A facile non-hydrogenated method for fabrication of black TiO\textsubscript{2-}\textit{x}/bacterial cellulose composites with improved photocatalytic performance

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Abstract
Black titanium dioxide (TiO\textsubscript{2-}\textit{x}) has attracted extensive attention owing to its visible light absorption and superior photodegradation activity. Here, black TiO\textsubscript{2-}\textit{x} nanocomposites are fabricated via a two-step method followed by a heat treatment process under an argon atmosphere, and then the black TiO\textsubscript{2-}\textit{x} is loaded onto the bacterial cellulose surface by surface grafting. The presence of Ti\textsuperscript{3+} species and oxygen vacancies is proved by XPS characterisation. Furthermore, the black TiO\textsubscript{2-}\textit{x} exhibits excellent photocatalytic activity for pollutants degradation.

1 | INTRODUCTION

In the past few decades, titanium dioxide (TiO\textsubscript{2}) nanomaterials have been widely used. TiO\textsubscript{2} nanomaterials are used as important photocatalyst for hydrogen production [1], environmental pollutant removal [2–4], and photochemical sensors [5]. There are four common crystal phases for TiO\textsubscript{2}: Rutile, anatase, brookite, and monoclinic crystal, in which the rutile and anatase phases TiO\textsubscript{2} are more widely studied due to their higher photocatalytic activity [6–9]. However, conventional white TiO\textsubscript{2} has poor visible light absorption (less than 5\%) due to its wide bandgap (3.0 eV for rutile and 3.2 eV for anatase) and its overall solar activity is thus very limited [10]. The photocatalytic activity depends on the number of working electrons and holes on the surface of the photocatalyst for the reaction [11]. In the photocatalytic process, TiO\textsubscript{2} absorbs light with energy larger than its bandgap and produces excited electrons in the conduction band and excited holes in the valence band. Therefore, in order to improve photocatalytic activity, it is important to improve light absorption and charge separation. In 2011, Chen et al. [6] obtained a black TiO\textsubscript{2} by hydrogenation, which is characterised by a light absorption range extending to the infrared light region. Hydrogenation significantly altered the structural, chemical, electronic, and optical properties of TiO\textsubscript{2} nanoparticles. The crystal-type disordered core-shell nanoparticles formed after the hydrogen treatment can absorb long waves, have structural and chemical defects and stronger conductivity.

At present, abundant works have been devoted to fabricate the black TiO\textsubscript{2} nanomaterials via a mass of synthetic approaches, including high-pressure hydrogen treatment [12], chemical reduction [13], chemical oxidation [14], solution evaporation method [15], hydrothermal method [18] and the like. Studies have shown that the black TiO\textsubscript{2} prepared by the above methods will appear to have a surface disorder and valence red shift, accompanied by the formation of Ti\textsuperscript{3+} and...
oxygen vacancies [16–21]. Along with many advantages, many problems and challenges have followed. First of all, the nature of controlling black TiO$_2$ is still only a scientific assumption at present due to the differences in experimental design and details. Second, the photocatalytic activity of black TiO$_2$ in the visible and near-infrared regions is still not satisfactory. Finally, the resolution of the properties of black TiO$_2$ remains a challenge. Theoretical and experimental conclusions have not yet been proposed. Thus, mass efforts need to be adopted in theoretical and experimental research to promote the application of this new material to various fields. However, both traditional TiO$_2$ and black TiO$_2$ powder are difficult to separate, recover, and recycle, and therefore a support material is required to fix TiO$_2$. In fact, fixing TiO$_2$ on a substrate with a large specific surface area has important research significance. Bacterial cellulose (BC) is a typical biomass material composed of interconnected cellulose nanofibers that can be constructed into a three-dimensional (3D) network structure. Compared to the plant cellulose, BC exhibits greater cellulose content (close to 100%), a greater degree of polymerisation (from 300 to 10,000) and a higher degree of crystallinity (up to 84%–89%). The use of BC as a support material not only provides extremely high surface area but also high porosity and flexibility, avoids filtering of photocatalyst powder, and improves photocatalytic performance. In this work, the TiO$_2$ nanoparticles are fixed on the surface or inside of the BC by some means to form a solid substrate with special functions.

