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Porous Bamboo Charcoal/TiO_2 Nanocomposites: Preparation and Photocatalytic Property

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Abstract: Here we report a novel surface modified bamboo charcoal/TiO_2 (SMBC/TiO_2) nanocomposites with high adsorption and photocatalytic property. SMBC were prepared by a wet oxidization method of cheap natural bamboo charcoal (BC) with good absorbent and chemical stabilities. After modification, high density of carboxyl groups were generated on the surface of BC, thus SMBC particles can be easily dispersed in water and have stronger interactions with TiO_2 nanoparticles, which ensure SMBC uniformly coated on TiO_2. And SMBC/TiO_2 nanocomposties have much higher specific surface area than BC/TiO_2, which could offer higher adsorption capacity. The saturated adsorption capacity of SMBC/TiO_2 is approximately 1.6 times, 12.1 times as great as BC/TiO_2 and pure TiO_2, respectively. The synergetic effect of adsorption and catalysis endow SMBC/TiO_2 composites much higher photocatalytic activity than BC/TiO_2 and pure TiO_2 for MB degradation, and the rate constant for MB photocatalytic degradation of SMBC/TiO_2 was almost 7 times and 6 times as large as BC/TiO_2 and pure TiO_2, respectively.

Key words: TiO_2; porous materials; wet oxidization; photocatalysis; adsorption

Heterogeneous semiconductor photocatalysis have received great attention due to the effectiveness and economy in environmental protection[1]. TiO_2 is one of the most suitable photocatalysts because of its high activity, low price, safety and excellent stability[2-4]. TiO_2 nanoparticles are easy to agglomerate, which will cause a remarkable deterioration of photocatalytic property. To overcome these problems, it is vital to find a promising support material to uniformly load TiO_2[5-7]. Many studies have been reported porous materials can be used as suitable candidates for supporting TiO_2 to obtain high active catalysts. For example, Hiromi, *et al*[8] showed that TiO_2-loaded MacroMeso-SiO_2 exhibited unique adsorption properties and enhanced photocatalytic degradation properties for organic dye. Particularly, the combination of TiO_2 nanoparticles with a number of carbonaceous materials is considered to be an effective method for enhancing photocatalytic efficiency. Fan, *et al*[9] demonstrated that uniform dispersion of TiO_2 on graphene was critical for improving photocatalytic efficiency of the photocatalyst.

Bamboo charcoal (BC) will be an ideal substrate due to its porous structure, high surface area and good mechanical and chemical stability. In addition, BC has high electrical conductivity, which can better transport photoinduced charges in TiO_2 under light[10]. Moreover, BC is one of the fastest growing plants on the earth and it's very cheap[11]. However, the poor water-dispersibility of pristine BC will hinder the uniform loading of TiO_2 nanoparticles. Therefore, it is of significant value to improve the dispersibility of BC in water. In recent years, many researches have been devoted to the surface functionalization of carbon materials[12-14]. A very significant method is that using wet oxidation process to modify BC. This way not only increases oxygen-containing functional groups on BC but also improves its water-dispersibility. In this article, the synthesis and characterization of SMBC/TiO_2 nanocomposites using SMBC as supporting materials by a simple and green method was reported. Adsorption and photocatalytic activities of pure TiO_2, BC/TiO_2 in comparison to SMBC/TiO_2 nanocomposites were also investigated. The characteristic micro-nano hierarchical structures of SMBC/TiO_2 nanocomposites can improve the light utilization efficiency of TiO_2 and promote the effective contact between TiO_2 nanoparticles and photocatalytic reactants. Thus the SMBC/TiO_2

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nanocomposites prepared here would exhibit a higher adsorption and photocatalytic activities.

1 Experimental

1.1 Materials and synthesis

Titanium dioxide (TiO_2, anatase), absolute ethanol (≥99.7%), ammonium persulfate (APS, ≥98%), nitric acid (HNO_3, 65%-68%), sulphuric acid (H_2SO_4, 95%-98%) and methylene blue were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Bamboo charcoal (BC, laboratory prepared from 3-5 years of moso bamboo sheets) were used directly.

