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Effect of Tourmaline Powder on the Photocatalysis of Nano-TiO_2*

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The mechanism for tourmaline powder improving the photocatalysis effect of nano-TiO_2 was studied by electron-spin resonance (ESR). It was found an increase of the intensity of the symbol of hydroxyl free radical produced by the mixture of the tourmaline and nano-TiO_2 through 355nm wavelength ultraviolet radiating. The tourmaline particle could promote the photocatalysis of nano-TiO_2, which maybe due to the surface electric field of the tourmaline. On the one hand, the surface electric field can make the water molecule ionize and form H^+ and OH^-, and the large quantity OH^- can catch the hole produced by nano-TiO_2. On the other hand, the surface electric field can reduce the photogenerated hole-electron recombination. These two aspects can improve the photons efficiency, and increase the quantity of hydroxyl free radical.

Key words: tourmaline powder, nano-TiO_2, hydroxyl free radical

1. INTRODUCTION

Since Fujishima[1] found the properties of photocatalysis of TiO_2 film, many scientists[2,3] have committed themselves to the studies on how to improve the effect of photocatalysis of nanometer semiconductor materials and how to choose the carriers of nano-materials. Up to now, many inorganic materials have been used as the carrier of photocatalysis materials, such as zeolite and montmorillonite. Tourmaline, as a kind of mineral environment material, has spontaneous polarity at room temperature, so it has a great applied value in protecting environment and promoting people's health[4,5]. The surface electric field exists on a particle of tourmaline along its polar axes, so the granular tourmaline can regulate the pH value of water to about 7.5[6]. The one of reasons why the photocatalysis of nano-TiO2 is low photons' efficiency is because the photoelectrons may return to value band to annihilate the holes. The tourmaline is a kind of polar mineral with surface electric field[7,8].The electric field may influence the photoelectrons transference on the surface of nano-TiO_2, so the photocatalysis effect of TiO_2 may be improved if the tourmaline powder and nano-TiO_2 are mixed together. The mechanism for tourmaline powder improving the photocatalysis effect of nano-TiO_2 was studied by electron-spin resonance (ESR). The experiment results showed that the tourmaline could enhance the production of hydroxyl free radicals (OH).

2. EXPERIMENTS

2.1 The observation of surface electric field

The tourmaline powder was observed by scanning electron microscope (SEM Philips XL30-TMP) and Tunnel Scope2400 made in Danmark (STM). The scanning voltage was 2.5V, the scanning current 0.04nA, and scanning speed 8000nm/s when the tourmaline powder was observed by STM. A mono-energetic electron beam had been employed on tourmaline particle, whose cross-section and the driving voltage being respectively 3nm and 25kV, and the current density of the incident electron beam was 33 μA when the tourmaline powder sample was observed by SEM. The

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powdered tourmaline sample was schorl-dravite crystal (R3m, a=b= 1.59782nm, c=0.715569nm).

2.2 Experiment for tourmaline improving photocatalysis

Tourmaline samples were produced from Inner Mongolia. Nano-TiO_2 (diameter between 20-40nm) was anatase produced by Zhoushan nano-materials factory in Zhejiang province. Two powders were mixed by a certain ratio. The hydroxyl free radical was tested by electron-spin resonance spectrometer (ESP300E) made in Switzerland. During the experiment process, the hydroxyl free radical was captured by DMPO-OH and the sample was radiated by 355nm wavelength UV-light. The scanning time was 160s.

3. RESULTS AND DISCUSSION

3.1 The electric field on the surface of tourmaline

Fig.1 shows the STM image of tourmaline powder on conducting electricity glass. This image displays the particles line one by one which reflects that the tourmaline particles exist electric dipole.

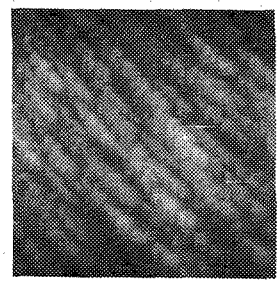


Fig.1 STM image of tourmaline powder, Scanning scope: 4 micron×4 micron

Fig.2 b_1 and Fig.2 b_2 show the sample's SEM images before and after electron beam bombardment, respectively. In Fig.2 b_2, a new phenomenon was found that an electron beam hitting spot in a shape of dumbbell appeared on the particle, and one half of the spot was brighter than the other half. This phenomenon was found by chance when we used electron probe to analyze the elements of tourmaline. The existence of bombardment spot displays the difference of electron density between the spot and other part on the surface of tourmaline. If the spontaneous polarization exists, its direction should be along reversely with c axis of tourmaline crystal, because the copper ion is absorbed on the antilogous end of tourmaline[9].

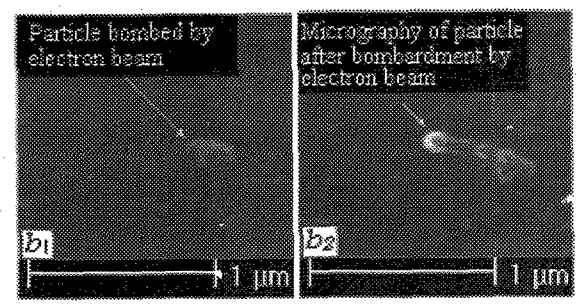


Fig.2 Image of the spot shape that one half was bright and the other was dark: b_1 and b_2 before and after it was bombed, respectively.

