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Geopolymer-TiO_2 Nanocomposites for Photocsatalysis: Synthesis by One-Step Adding Treatment Versus Two-Step Acidification Calcination

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Abstract: Geopolymer-TiO_2 nanocomposites were prepared by two different techniques, namely the two-step acidification calcination treatment and one-step adding method. The potential photocatalytic activities of geopolymer-TiO_2 nanocomposites prepared by the two different methods were tested and compared. Nanocomposites prepared via the one-step process showed better photocatalytic activity. The amount of TiO_2 particles loaded on the surface of the foaming materials was investigated by XRD and SEM-Mapping. By comparing with the sample obtained from two-step treatment, the TiO_2 particles were distributed uniformly on the surface of the foaming materials for the sample obtained from the one-step method in this study. Results showed that the specific surface area of the geopolymer-TiO_2 prepared by the one-step treatment process (28.67 m^2/g) was significantly lower than the two-step acidification calcination process (215.04 m^2/g), while the photocatalytic efficiency with methylene blue trihydrate (MB) was better. This is due to the more stable structure of geopolymer-TiO_2 nanocomposites, the better dispersion and more loading of TiO_2 particles on the foaming materials surfaces, leading to the enhanced photocatalytic activity.

Keywords: fly ash; porous materials; TiO_2; one-step; photocatalytic; functional

1. Introduction

Recently, metal dioxides with excellent photocatalytic activity have been attracting attention [1]. Among the various metal dioxides, TiO_2 is usually used as a photocatalyst to treat water pollution for the removal of chemical contaminants [2,3]. Nevertheless, the recovery and the agglomerates of TiO_2 nanoparticles are two inevitable problems [4]. Therefore, developing new TiO_2 supported catalysts is an urgent problem requiring action.

Coal fly ash (CFA) is generally derived from thermal power generation plants and can negatively impact the environment [5]. Some researchers have concentrated on the preparation of environmentally friendly products from CFA through geopolymerization [6,7]. Geopolymers can be used as supported materials, which not only solves the agglomeration of nanomaterials, but also adsorbs a certain amount of harmful substances [8]. Alouani et. al. removed methylene blue from aqueous solution by using fly ash based geopolymer powder [9]. Further, metakaolin based geopolymer was applied to absorb multi- and mono- cations in aqueous solution by Onutai's team [10]. Those studies suggest the possibility of using geopolymer as supports for photocatalyst. In order to increase the amount of the loadable nanoparticles and the contact surface with water, geopolymer could be prepared as a porous structure. However, the existing literature is scarce.

Therefore, we focused on the synthesis of a porous geopolymer supported TiO_2 nanocomposite. Two different methods were used in this study. The first one is the one-step method. Geopolymer-TiO_2

nanocomposites were fabricated by adding TiO_2 particles directly during the preparation of the foamed CFA geopolymer. In the two-step method, foamed CFA geopolymer was first prepared and then TiO_2 particles were loaded on the surface. In order to explore the relationship between the structural properties of the nanocomposites and the synthesis methods, multiple techniques, including SEM, XRD, and BET were applied to investigate the properties of the geopolymer-TiO_2 nanocomposites. The photocatalytic activities of the geopolymer-TiO_2 nanocomposites were monitored via testing the degradation time for MB. Therefore, the objective of this work was to investigate if the one-step convenient process could have an obvious effect on enhancing photocatalytic performance by comparing with the two-step method. Although fly ash-TiO_2 composites have been investigated by some researchers previously, geopolymer-TiO_2 composites were prepared here by the one-step process for the first time, to the best of our knowledge.

2. Materials and Methods

CFA was collected from Shenhua Junggar Energy Corporation in Junggar, Inner Mongolia, China, and calcined at 850 °C for 4 h before use. Analytical grade sodium hydroxide, H_2O_2 solution (30%), grade oleic acid, TiO_2 (P25), methylene blue trihydrate, and nitric acid (HNO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial sodium water glass with original modulus of 3.2 was purchased from Guangdong Foshan Zhongfa Co., Ltd., China, and deionized water is self-made in the laboratory.

The foam materials were prepared based on our previous literature [11]. The alkaline activator (the modulus is 1.2) was thoroughly stirred at 1800 rpm for 8 min. Then CFA (50 g) was mixed at 1800 rpm for 5–6 min after adding to the activator solution. Oleic acid (0.3 g) was added and mixed for another 3–5 min, then H_2O_2 solution (2.25 mL) was added to the mixture, stirring at 2000 rpm for 3–5 min to make geopolymer foam. Finally, the foam mixture was cast into a silica gel mold and cured at 80 °C for 24 h. The material was named as GF.