30 mL of 1 mol/L APS solution (prepared in 2 mol/L H_2SO_4 and 1 mol/L HNO_3) was added to a round bottom flask containing 0.5 g of BC. The mixture was stirred and refluxed at 60 ℃ for 12 h. SMBC were obtained by collecting the precipitation after centrifugation of resultant reaction mixture, then washed thoroughly with water and dried at 60 ℃ under vacuum overnight.

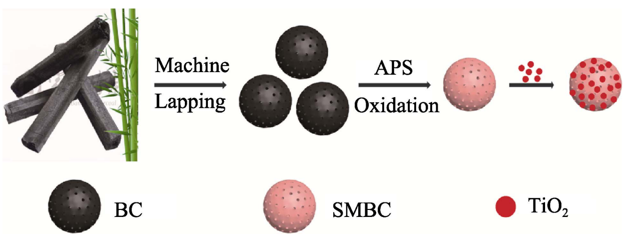
TiO_2 (0.3 g), SMBC (0.5 g) and deionized water (50 mL) were added into a 100 mL round bottom flask. And the mixture was stirred for 10 h at room temperature. The resultant mixture was centrifuged and the precipitation was collected, then dried in vacuum at 60 ℃ for 24 h to obtain SMBC/TiO_2 nanocomposites.

1.2 Characterizations

Fourier transform infrared spectroscopy (FT-IR) analysis of the samples was taken on a Spectrum One FT-IR spectrometer (Perkin-Bhaskar-Elmer Co, USA). The morphology of the samples was determined by field emission scanning electron microscopy (FESEM, JSM7100F, Japan). Crystallinity study of the samples were performed on an X-ray diffraction (XRD, D/MAX-IIIC, Japan), taken from 5° to 80° with Cu−Kα (λ = 0.154 nm) radiation to the sample at the scanning rate of 10°/min. N_2 adsorption-desorption isotherms were measured at −196 ℃ with JW-BK112 analyzer.

1.3 Adsorption capacity and photocatalytic activity measurements

The adsorption capacity and photocatalytic activities of synthesized samples were quantitatively studied by using a typical photocatalytic model reaction: 12 mg of SMBC/TiO_2 composite photocatalysts or pristine BC/TiO_2 composite photocatalysts were homogeneously dispersed into the 100 mL of 15 mg/L methylene blue (MB) aqueous solutions. For comparison purposes, pure TiO_2 nanoparticles were also homogeneously dispersed into 100 mL of 15 mg/L MB aqueous solutions at mass ratio maintaining a similar amount of TiO_2. The prepared dispersion were irradiated in air with a lamp that simulated solar irradiation (LanPu-XQ 350 W adjustable xenon lamp). The distance of light source to the experimental dispersion was setted to 10 cm and optical power of reactor was found to be 50 W/m^2. Before illumination, the dispersion were stirred in dark for 30 min at room temperature, enabling adsorption-desorption equilibrium. Then 5 mL of the solution were taken from the reactor and then separated by centrifuging (12000 r/min, 10 min) to separate the catalyst. At beginning, 5 mL solution was sampled every 10 min during one hour of illumination. MB degradation was determined using a UV-Vis spectrophotometer (UV-3600, Shimadzu) at 664 nm wavelength.



