Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2012, Article ID 264186, 4 pages
doi:10.1155/2012/264186

Research Article

Preparation and Photocatalytic Property of TiO_2/Diatomite-Based Porous Ceramics Composite Materials

Shuilin Zheng,[1] Chunhua Bai,[1] and RuQin Gao[2]

[1] *School of Chemical and Environmental Engineering, China University of Mining and Technology, Beijing 100083, China*
[2] *Institute of Environmental Engineering, North China Institute of Water Conservancy and Hydroelectric Power, Zhengzhou 450011, China*

Correspondence should be addressed to Chunhua Bai, baichunhua1978@163.com

Received 13 July 2011; Revised 11 September 2011; Accepted 16 October 2011

Academic Editor: Jiaguo Yu

The diatomite-based porous ceramics was made by low-temperature sintering. Then the nano-TiO_2/diatomite-based porous ceramics composite materials were prepared by hydrolysis deposition method with titanium tetrachloride as the precursor of TiO_2 and diatomite-based porous as the supporting body of the nano-TiO_2. The structure and microscopic appearance of nano-TiO_2/diatomite-based porous ceramics composite materials was characterized by XRD and SEM. The photocatalytic property of the composite was investigated by the degradation of malachite green. Results showed that, after calcination at 550°C, TiO_2 thin film loaded on the diatomite-based porous ceramics is anatase TiO_2 and average grain size of TiO_2 is about 10 nm. The degradation ratio of the composite for 5 mg/L malachite green solution reached 86.2% after irradiation for 6 h under ultraviolet.

1. Introduction

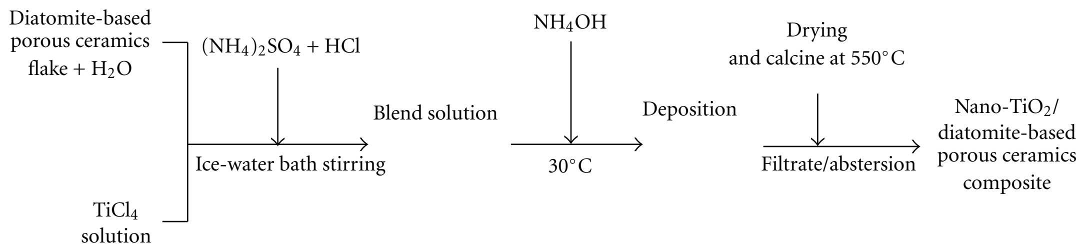
Among various oxide semiconductor photocatalysts, titania appears to be a promising and important prospect for using in environment purification due to its strong oxidizing power, photoinduced hydrophilicity, nontoxicity, considering cost, and chemical and photochemical stability [1–3]. And its photocatalytic performance may be further improved, through surface modification, or made into special shape like nanotubular [4, 5]. But nano-TiO_2 is not convenient to use and hard to recycle after using, so it has been an important research direction for nano-TiO_2-photo catalysis that the nano-TiO_2 is made to load on some porous material, such as charcoal, silica, hierarchical flower-like boehmite superstructures (HFBS), hierarchical flower-like β-$Ni(OH)_2$ superstructures, montmorillonite, and diatomite [6–10].

The diatomite is a natural mineral materials with amorphous silica as main composition, which is low in bulk density, stable in chemical property, and large in specific area. Many researchers have reported on the photocatalytic material with diatomite as substrate. However, few were about the loaded nano-TiO_2 on the surface of diatomite-based porous ceramics. In this paper, taking diatomite as base and adding an amount of ultrafine tourmaline and sintering additive, we prepared the diatomite-based porous ceramics by low-temperature sintering and analyzed its characterization, and then the nano-TiO_2/diatomite-based porous ceramics composite was made by hydrolysis deposition method with titanium tetrachloride as the precursor of TiO_2 and diatomite-based porous as the supporting body of the nano-TiO_2. The photocatalysis property of the composite for the degradation of malachite green was tested.

2. Experimental Section

The diatomite is from Linjiang Meston Powder Material Co., Ltd., whose main composition is SiO_2 80.39%, Al_2O_3 4.07%, and Fe_2O_3 1.87%. Its median particle size is 7.8 μm, specific surface area 20.88 m^2/g. Other materials are ultra-fine tourmaline (median particle size 2.80 μm), sintering assistant, cementing agent, and dispersing agent.