2.1. Preparation of Geopolymer-Supported TiO_2 by One-Step Process

Subsequently, 5 g TiO_2 (10 mass%) was added to the foamed geopolymer paste, and stirred for further 3–5 min. The final product was named as GFT1.

2.2. Preparation of Geopolymer-Supported TiO_2 by Two-Steps Process

As specified in previous studies [12], 3.0 g TiO_2 was dissolved in 100 mL HNO_3 (1 M), 500 mL deionized water was then added and stirred an hour under the condition of 70 °C. Then 10 g geopolymer was added to the solution and stirred for about 1 h. The materials were washed four times with deionized water for removing excess unloaded TiO_2 and calcined at 500 °C for 2 h, gradually. The product was named as GFT2.

X-ray powder diffraction (XRD) (D8-FOCUS, BrokerAXS (Beijing) Technology Co., Ltd., Beijing, China, Cu-Kα radiation) was used to measure the crystalline phases. The surface morphology of geopolymer-TiO_2 composites was characterized by scanning electron microscope (SEM, Hitachi SU8010, Hitachi, Tokyo, Japan). The measurements of specific surface area and pore volume were carried out via measuring N_2 adsorption-desorption isotherms at 77 K using a Micromeritics ASAP 2020 apparatus (Micromeritics Instrument (shanghai) Ltd., Shanghai, China). Photocatalytic activity was tested using a 300 W Xe lamp (CEL-HXF300, Beijing Zhongjiao Jinyuan Technology Co., Ltd., Beijing, China). 0.04 mg catalyst synthesized by one-step method and by two step process was separately adjunct to MB solution (50 mL) of 10 mg/L concentration. The mixture was stirred in dark condition for 30 min in order to reduce the error caused by adsorption-desorption. After irradiation, the degradation of MB was measured by a UV/vis spectrometer (Lambda 35, Perkinelmer, Guangzhou, China) at 665 nm, which was calculated to concentration by the Beer–Lambert law.

3. Results and Discussion

3.1. XRD Analysis

Figure 1 shows the XRD patterns of the geopolymer and the geopolymer-TiO_2 composites synthesized by different preparation approaches. The geopolymer (GF) owns one "hump" located at around 26.0–28.0° (2θ). For GFT1, the diffraction peak of the anatase phase of titania appears at 2θ = 25.3° (JCPDS NO. 65-5714), and the other diffraction peak is ascribed to the faujasite zeolite (JCPDS NO. 26-0897). Compared to GFT2, the anatase phase of titania exhibits greater sharpness and more intensity (101) of reflection in the GFT1 sample. A part of TiO_2 was lost in the two-step method during the activation process of TiO_2 in dilute acid solution, while one-step method could avoid the waste of TiO_2 on the surface of the support material. This means that the one-step method is more conductive to the preparation of the geopolymer-TiO_2 composite.

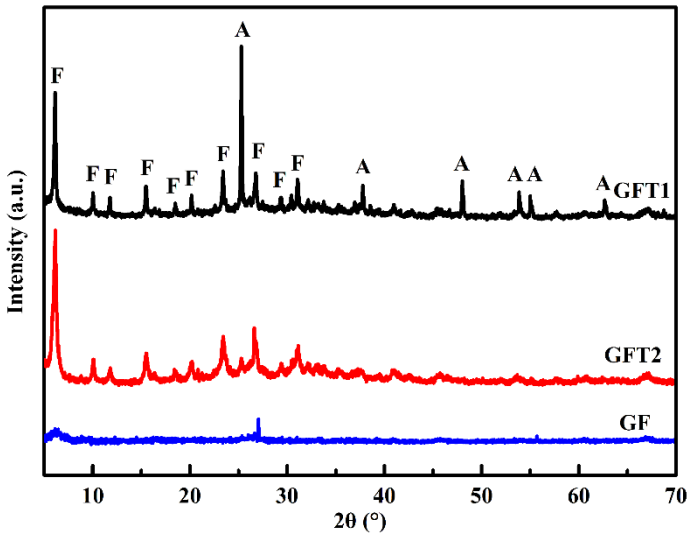

Figure 1. XRD patterns of the geopolymer (GF) and the geopolymer-TiO_2 composites obtained by two different approach. A—anatase, F—faujasite.