Herein, we have reported a facile synthetic strategy. Black TiO$_{2-x}$ nanocomposites are fabricated via a two-step method followed by a heating treatment process under an argon atmosphere. NaBH$_4$ was chosen to be used for the production of black TiO$_2$ at different mass ratios ($x=0.3, 0.5, 0.7, 1.0$), and then the BC/TiO$_{2-x}$ composites were prepared by ex-situ fixation approach for inserting the TiO$_{2-x}$ into the BC matrix. The as-fabricated composites exhibit excellent visible light absorption, which highly increases photocatalytic activity.

2 EXPERIMENTAL SECTION

2.1 Materials

Tetrabutyl titanate (TBOT, CP, 98%), hydrochloric acid (AR, 37 wt%) and ethanol were purchased from Cdkelong Co., Ltd. and used without further purification. Deionised water (DI H$_2$O) was used for all the experiments.

2.2 Synthesis of black TiO$_{2-x}$ nanomaterials

The black TiO$_{2-x}$ nanoparticles were synthesised via a solvothermal reaction and chemical reduction method. In a typical process, 8 ml of TBOT and 32 ml of ethanol were mixed, recorded as solution A and a compound of 2.0 ml DI H$_2$O, 35.0 ml ethanol and 0.5 ml nitric acid, recorded as solution B. Afterwards, solution A was added dropwise to solution B and the mixture was stirred vigorously for 20 min. Subsequently, the mixture was transferred to a 100 ml Teflon-lined stainless steel autoclave, maintained at 180°C for 12 h. After this, the white powder was collected by washing with distilled water several times, centrifugation, drying, grinding and calcination. Finally, the TiO$_2$ powders were placed into a magnetic boat with NaBH$_4$ at different mass ratios ($x=0.3, 0.5, 0.7, 1.0$) and transferred to tube furnace heated to 550°C at a temperature rate of 5°C min$^{-1}$ and maintained for 1 h under an argon atmosphere. Ultimately, the black TiO$_{2-x}$ nanoparticles were rinsed with DI H$_2$O and dried in the oven.

2.3 Preparation of BC membranes

Acetobacter xylinum NUST5.2 was incubated in an agitated culture at 29°C for 7 days. This culture was composed of D-glucose, sucrose, yeast extract, (NH$_4$)$_2$SO$_4$, KH$_2$PO$_4$, and MgSO$_4$ dissolving in DI H$_2$O to form concentrations of 20, 21, 10, 4, 2, and 0.4 g/L$^{-1}$. The pH of the medium was adjusted to 6.0–6.2 by 2.5 M NaOH. BC membranes were purified by soaking in DI H$_2$O at 70°C for 3 h and then 1 M NaOH in DI H$_2$O at 70°C for 90 min. Samples were rinsed with DI H$_2$O to pH $\approx$ 7 and stored in the refrigerator at 4°C prior to use.

2.4 Fabrication of black TiO$_{2-x}$/BC composites

The BC/TiO$_{2-x}$ composites were prepared by ex-situ fixation approach for inserting the TiO$_{2-x}$ into the BC matrix. First, 0.3 g of TiO$_{2-x}$ nanoparticles were mixed with 30 ml DI H$_2$O to form a suspension in a 150 ml beaker, and several BC membranes (cut into 2 $\times$ 2 cm) were added into the above mixture. The beaker was set on an orbital shaker and continuously stirred at 150 rpm under a temperature of 30°C for 7 h to ensure that the TiO$_{2-x}$ nanoparticles were fully fixed on the BC hydrogels (the detailed process is shown in Figure S5). Afterwards, the composites were rinsed with DI H$_2$O to remove the residues thoroughly and freeze-dried.

