-TiO\textsubscript{2} (anatase)/tourmaline beads photo-catalyst were loaded into the reactor column, respectively. The solution MO (50 ml, 1 × 10\textsuperscript{-5} mol·L\textsuperscript{-1}) was poured into the reactor column and kept 30 min in dark place. After that the reactor was irradiated under UV irradiation for different time intervals. Then the sample was separated and analyzed by UV-visible spectrophotometer (Lambda 950, PerkinElmer). The absorbance at 464 nm for methyl orange (absorption peak methyl orange) was measured. Photocatalytic activity performance will be indicated by the apparent degradation rate of MO, as shown in Formula (1).

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\text{Degradation rate} = \frac{A_0 - A}{A_0} \times 100\% \quad (1)
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3. Results and discussion

3.1. Structural evaluation of the gradient coatings

The crystalline structure of the gradient coatings was evaluated by XRD. The TiO\textsubscript{2} calcined at different temperatures were shown in Fig.1. The peak at 25.3\textdegree corresponded to characteristic peak of anatase (101) crystal plane. The width of (101) plane diffraction peak of anatase became narrower with the calcination temperature increasing. The diffraction peak of anatase phase has appeared at 380\textdegree, It could be shown that the gel have been crystallized into the anatase structure. At 400\textdegree anatase and rutile coexist to form a mixed crystal, indicating that the anatase phase have begin to transform to rutile. The diffraction peaks of rutile phase were significantly enhanced with the annealing temperature increasing. According to our knowledge, Titanium (IV) oxide exhibits three polymorphs viz., anatase, brookite and rutile. Out of the three polymorphs, the anatase phase draws wide attention because of its activity as a photocatalyst [11]. Therefore, the optimum calcining temperature must be 400\textdegree, and the obtained product has a pure anatase phase and good crystallinity.
Morphological characterization of TiO$_2$ gradient coatings were carried out by SEM, as shown in Fig. 2. It could be seen that the gradient coatings of TiO$_2$ is uniform distribution and highly adherent on tourmaline beads. It could enlarge specific surface area of the catalyst films to improve its photocatalytic activity. From A to B line scan shows that titanium elements have infiltrated into the tourmaline carrier (Fig. 3).

3.2. Photocatalytic activity of Nano-TiO$_2$ (anatase) Gradient Coating on Tourmaline Beads

Fig. 4 shows the photocatalytic degradation efficiency of methyl orange (MO). The result indicated that pure tourmaline beads have a weak effect on degradation of methyl Orange, and the MO degradation ratio is 5.8%. Under UV excitation the anatase TiO2 powders prepared by sol-gel method, have certain catalytic effect of MO. The rate of degradation of MO is 38.2% after reaction 4h. While the MO degradation ratio approached 70.4% by gradient nano-TiO$_2$ (anatase)/tourmaline beads, much better than the other two types of catalysts. This is because the surface electric field of tourmaline can inhibit the re-composite of TiO$_2$ photo-electron and hole, and the photo-electron were firmly adsorbed on the anode of tourmaline, while the photo-hole stayed the surface of TiO$_2$ will combine with surface hydroxyl of gradient material to form hydroxyl free radicals, and improve the photocatalytic reaction efficiency[12].

Fig. 2 displayed the SEM images of tourmaline beads (Fig. 2a) and TiO$_2$ gradient coatings (Fig. 2b) on tourmaline beads.

![Fig. 2](image)

![Fig. 3](image)

![Fig. 4](image)
The photocatalytic activities of TiO$_2$ gradient material at different coating times were shown in Fig.5. With the coating time increase, the photocatalytic efficiency of gradient material can be improved. But when the coating times exceed a certain value, the catalytic effect is decreased. Photocatalytic activity is mainly related to the crystal structure of TiO$_2$. When the coating time is less, nanoparticle film load on tourmaline surface is not uniform, even a small amount of blank area is not covered, TiO$_2$ anatase structure is not perfect and has a big defect, which make the composite risk of photo-electron and hole increased, and activity of gradient material lower. When the load increases the number, the TiO$_2$ nano-granular layer on tourmaline surface also thicken, the activity of gradient composite catalyst rise. Load for 3 times, tourmaline surface of TiO$_2$ anatase crystalline phase structure has been more perfect, and then increase the amount of TiO$_2$ crystalline structure of the TiO$_2$ film has little effect. Under this load, TiO$_2$ nanoparticles completely cover the surface of the carrier, and even a small amount of stuffing. Photocatalytic reaction generally occurs on catalyst surface, the migration of electron-hole has a certain depth. So in actual reaction, real motivated to produce photo-generated carrier only outer certain thickness of the catalyst, the inner layer of TiO$_2$ role is minimal. Preparation of composite photocatalyst, if the load is too many times, the coating layer is too thick, the outer layer of TiO$_2$ particles farther away from the tourmaline surface distance. By tourmaline surface field strength formula($E_r = (2/3)E_o (a/r)^3$) known, the electric field around tourmaline abate rapidly with the increase distance between outer layer of TiO$_2$ and tourmaline surface, and the interaction The interaction between the two weakened, tourmaline not achieve the role of the electron-trapping agent, the activity is decreased. Therefore optimums coating time was three times.

4. Conclusions
We reported the preparation of gradient nano-TiO$_2$ (anatase) /tourmaline beads by sol impregnated method. The photocatalytic activity was determined by degradation of MO under UV light. Gradient materials have significant effect on enhancing the photocatalytic efficiency than pure nano-TiO$_2$ (anatase), tourmaline beads. In this work, it was found that the MO degradation ratio approached 70.4% by gradient nano-TiO$_2$ (anatase) /tourmaline beads. The surface electric field of tourmaline can inhibit the re-composite of TiO$_2$ photo-electron and hole, and the photo-electron were firmly adsorbed on the anode of tourmaline, while the photo-hole stayed the surface of TiO$_2$ will combine with surface hydroxyl of gradient material to form hydroxyl free radicals, and improve the photocatalytic reaction efficiency.

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References
[1] Dong F-A, He D-L and Yuan Ch-L 2005 Journal of Functional Materials 10 1485
[2] Zhang X-J, Wu R-H and Tang Y-H 2004 China Non-metallic Mining Industry Herald 3 39
[3] Ji H-W, Ma W-H and Huang Y-P 2003 Chinese Science Bulletin 21 2199
[4] Xue W, Zhang G and Xu X 2011 Chem. Eng. J 167 397
[5] Ch S-Zh, Zhang P-Y and Zhu W-P 2004 Progress In Chemistry 4 613
[6] Yuan Ch-L and Dong F-Q 2006 Acta Minalogica Sinica 2 233
[7] Ren M, Zhang Y-J, Liu S-W, Ma X and Xiu Zh-L 2006 Journal of Ji Nan University(Science and Technology) 4 15
[8] Peng F, Huang L and Chen Sh-H 2006 Modern Chemical Industry 2 18
[9] Zhang X-H, Wu R-H and Ma H-W 2006 Non-Metallic Mines 3 325
[10] Wu H-J, Wu M, Xie M-S , Liu H, Yang M and Sun F-X 2000 Chinese Journal of Catalysis 5 399
[11] L. Jong, H.N. Wooseok and K. Misook 2003 Appl. Catal. A Gen 244 49
[12] Feng Y-W, Liang J-Sh, Liang G-Ch, Ding Y and Wang J 2003 Journal of Synthetic Crystals 6 569