Scheme 1 Schematic illustration of the formation for SMBC/TiO_2 nanocomposites

2 Results and discussion

The application of BC is seriously limited due to its poor water-dispersibility. Herein, we use a wet oxidation process to modify pristine BC for improving its water-dispersibility, after modification, a large amount of carboxyl groups are generated on the surface, which intensify interactions of SMBC with TiO_2 nanoparticles and would do favor to TiO_2 loading. Then commercial TiO_2 with a size of 10 nm are mixed with micron sized SMBC in deionized water to obtain SMBC/TiO_2 nanocomposites with micro-nano hierarchical structures. The characteristic micro-nano hierarchical structures can improve the light utilization efficiency of TiO_2 and promote the effective contact between TiO_2 nanoparticles and photocatalytic reactants[4]. The detailed preparation process of SMBC/TiO_2 nanocomposites is illustrated in Scheme 1. Fig. 1(a) shows FT-IR spectra of BC and SMBC, the weak peaks at 2924 and 1450 cm^{-1} can be assigned to the stretching vibrations and bending absorption bands of $-CH_2$ groups of pristine BC, and the peaks at 3434 cm^{-1} are attributed to the stretching vibrations of active −OH or −COOH groups. After modification, all the characteristic peaks of $-CH_2$ groups turn weaker, revealing that most of $-CH_2$ groups were oxidized. And the characteristic peaks of C=O and C−O stretching vibrations of aliphatic carboxyl groups are observed at 1725 cm^{-1} and 1209 cm^{-1}, respectively. All these results indicate that a large amount of carboxyl groups generated on the surface of SMBC after modification.

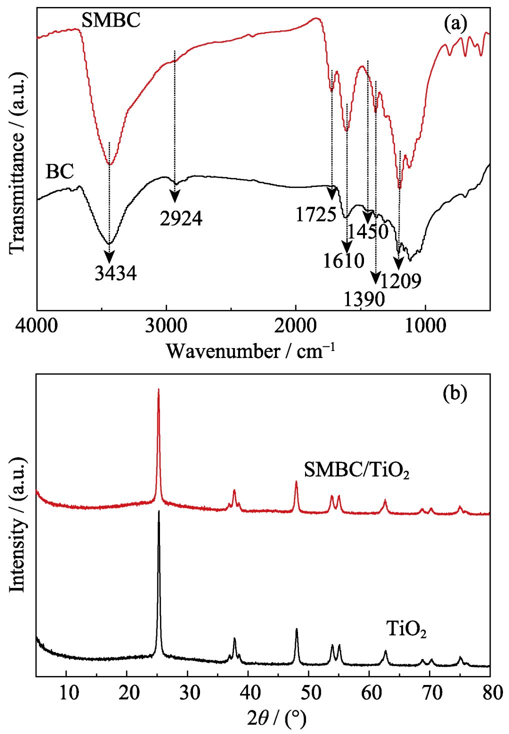


Fig. 1 (a) FT-IR spectra of BC and SMBC, (b) XRD patterns of pure TiO_2 and SMBC/ TiO_2 nanocomposites

XRD patterns of pure TiO_2 and SMBC/TiO_2 nanocomposites are shown in Fig. 1(b). The major peaks of pure TiO_2 at about 25°, 38°, 48°, 54°, 55°, 63° are corresponded to (101), (004), (200), (105), (211) and (204) crystal planes of anatase TiO_2[15]. After loading on the surface of SMBC, all the peaks appeared at the same position and no other peak was observed, indicating that the loading of TiO_2 doesn't change the crystal structure.

The morphologies of the samples were characterized by FESEM and the images are presented in Fig. 2(a-d). Fig. 2(a-b) exhibit the images of BC/TiO_2 nanocomposites and reveal that most of TiO_2 nanoparticles are agglomerated. When using SMBC as supporting materials, it is clearly observed that TiO_2 nanoparticles are even covered on the surface of SMBC (Fig. 2(c-d)). This is attributed to the chemical adsorption between SMBC and TiO_2. The above phenomenon is in good consistence with the FT-IR results, in which the pristine BC modified by APS will have good water-dispersibilities and then be uniformly covered with TiO_2 nanoparticles.