3.2. SEM Observations

The surface morphology of GF without any TiO_2 (Figure 2a,b) and GFT1 (Figure 2c,d) or GFT2 (Figure 2e,f) are presented in Figure 2. From Figure 2a, the highly interconnected pores are observed on the surface of the geopolymer, and the material contains 45.91 mass% O, 10.51 mass% Na, 25.44 mass% Al, and 18.13 mass% Si (Figure 2b). Figure 2c–f indicates morphological changes and distribution of Ti in composites with the use of different preparation treatments. The SEM images of GFT1 (Figure 2c) reveal that the excellent porous material formed by the uniform combination of TiO_2 particles and CFA could be observed. From SEM elemental mapping images (Figure 2d), well-dispersed TiO_2 particles (about 6.63 mass%) throughout the composite samples is related to the one-step method [13]. The porous material with a smoother surface and a more uniform pore is shown in Figure 2e, and a small amount of TiO_2 (3.63 mass%, about half of one-step method) is supported on the surface of the porous material by the two step preparation process, which could be reflected by SEM elemental mapping images (Figure 2f). Different treatment methods caused not only a difference in the morphology of the composite materials, but also the amounts and the extent of dispersion of TiO_2 in the composite, which is consistent with XRD analysis.

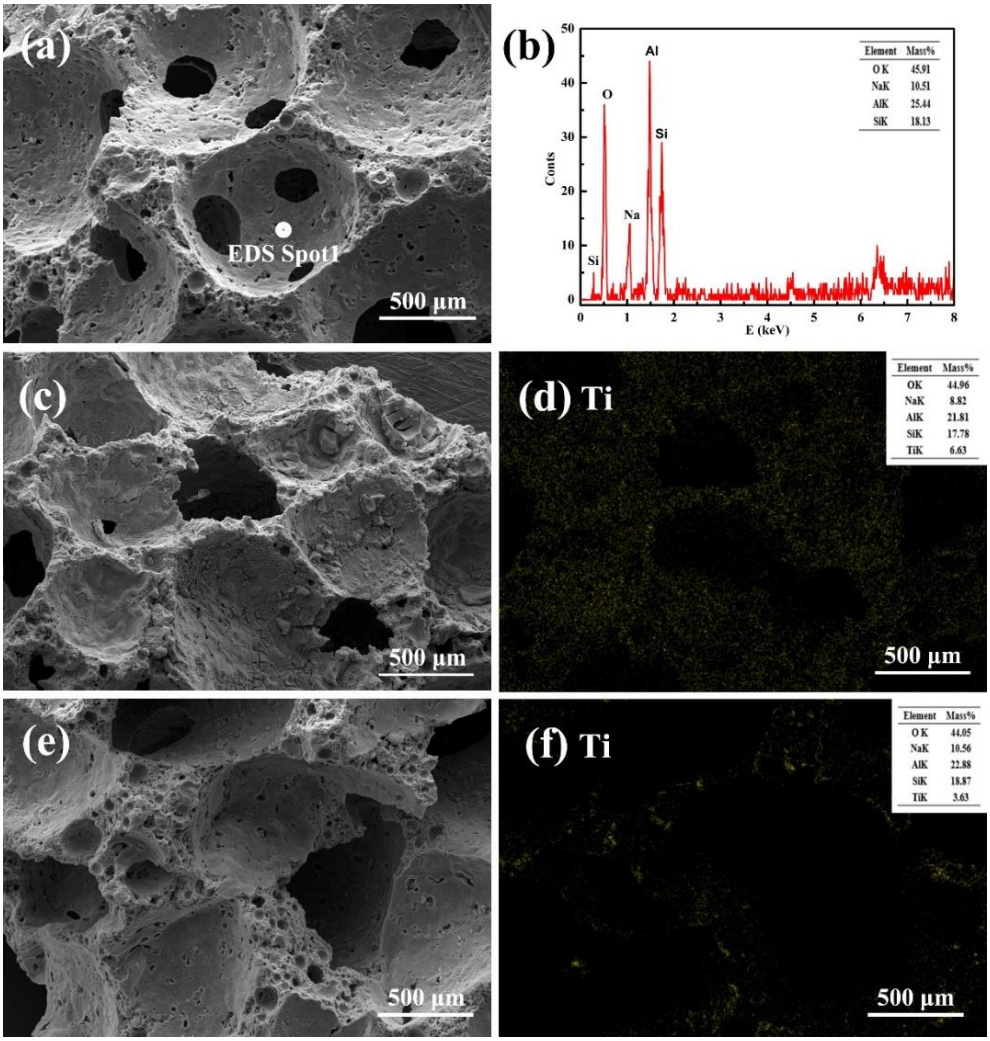

Figure 2. SEM images of geopolymer and geopolymer-TiO_2 composite synthesized via two methods: (**a**) GF, (**b**) EDS spectra of GF, (**c**) GFT1, (**d**) Ti-mapping of GFT1, (**e**) GFT2 and (**f**) Ti-mapping of GFT2.