2.5 Characterisation and measurements

The morphology of the samples was investigated by means of scanning electron microscope (SEM, JEOL JS-6380LV) and transmission Electron Microscope (TEM, JEM-2100). The crystallinity and the phase composition of samples were characterised by X-ray powder diffraction (XRD, Bruker D8 ADVANCE). UV-vis spectrum was recorded on a Cary 5000 spectrophotometer equipped with an integrated sphere accessory for UV-vis Diffuse reflectance spectroscopy (DRS). The spectroscopic properties of the samples were investigated by Fourier Transform infrared spectroscopy (FTIR, Bomen MB154S) and X-ray photoelectron spectroscopy (XPS, PHI-5300).
2.6 | Photocatalytic activity

P25 was used as a reference TiO$_2$ source and 30 mg/l rhodamine B (RhB) solution was used as a model pollutant. A set of photocatalytic degradation experiments was performed according to the following procedure: Suspensions of the samples (50 mg) in RhB solution were placed in a quartz reactor (200 ml) with a 300 W Hg lamp. Prior to the photoreaction, the solution was magnetically stirred in the dark for 30 min to reach adsorption–desorption equilibrium; then, the reaction was irradiated by the UV light from the top with stirring. During the photoreaction, samples were taken from the reaction mixture at 10-min intervals for assessment of photocatalytic activity.

3 | RESULTS AND DISCUSSION

We chose NaBH$_4$ as a reducing agent to prepare black TiO$_{2-x}$ with visible light absorption. The action of this reducing agent is thermally decomposed to produce active hydrogen (H$^-$) to induce defects (oxygen vacancies, OVs) on the surface of the material; schematic representation of the experimental section is shown in Figure S1. The XRD patterns of all the samples at different mass ratios of NaBH$_4$ as shown in Figure 1(a) indicated the diffraction peaks of the anatase phase (JCPDS No. 21–1272), with a peak shifting towards the lower diffraction angle (as shown in Figure 1(b)). As the number of the reductant increases, the intensity of the peaks reduced and peaks broadened of full width ($2\theta = 25.28^\circ$) compared with pure TiO$_2$. These phenomena reveal that the surface disordered of the titania through the reduction process. Not only that, along with the presence of a high amount of NaBH$_4$ ($x > 0.3$), some new crystalline phases have been formed. XPS is an effective means of studying the elemental composition and chemical state of the samples. Meanwhile, XPS analysis can confirm the existence of the defect such as oxygen vacancies formed on the surface of the samples. The binding energies of Ti 2p at 464.2 and 458.5 eV in all the samples can be assigned to the photoelectrons from Ti 2p 1/2 and Ti 2p 3/2 spin-orbital splittings of Ti$^{4+}$ species, binding energies of 463.1 and 457.6 eV, ascribed to Ti$^{3+}$ species. An obvious peak-shifting towards the lower binding energy of the Ti 2p 3/2 peaks demonstrates the existence of Ti$^{3+}$ in the TiO$_{2-x}$ nanoparticles. The content of Ti$^{3+}$ species increase with the amount of NaBH$_4$ used, perhaps due to more reduction (as shown in Figures 1(c) and (d)).

The degradation of RhB is used to test the photocatalytic performance of different samples under UV-light irradiation. In order to exclude the possibility of self-degradation of RhB, a blank experiment was carried out as displayed in Figure 2(a), and the self-degradation process can be ignored after 80 min under light irradiation. The degradation efficiency of P25 is very high, but it is still not as good as black TiO$_2$ ($x = 0.3$). The degradation rates of the other reduced black TiO$_2$ are 69.8% ($x = 0.5$), 62.1% ($x = 0.7$) and 41.9% ($x = 1.0$), respectively. It is worth noting that the degradation rate of black TiO$_2$ ($x = 0.3$) is 94%, which indicates that the RhB can be removed. Furthermore, the photocatalytic degradation experiments after combining with BC were also performed as shown in Figure 2(b). Obviously, the 30-min dark adsorption test proved the adsorption capacity of the BC material with an adsorption rate of 27%. It can be observed that the degradation ability of TiO$_{2-x}$/BC
CONCLUSION