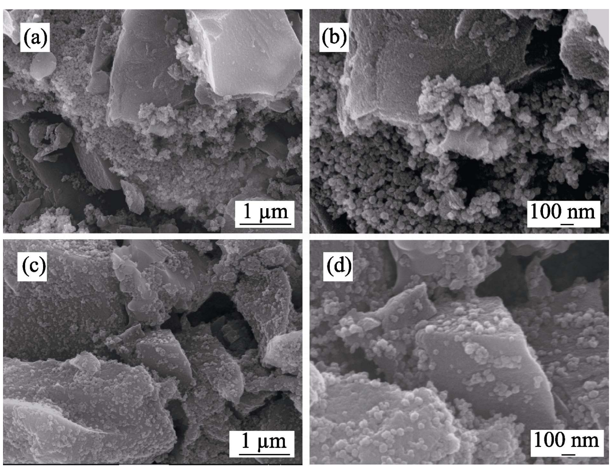


Fig. 2 FESEM images of nanocomposites
(a-b) BC/TiO_2; (c-d) SMBC/TiO_2

N_2 adsorption-desorption isotherms of BC/TiO_2 and SMBC/TiO_2 nanocomposites are shown in Fig. 3. The curves show a classical type-IV characteristic, suggesting the presence of mesopores. Then the textural properties of nanocomposites were analyzed by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. Table 1 shows the specific surface area (S_{BET}), pore size, and pore volume (V_t) of BC/TiO_2 and SMBC/TiO_2 composites. Due to the aggregation of TiO_2 nanoparticles and poor water-dispersibilities of BC, S_{BET} of BC/TiO_2 nanocomposites was only 71 m^2/g. By using SMBC as supporting materials, TiO_2 nanoparticles can be loaded uniformly on the surface and SMBC/TiO_2 nanocomposites display much higher S_{BET} and pore volume. S_{BET} is 155 m^2/g, nearly 2.2 times as large as BC/TiO_2. The higher S_{BET} and V_t would offer more surface active sites and do favor to improve the adsorption and photocatalytic degradation performance.

Fig. 4(a) shows MB removal efficiency of pure TiO_2, BC/TiO_2 and SMBC/TiO_2 nanocomposites under the same condition. Before photocatalysis, all samples are allowed to stand for 30 min to ensure saturated adsorption. Clearly, TiO_2 has almost no adsorption capacity and SMBC/TiO_2 shows a higher MB adsorption efficiency than BC/TiO_2 in dark. It is generally known that the adsorption activity of materials can be greatly influenced by the structural features and surface chemistry[5]. As for BC/TiO_2, the introduction of BC can greatly increase the adsorption capacity

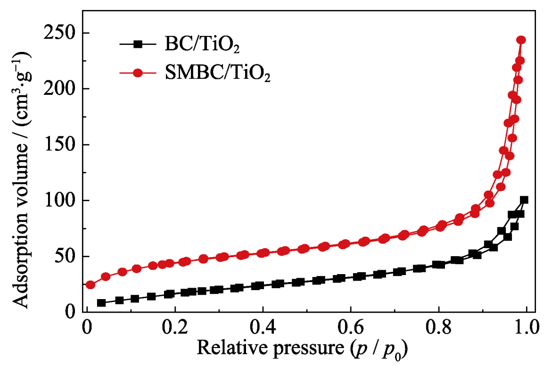


Fig. 3 N_2 adsorption-desorption isotherms of BC/TiO_2 and SMBC/TiO_2 nanocomposit

Table 1 Textural properties of different materials

Sample	$S_{BET}/(m^2 \cdot g^{-1})$	$V_t/(cm^3 \cdot g^{-1})$	Pore size/nm
BC/TiO_2	71	0.17	7.7
SMBC/TiO_2	155	0.36	13.7