3.3. BET Analysis

Table 1 summarizes the pore structure of GFT1 and GFT2. By comparing with GFT1, the total pore volume of GFT2 increases from 0.13 to 0.26 cm^3/g, the *t*-plot micropore area increases from 0 to 135.39 m^2/g and the BET surface area increases from 28.67 to 215.04 m^2/g. GFT1 synthesized by the one-step method has a BET surface area of 28.67 m^2/g, which is significantly lower than GFT2. The *t*-plot micropore area for GFT1 is 0 and the total pore volume is only half of GFT2. This phenomenon is caused by the well-distribution of TiO_2 nanoparticles for sample GFT1, which is in favor of improving the photocatalytic efficiency.

Table 1. Comparison of product properties between GFT1 and GFT2.

Sample	Surface Area (m^2/g)		V_{Total} (cm^3/g)
	S_{BET}	$S_{t\text{-plot}}$	
GFT1	28.67	0	0.13
GFT2	215.04	135.39	0.26

*V*total, total pore volume; *St*-plot, *t*-plot micropore area; S_{BET}, BET surface area.

3.4. Photocatalytic Activity

For exploring the influence of geopolymer and geopolymer-TiO_2 composites prepared by two methods on the photocatalytic efficiency, the photocatalytic degradation performance of MB is compared. As shown in Figure 3, GFT1 synthesized by one-step convenient method exhibited better photocatalytic efficiency for MB. The degradation is completed in ca. 15 min. However, GFT2 synthesized by the two-step method presented lower activity than GFT1. The MB is degraded after 45 min of irradiation. Although the photocatalysis property of geopolymer without any TiO_2 particles (GF) is relatively low, the material could fully degrade MB after 50 min. This may be caused by the high adsorption capacity of the geopolymer and some precious metals that have photocatalytic effect contained in the geopolymer [11,14]. The lower amount of anatase phase of TiO_2 (Figure 1), and uneven dispersion of TiO_2 on the surface of the GFT1 sample (Figure 2) suggest that the GFT1 sample could be a potential candidate for the treatment of industrially discharged wastewater.

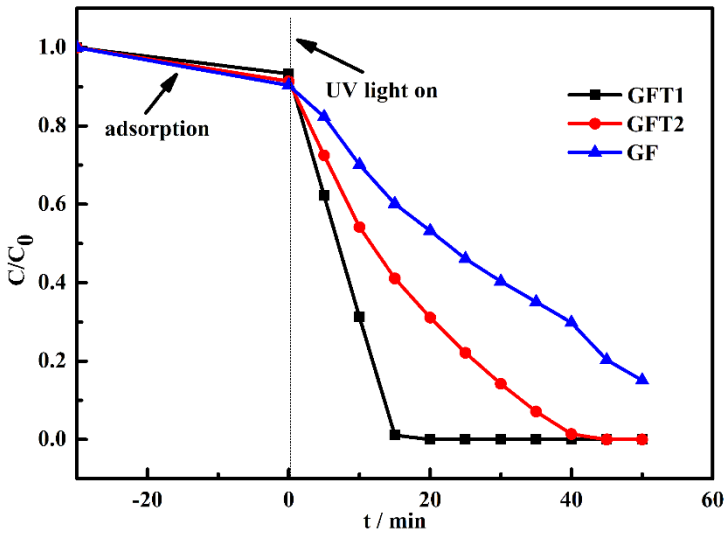

Figure 3. Change in MB concentration versus irradiation time of geopolymer and geopolymer-TiO_2 composites obtained by two preparation approach.

4. Conclusions

In summary, the geopolymer-TiO_2 nanocomposites were prepared via two different processes, namely the one-step method and two-step treatment. The preparation process was found to significantly affect the TiO_2 loading amount, dispense extent, porosity, and surface area of the resultant products. TiO_2 can be uniformly distributed under the condition of high-speed stirring by the one-step process. In addition, the one-step method avoided the waste of TiO_2, and increased the loading amount of the composites. Composites prepared by the one-step method were superior to those synthesized by the two-step method for not only improving the crystallite loading and distribution, but also enhancing the photocatalytic performance.

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