Titanium tetrachloride, ammonium sulfate, is from Beijing Yili Fine Chemical Co., Ltd. Malachite-green is from Beijing Beihua Chemical Co., Ltd. First, the diatomite, tourmaline, sintering assistant with water, some dispersing agent,



Scheme 1

and cementing agent were mixed and milled to 1.2 μm average particle size in the sand mill Mini-Zeta and then dried in oven at 105°C and formed under 40 MPa, sintered at 960°C. The preparation route of the composite of nano-TiO_2 supported on diatomite-based porous ceramic is as in Scheme 1.

The phase composition of the carrier and titanium dioxide thin membrane has been confirmed by Dutch X-ray diffraction (tube voltage 40 kV, tube electric current 40 mA, Cu target, length of stride $A = 1.5406\,\lambda$, the rate of march 5°/min, collects diffraction data scope 20°~80°). The microstructure of porous ceramics composite was observed with scanning electronic microscope (SEM, ST-2000).

Photocatalytic activity experiments of the nano-TiO_2/diatomite-based porous ceramics composites was carried out in a photo-catalytic test equipment shown in Figure 1, taking 5 mg/L, 10 mg/L, and 20 mg/L malachite green solution as initial density. First, the composites were soaked 24 h in the malachite green solution then dried and put on the support in the beaker (1 g sample for 100 g malachite green solution). The position of the composites is 5 mm under the liquid level, and the distance between the liquid level and ultraviolet tube is 50 mm. The 5 mL reaction suspension sample was taken in space for 30 min. The absorbency of suspension in irradiated photo-catalytic degradation processing (in the lens hood) was tested with a spectrophotometer (UV-2000, Shanghai) at solution characteristic wavelength (malachite green $\lambda_{\max} = 618$ nm). Photo-catalytic activity of the nano-TiO_2/diatomite-based porous ceramics composites was characterized by malachite green solution degeneration rate or decoloration rate. According to Langmuir law, there is a linear relation between the absorbency and the density at the characteristic wavelength. The decoloration rate calculates as follows:

$$\eta = \frac{(A_0 - A_t)}{A_0} \times 100\%. \quad (1)$$

Herein, η stands for the malachite green solution decoloration rate, A_0 stands for the absorbency of malachite green solution, and A_t stands for the absorbency after illumination t time.

3. Results and Discussion

Figure 2 shows the SEM photograph of diatomite-based porous ceramics (Figure 2(a)) and the nano-TiO_2/diatomite-based porous ceramics composite (Figure 2(b)). As in Figure 2(a), plentiful diatomaceous primitive hole and the crevice formed by the pellet stack in the diatomite-based porous ceramics can be observed, the aperture of which is tiny. As in Figure 2(b), on the diatomite-based porous ceramics surface and the opening wall, the size of grain that is dispersed evenly in the diatomite-based porous ceramics surface and the passageway is about 10 nm. This kind of microstructure is important to increase the active sites of the photochemical catalysis and improve the photochemical catalysis efficiency. And the BET surface area of composite is 28.9 m^2/g.

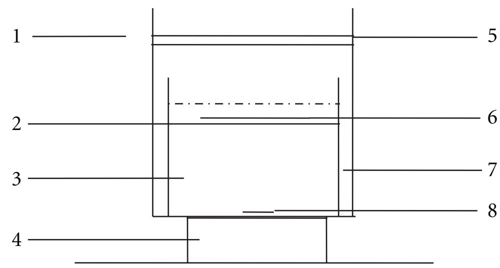
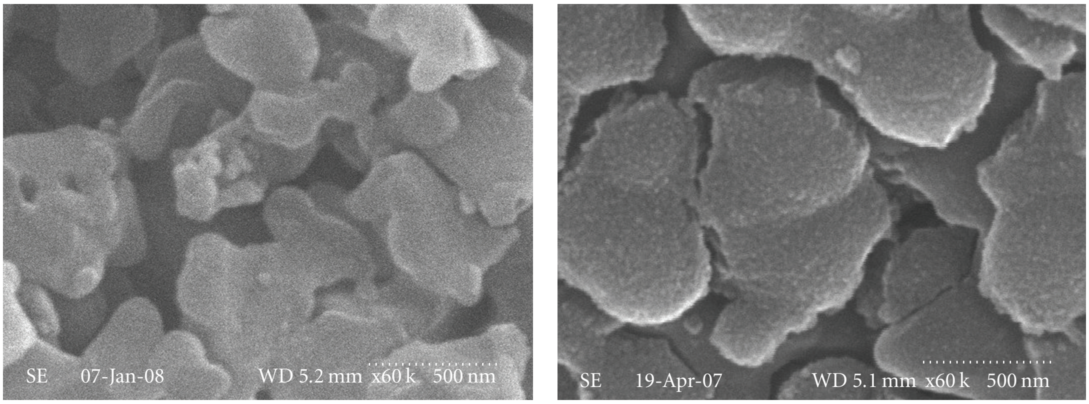