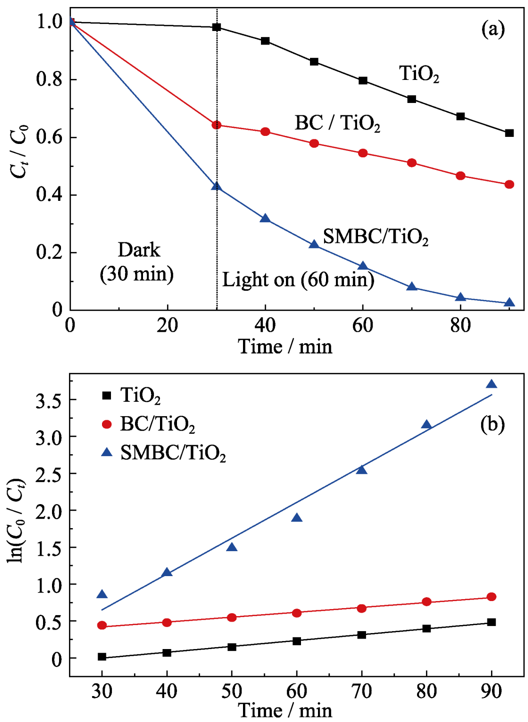


Fig. 4 (a) Changes of relative concentration of MB in the presence of TiO_2, BC/TiO_2 and SMBC/TiO_2 under the same condition, and (b) ln(C_0/C_t) *vs.* time of MB photocatalytic degradation for pure TiO_2, BC/TiO_2 and SMBC/TiO_2

of MB. Furthermore, SMBC with many oxygen-containing functional groups on the surface can improve chemical adsorption. The specific values for maximum adsorption capacities (Q) of all samples are presented in Table 2. As shown in Fig. 4(a), MB are rapidly removed under light irradiation with SMBC/TiO_2 nanocomposites. Specifically speaking, more than 97% of MB with SMBC/TiO_2 has been removed within 1.5 h. Nevertheless, only about 56% of MB could be removed with BC/TiO_2 and 38% removed with pure TiO_2.

As is known to us, when the initial concentration is very low (30 mg/L for MB), the kinetic linear curves of photocatalytic degradation of MB is fitted by Langmuir-Hinshelwood first-order rate law[2], and the reaction rate constant can be calculated by the following equation:

$$\ln(C_0 / C_t) = kt \qquad (1)$$

Where k is the rate constant, C_0 is initial concentration of MB, C_t is MB concentration at time t. The rate constants can be obtained from the slope of linear fitting. As shown

Table 2 Saturated adsorption capacity of MB in dark and kinetic data of photocatalytic degradation in the presence of different catalysts

Sample	Q/(mg·g^{-1})	k/(×10^{-2}, min^{-1})
TiO_2	5.9	0.79
BC/TiO_2	44.7	0.66
SMBC/TiO_2	71.5	4.85

in Fig. 4(b), it can be seen that the MB photocatalytic degradation efficiencies of SMBC/TiO_2 are clearly superior to BC/TiO_2 and TiO_2. The reaction rate constant of SMBC/TiO_2 is almost 7 times and 6 times as high as BC/TiO_2 and TiO_2, respectively. The values of reaction rate constant for all samples are listed in Table 2. That BC/TiO_2 shows a little lower photocatalytic degradation rate than TiO_2 may be attributed to the shading effect of BC.

In addition, time-dependent UV-Vis spectra of MB aqueous solution in the presence of all photocatalysts are shown in Fig. 5. Because of the adsorption effect of BC, a sharp drop of absorption intensity were shown at the first 30 min for both BC/TiO_2 and SMBC/TiO_2 (Fig. 5(b) and (c)), while pure TiO_2 basically remained unchanged (Fig. 5(a)). Under UV irradiation, the absorption intensity of MB in the presence of pure TiO_2 or BC/TiO_2 decreased slowly due to the aggregation of TiO_2, while the