The chemical composition of the different samples, the high-visible absorption, which is consistent with the TiO$_2$ showing a bandgap of around 3.2 eV, while the reduced samples exhibit 1.50, 1.37, 1.13, 1.00 eV for the pure TiO$_2$, which agrees to the characteristic of the anatase phase. S2(a), the absorption edge is located near 390 nm for pure TiO$_2$, which further indicates the reduction of Ti$^{4+}$ species successfully and the existence of the Ti$^{3+}$ species on the surface of the sample. With the increasing amount of reductant, the intensity of peak at 457.3 eV becomes stronger, which further indicates an increase in the concentration of Ti$^{3+}$ species on the surface of the sample (as shown in Figures S3(b) to (d)).

During the heating process, the active substance hydrogen is thermally decomposed by NaBH$_4$ and reacts with lattice oxygen, which caused the formation of oxygen vacancies on the surface of TiO$_2$. After analysing the experimental data, the XPS spectra of O 1 s can be divided into two characteristic peaks for all samples as displayed in Figure S4. The peaks at 531.2 and 529.6 eV correspond to surface hydroxyl group (O-H) and Ti-O, respectively. The O 1 s (O-H) that existed in the reduced samples are attributed to the reaction of oxygen vacancies with water in the air. As the amount of NaBH$_4$ increases, the peak area of O 1 s (O-H) increases, which indicates an increase in the oxygen vacancies concentration on the sample surface. Meanwhile, the elemental abundances determined by XPS in TiO$_{2-x}$ samples are displayed in Figure S2(a).

In summary, black TiO$_{2-x}$ nanoparticles and TiO$_{2-x}$/BC composites have been fabricated by a two-step method followed by an in-situ reduction process under an argon atmosphere; subsequently, TiO$_{2-x}$ nanoparticles are inserted into the BC matrix by ex-situ fixation approach. The black TiO$_{2-x}$ nanoparticles are provided with improved light absorption ability, and its photocatalytic properties for degradation of dye has been enhanced than that of P25. The colour of TiO$_2$ changed from white to black after NaBH$_4$ reduction and can be attributed to the formation of oxygen vacancies. The results show that the appropriate OV concentration can greatly improve the photocatalytic performance, and excessive OV concentration will actually inhibit photocatalytic activity.

TABLE 1 Elemental abundances determined by XPS in titania samples

| Samples        | Ti   | O    | C    | B    |
|----------------|------|------|------|------|
| Pure TiO$_2$   | 25.1 | 51.5 | 23.4 | 0.7  |
| X = 0.3        | 17.9 | 45.4 | 34.5 | 2.2  |
| X = 0.5        | 17.3 | 51.8 | 26.4 | 4.6  |
| X = 0.7        | 16.7 | 49   | 28.5 | 5.8  |
| X = 1.0        | 12.7 | 50.2 | 30.9 | 6.2  |

4 | CONCLUSION

In summary, black TiO$_{2-x}$ nanoparticles and TiO$_{2-x}$/BC composites have been fabricated by a two-step method followed by an in-situ reduction process under an argon atmosphere; subsequently, TiO$_{2-x}$ nanoparticles are inserted into the BC matrix by ex-situ fixation approach. The black TiO$_{2-x}$ nanoparticles are provided with improved light absorption ability, and its photocatalytic properties for degradation of dye has been enhanced than that of P25. The colour of TiO$_2$ changed from white to black after NaBH$_4$ reduction and can be attributed to the formation of oxygen vacancies. The results show that the appropriate OV concentration can greatly improve the photocatalytic performance, and excessive OV concentration will actually inhibit photocatalytic activity.

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SUPPORTING INFORMATION

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