3.2 Surface electric field of tourmaline enhance the production of hydroxyl free radical

Fig.3 shows the SEM image of a mixture of the tourmaline powder and nano-TiO_2 in the ratio of 1 to 2. From this image it could be found that the tourmaline particles were evenly covered with nano-TiO_2 powder. This result reflects the polar of tourmaline can absorb the particles of TiO_2. Fig.4 offers the energy spectra of X-ray about the mixture, in which the Al, Si, and Fe are the chemical component of tourmaline, and Ti element is the chemical component of nanometer TiO_2, and O element is the common element of Tourmaline and TiO_2.

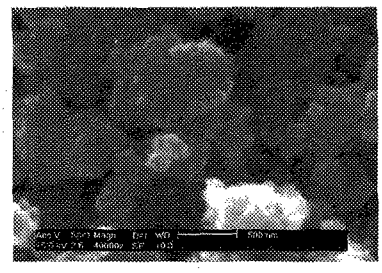


Fig. 3 SEM image of a physical mixture of tourmaline powder and Nano-TiO_2 1:2

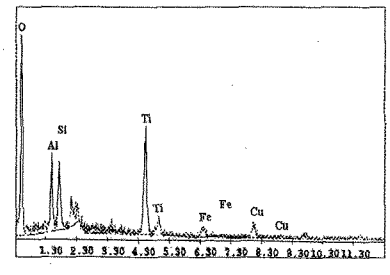
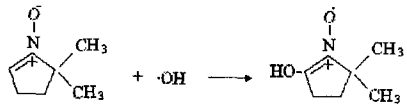


Fig.4 Energy spectra of X-ray about the mixture of tourmaline and Nano-TiO_2

In a word, because of the polarity of tourmaline particle and semiconductor nature of TiO_2 two kinds of powder can be mixed evenly by mechanical method.

The hydroxyl free radical was captured by DMPO-OH



and then, the signal of hydroxyl free radical was tested by ESR. In general, after the hydroxyl free radical is captured by DMPO, there will be 6 iso-intensity absorption peak on the ESR spectra, and may be 4 peaks in the intensity ratio is 1:2:2:1 because of the superposition of 2 peaks. In the experiments, 4 peaks appeared in the ESR spectra (Fig.5,6,7).

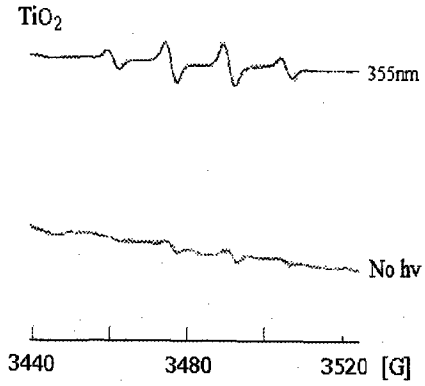


Fig. 5 ESR spectra for nano-TiO_2

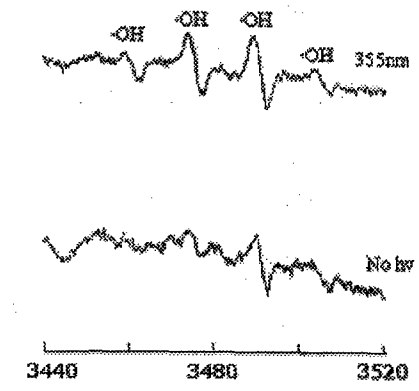


Fig.6 ESR spectra for the mixture of the tourmaline and nano-TiO_2 powder in the weight ratio of 1 to 2.

Comparing Fig.5 with Fig.6 and Fig.7, it could be found that the intensity of ESR absorption signal was higher for the mixture of tourmaline and TiO_2 than for the pure nanometer TiO_2. So, the tourmaline particle can help the nano-TiO_2 produce more hydroxyl free radical.

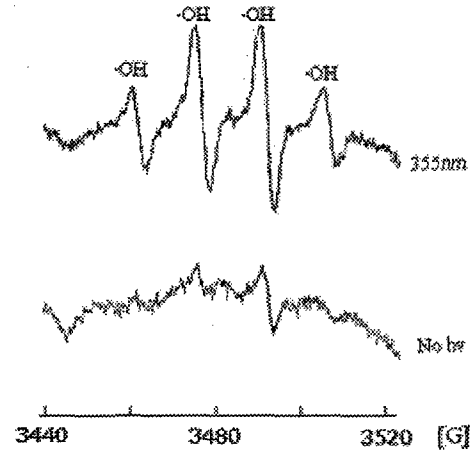


Fig.7 ESR spectra for the mixture of the tourmaline and nano- TiO_2 in the weight ratio of 1 to 5.

The mechanism may be that one hand the surface electric field of the tourmaline particle can break the cluster of water into smaller cluster [10], and enhance the water molecular to ionize,

$$(H_2O)_n \xrightarrow{\textit{Surface electric field of tourmaline particles}} nH_2O$$

$$H_2O \xrightarrow{\textit{Polar of tourmaline}} OH^- + H^+$$

on the other hand, the tourmaline particles can capture or repulse the photoelectrons, and reduce the rate of the photogenerated electrons backing to value band. Above two factors may make the hydroxyl OH^- capture more positive holes, and change into ·OH (hydroxyl free radical). So, tourmaline particle can improve the photocatalysis effect of nano-TiO_2.

4. CONCLUSION

Through electron-beam bombardment, the surface electric field of a tourmaline particle can showed up by the bombardment spot. Tourmaline particle can be evenly covered by nano-TiO_2, and the surface electric field can reduce the photogenerated electron-hole recombination, and enhance the production of hydroxyl free radical.

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