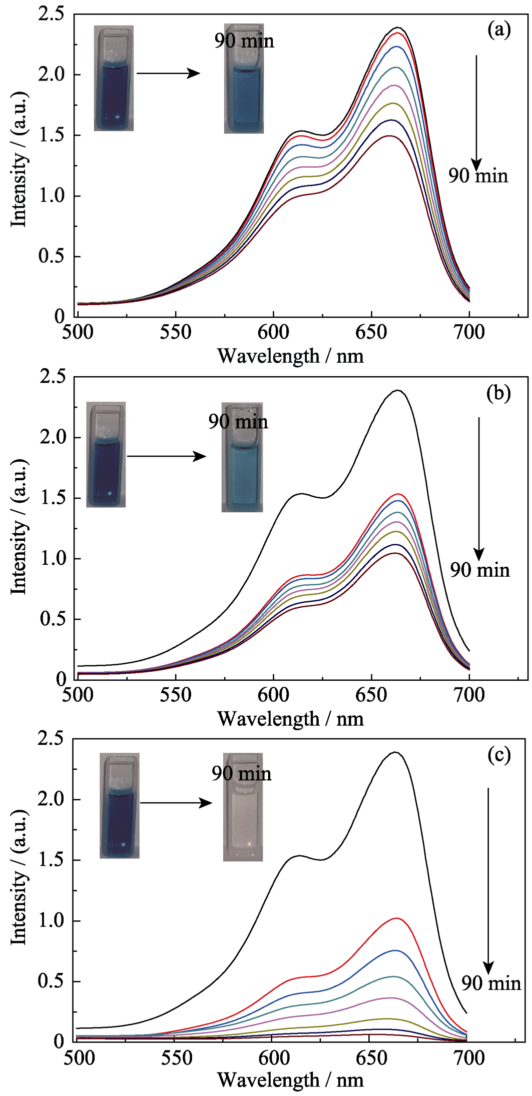


Fig. 5 Time-dependent UV-Vis spectra of MB aqueous solution in the presence of pure TiO_2 (a), BC/TiO_2 (b) and SMBC/TiO_2 (c). The insets show the corresponding changes of MB aqueous solution in color

intensity for SMBC/TiO_2 decreased obviously, indicating that the homogeneous dispersion of TiO_2 on the surface of SMBC enhanced its photocatalytic activity. This superior performance of SMBC/TiO_2 could also be confirmed according to the inset photographs by comparing the color difference of the remaining MB solutions after 90 min irradiation under UV.

3 Conclusion

In summary, a kind of novel surface modified bamboo charcoal/TiO_2 (SMBC/TiO_2) nanocomposites was prepared by a simple and green wet oxide method. The prepared SMBC/TiO_2 nanocomposites exhibit a higher adsorption and photocatalytic activities as compared to pure TiO_2 and unmodified BC/TiO_2 composites. The saturated adsorption capacity of SMBC/TiO_2 nanocomposites was approximately 1.6 times, 12.1 times as great as BC/TiO_2 and pure TiO_2, respectively. And the rate constant for MB photocatalytic degradation of SMBC/TiO_2 was almost 7 times, 6 times as high as BC/TiO_2 and pure TiO_2, respectively. The synergetic effect of adsorption and catalysis gives SMBC/TiO_2 nanocomposites much higher photocatalytic activity for degradation of MB under UV irradiation. Thus SMBC/TiO_2 composites prepared in this work would be potentially applied in waste water treatment.

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多孔竹炭/二氧化钛纳米复合材料制备及其光催化作用

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摘 要: 本工作合成了一种具有高吸附性能和光催化性能的表面改性竹炭/二氧化钛(SMBC/TiO_2)纳米复合材料。通过湿法氧化处理廉价、天然绿色的竹炭(BC), 制备了具有良好吸附性、化学稳定性的表面改性竹炭(SMBC)。经过改性, BC 表面生成大量含氧官能团, 因此 SMBC 粒子易分散于水中, 并且与 TiO_2 有较强的相互作用, 确保 TiO_2 均匀地负载在 SMBC 表面。SMBC/TiO_2 比 BC/TiO_2 有更大的比表面积, 能提供更强的吸附性能。SMBC/TiO_2 的饱和吸附容量大约是 BC/TiO_2 的 1.6 倍, 是 TiO_2 的 12.1 倍。吸附和催化的协同作用使 SMBC/TiO_2 复合材料降解 MB 具有更高的光催化活性, SMBC/TiO_2 光催化降解 MB 的速率常数分别是 BC/TiO_2 和 TiO_2 的 7 倍和 6 倍。

关 键 词: TiO_2; 多孔材料; 湿法氧化; 光催化; 吸附

中图分类号: TF125 **文献标识码:** A