Figure 1: The instrument of degradation on malachite-green 1-Lens hood; 2-support; 3-malachite green solution; 4-magnetic force stirrer; 5-high-pressure mercury lamp; 6-diatomite-based porous ceramics loaded titanium dioxide; 7-cooling water; 8-roter.

The XRD patterns of samples of diatomite-based porous ceramics and nano-TiO_2/diatomite-based porous ceramics composites are shown in Figure 3. The peaks at $2\theta = 26.8°$, 36.8° are characteristic peaks of silica, which show that silica is the primarily composition of diatomite-based porous ceramics. For the nano-TiO_2/diatomite-based porous ceramics composite, the characteristic peaks of anatase crystal TiO_2 have been shown at $2\theta = 25.2°$ (101), 37.7° (004), 48.0° (200), and so on, which explains that the tiny grain deposited on surface of the diatomite-based porous ceramics was anatase.

By diffraction peak width B at half intension of Figure 3(2), the average grain size of TiO_2 calculated by Scherrer's formula is 10.6 nm, which is consistent with Figure 2(b) observed.

Figure 4 is EDS spectra of diatomite porous ceramics and nano-TiO_2/diatomite-based porous ceramics composites. As in Figure 4(a), diatomite-based porous ceramics is mainly composed of Si, O, Al, K, Fe, Si, and so forth, and the Si, O element content is outstanding, which is consistent with its X-diffraction pattern of diatomite-based porous ceramics. For the nano-TiO_2/diatomite-based porous ceramics composite, the Ti element peaks may be seen from Figure 4(b).



(a) (b)

Figure 2: SEM photograph of diatomite-based porous ceramics (a) and nano-TiO_2/diatomite-based porous ceramics composite (b).

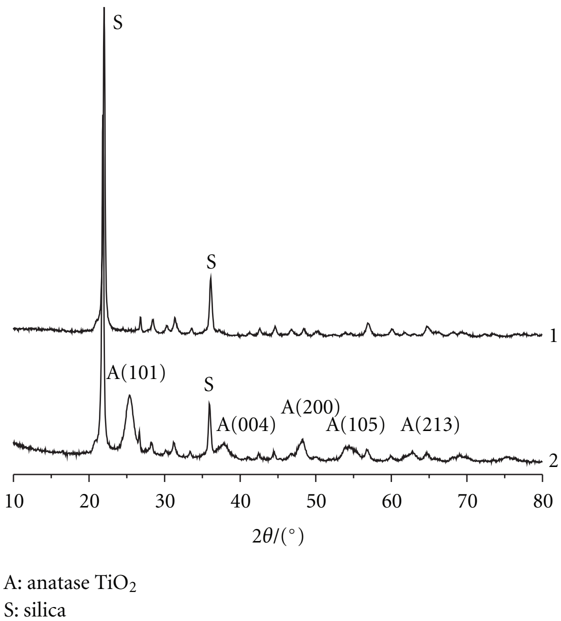


Figure 3: XRD patterns of samples. 1: diatomite-based porous ceramics. 2: nano-TiO_2/diatomite-based porous ceramics composite.

Because of Ti element in surface layer of the diatomite-based porous ceramics, Si, Al, and other elements peaks intensity is obviously dropped. And the TiO_2 concentration of the composite obtained through EDS spectra is about 10.11%.

Figure 5 is the degradation rate curve of different initial densities of malachite green solution with the illumination time. The results indicate that degeneration rate rises gradually with the illumination time. At first, the degradation speed is quick, which slows down after 3 h. With illumination time increases, the intermediary products increase, accumulate on the TiO_2 film, and then reduce the active sites participating in the response, which decrease the photocatalytic activity. The higher the initial density is, the lower is the photocatalysis degradation rate. With the malachite green density thickens, the solution light-admitting quality drops as well as the ultraviolet light intensity which irradiates to the film surface to stimulate photochemical catalysis reduces. When initial density of the malachite green solution is 5 mg/L, the degradation rate of it is at its maximum, which reaches 82.4% and is higher than pure TiO_2 (74.5%) in 6 h.

Nano-TiO_2/diatomite-based porous ceramics composites can improve the photocatalysis effect for malachite green solution, which is related to the properties of support material. Firstly, the porous ceramics surface and the opening wall are quite rough, the specific surface area is high, and the physical adsorption force between ceramics and the TiO_2 particles is strong. Once they contact, opposite electric charges will accumulate in the contact surface for electron transporting, which attract mutually, and strengthen the adsorption of TiO_2 thin film to carrier. Secondly, the pore structures of the diatomite-based porous ceramics provide more surface activity sites and increase illumination area of TiO_2 thin film and the number of the catalyst granule, which is advantageous to improve the photocatalysis efficiency. The primary cause of low nano-TiO_2 photocatalysis quantum efficiency is when the valence band electrons jump to conduction band after absorbed proper photon, lots of electrons in conduction band will return and recombine with holes in valence band. Electrons and holes will be excitated, when nano-TiO_2 loaded on diatomite-based porous ceramics contact with light. Although the photocatalyst of the inner pore cannot obtain illumination, which is advantageous to the electron transporting. It will reduce the recombination probability of surface layer holes and electrons and improve the photocatalysis activity.

Moreover, the ultrafine tourmaline introduced in the diatomite-based porous ceramics will increase the photocatalytic activity of the material. The tourmaline itself in the diatomite-based porous ceramics has permanent electrode, and strong electric field (superficial field intensity achieves 10^7 V/cm^3) existing on the surface will affect nano-TiO_2 under ultraviolet illumination. The conduction band electrons stimulated by high-energy photon are shifted to other mediums or the tourmaline-positive electrode in the tourmaline electric field, which reduces the compound probability of the holes and the electrons and raises the photoproduction hole applying factor.

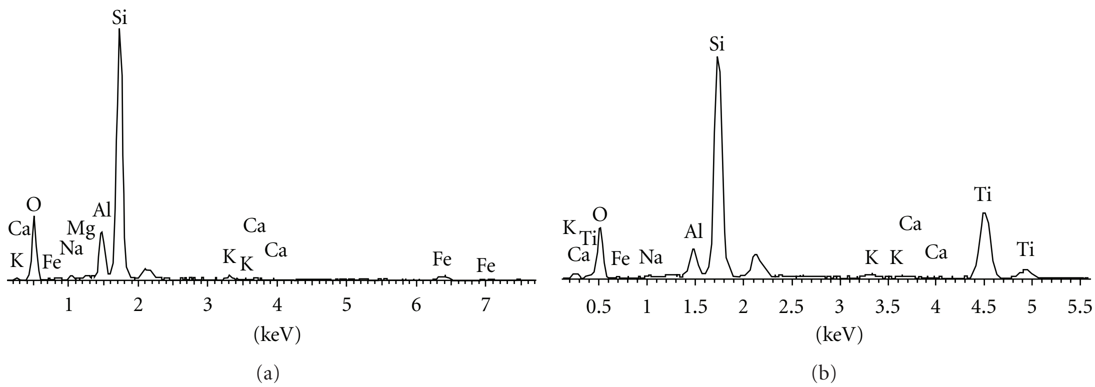


Figure 4: EDS spectra of diatomite-based porous ceramics (a) and Nano-TiO_2/diatomite-based porous ceramics composite (b).

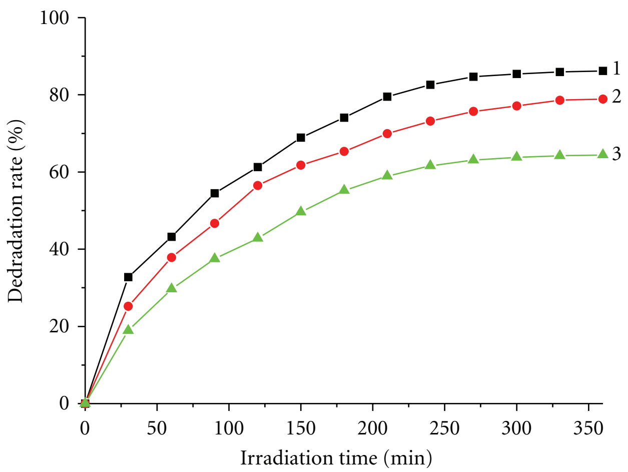


Figure 5: Photocatalysis degeneration curves of malachite green. 1 : 5 mg/L; 2 : 10 mg/L; 3 : 20 mg/L.

4. Conclusions

Taking diatomite as the main material with same ultrafine tourmaline powders and sintering additive added, the porous ceramics with tiny apertures has been made by sintering at low temperature.

Nano-TiO_2 diatomite-based porous ceramics composites with titanium tetrachloride as the precursor has been made by hydrolysis deposition. TiO_2 thin film loaded on the surface of diatomite-based porous ceramics is anatase TiO_2 crystal, and the average grain size of TiO_2 is about 10 nm.

Using the nano-TiO_2 diatomite-based porous ceramics composites to catalyze the malachite green, the degradation ratio of the malachite green reached 86.2% after irradiation 6 h under ultraviolet with initial density of malachite green solution 5 mg/L.

References

[1] J. A. Byrne, P. A. Fernandez-Ibañez, P. S.M. Dunlop, D. M.A. Alrousan, and J. W.J. Hamilton, "Photocatalytic enhancement for solar disinfection of water: a review," *International Journal of Photoenergy*, vol. 2011, Article ID 798051, 12 pages, 2011.

[2] G. F. Shang, H. B. Fu, S. G. Yang, and T. G. Xu, "Mechanistic study of visible-light-induced photodegradation of 4-chlorophenol by $TiO_{2-x}N_x$ with Low Nitrogen Concentration," *International Journal of Photoenergy*, vol. 2012, Article ID 759306, 9 pages, 2012.

[3] J. Yu, J. F. Xiong, B. Cheng, and S. Liu, "Fabrication and characterization of Ag-TiO_2 multiphase nanocomposite thin films with enhanced photocatalytic activity," *Applied Catalysis B*, vol. 60, no. 3-4, pp. 211–221, 2005.

[4] W. C. Oh and M. L. Chen, "The improved photocatalytic properties of methylene blue for V_2O_3/CNT/TiO_2 composite under visible light," *International Journal of Photoenergy*, vol. 2010, Article ID 264831, 5 pages, 2010.

[5] N. H. Lee, H. J. Oh, S. C. Jung, W. J. Lee, D. H. Kim, and S. J. Kim, "Photocatalytic properties of nanotubular-shaped TiO_2 powders with anatase phase obtained from titanate nanotube powder through various thermal treatments," *International Journal of Photoenergy*, vol. 2011, Article ID 327821, 7 pages, 2011.

[6] P. Pucher, M. Benmami, R. Azouani et al., "Nano-TiO_2 sols immobilized on porous silica as new efficient photocatalyst," *Applied Catalysis A*, vol. 332, no. 2, pp. 297–303, 2007.

[7] X. X. Yu, J. Yu, B. Cheng, and M. Jaroniec, "Synthesis of hierarchical flower-like AlOOH and TiO_2/AlOOH superstructures and their enhanced photocatalytic properties," *Journal of Physical Chemistry C*, vol. 113, no. 40, pp. 17527–17535, 2009.

[8] G. K. Zhang, X. M. Ding, F. S. He et al., "Low-temperature synthesis and photocatalytic activity of TiO_2 pillared montmorillonite," *Langmuir*, vol. 24, no. 3, pp. 1026–1030, 2008.

[9] J. Yu, W. Wang, and B. Cheng, "Synthesis and enhanced photocatalytic activity of a hierarchical porous flowerlike *p-n* junction NiO/TiO_2 photocatalyst," *Chemistry*, vol. 5, no. 12, pp. 2499–2506, 2010.

[10] Y. Jia, W. Han, G. Xiong, and W. Yang, "Layer-by-layer assembly of TiO_2 colloids onto diatomite to build hierarchical porous materials," *Journal of Colloid and Interface Science*, vol. 323, no. 2, pp. 326–331, 2008.