Photocatalytic Degradation and Hydrogen Production of TiO$_2$/Carbon Fiber Composite Using Bast as a Carbon Fiber Source

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TiO$_2$/carbon fiber composite is achieved by loading TiO$_2$ nanoparticles on biomass carbon fiber, which originates from the carbonized natural bast. The carbonized process and the loading amount of TiO$_2$ are researched in detail. It is found that the carbonized bast fiber shows robust adsorption characteristics for TiO$_2$ nanoparticles in aqueous dispersion, and TiO$_2$ nanoparticles with ~15 wt.% in total weight are uniformly loaded onto the fiber surface. The photocatalytic properties of TiO$_2$/carbon fiber composite are evaluated by photocatalytic degradation of rhodamine B and water splitting for hydrogen production. The results indicate that 90% RhB molecules could be attacked in 60 min under UV light irradiation, and the hydrogen production rate of water splitting is up to 338.51 μmol/h. The highlight is that TiO$_2$/carbon fiber composite is easy to be recycled due to the incorporation of macroscopical biomass carbon fiber.

1. Introduction

Since Fujishima and Honda reported the groundbreaking research work on splitting water to produce hydrogen on TiO$_2$ electrode [1], the photocatalysis had aroused great interest. TiO$_2$ nanomaterials possess commendable performance in terms of its nontoxic, cost effectiveness, strong oxidizing activity, and long-term stability against photocorrosion, which have a very broad application prospect in many fields, such as air pollution, waste water treatment, hydrogen production, and sterilization [2–7]. The application of TiO$_2$ nanomaterials is greatly limited due to the poor visible light response and high charge recombination rate, originating from the wide band gap (3.2 eV for anatase and 3.0 eV for rutile) and the relatively high electrical resistance. TiO$_2$ is combined with carbon species such as carbon nanotubes, graphene, carbon fiber, and graphite-like carbon to form TiO$_2$/carbon composites [8–12] due to the good adsorbability and strong charge transport ability [13, 14].

Carbon fiber is a kind of one-dimensional carbon material with excellent properties, such as high tensile strength, low weight, high chemical resistance, high temperature tolerance, and excellent electrical conductivity, making them very popular in many fields. However, commercialized carbon fiber is relatively expensive due to the raw materials and fabrication process, which is not conducive to the photocatalyst application in the wide range. Biomass fiber carbonization is a feasible route to obtain low-cost carbon fiber, which can meet some applications with no high requirement on mechanical behavior, such as photocatalyst and solar cells.

In the liquid phase system, TiO$_2$ nanomaterials are difficultly recycled after reaction; the poison and aggregate of TiO$_2$ powder are also disadvantageous factors [15]. They all seriously restrict the practical application of photocatalysis. Therefore, it is an effective way to solve the recovery of photocatalyst by combining TiO$_2$ nanomaterials with carbon fiber. Natural bast fiber was used in textile in the ancient times. Its main component is cellulose, which takes up about 75% content of the fiber. The bast becomes a kind of high-
strength, low elongation fiber, so it is an ideal raw material of biomass carbon fiber. However, the electrical conductivity, high temperature resistance, and the chemical and physical adsorptions of bast fiber are disadvantageous. Biomass fiber carbonization is a suitable way to improve electrical conduction and structural properties, including increasing porous structure and fiber roughness, which are conducive to enhance the adhesion and load amount of TiO₂ nanomaterials on the surface of biomass carbon fiber. Because bast fiber is widely accessible and low cost, the biomass carbon fiber using bast fiber as a raw material has great advantages in practical application of catalyst carrier.

Here, the bast was carbonized to get biomass carbon fiber. Then, the carbon fiber was put into TiO₂ nanoparticle dispersion with different concentrations to obtain optimal TiO₂/carbon fiber composite. Using the recycled photocatalyst, the photocatalytic degradation of rhodamine B (RhB) and water splitting for hydrogen production were performed, 90% RhB molecules were attacked in 60 min under UV light irradiation, and the hydrogen production rate was up to 338.51 μmol/h. A theoretical model was proposed to explain the photocatalytic mechanism of the composites.

2. Experimental Section

2.1. Preparation of the Sample. TiO₂/carbon fiber composites were prepared by the following process. A certain amount of bast fiber was located into the tube furnace. In the hydrogen ambience with 100 sccm, the fiber was heated to 300°C at a rate of 10°C/min and then maintained for 1.5 h. The biomass

![Figure 1: The Raman spectrum (a) and SEM image (b) of biomass carbon fiber.](image1)

![Figure 2: XRD patterns (a) and Raman spectra (b) of TiO₂/carbon fiber micronanocomposites.](image2)
carbon fiber was obtained after cooling down. Different amounts of TiO$_2$ nanoparticles (P25) were dispersed into 50 mL deionized water with strong ultrasonic to attain homogenous dispersion (5, 10, 15, and 20 g/L, resp.). After immersing the biomass carbon fiber into TiO$_2$ dispersion for several minutes, the composites were annealed at 450°C under H$_2$ ambience. TiO$_2$/carbon fiber composites with different concentrations of TiO$_2$ dispersions, labelled as TCF05, TCF10, TCF15, and TCF20, could be achieved by repeating the above-depicted procedures to increase the load amount. The load amount of TiO$_2$ nanoparticles was estimated to be about 15 wt.% in total mass.

2.2. Characterization. The morphology of the samples was characterized by field emission scanning electron microscopy (FESEM, Hitachi S4800). Raman spectroscopy (Horiba Jobin Yvon LabRAM HR8000) and grazing-angle X-ray diffraction (Rigaku D/MAX-2400) were employed to characterize the crystal structure of the samples. UV-visible absorption spectrum was recorded using Hitachi U-3900H spectrophotometer to evaluate the photocatalytic degradation performance. Water splitting for hydrogen production was applied to evaluate the photocatalysis on photocatalytic hydrogen production system (Labsolar-IIIAG, Perfectlight Technology Co. Ltd., China).

2.3. Photocatalytic Activity Test

2.3.1. Photocatalytic Degradation of RhB Molecules. The photocatalytic activities were evaluated by photodegradation of RhB molecules. The procedures had been reported in the previous works [16–18]. 0.2 g TiO$_2$/carbon fiber composite was dispersed into 100 ml RhB solution (10 mg/L). The suspensions were magnetically stirred in dark for 30 minutes to reach the adsorption-desorption equilibrium. The degradation was carried out under high pressure xenon lamp (300 W) with a cutoff filter (λ ≥ 400 nm). During the irradiation, 4.5 ml dispersion was collected and centrifuged to remove the catalysts with a time interval. The filtrates were analyzed by recording the changes of the absorption bands (around 554 nm) of RhB using Hitachi U-3900H spectrophotometer. After the photocatalyst reaction, TiO$_2$/carbon fiber composite was rinsed by ethanol and deionized water and dried for recycling.

2.3.2. Photocatalytic Hydrogen Production from Water Splitting. 0.15 g TiO$_2$/carbon fiber composite was added into
the solution mixed by 90 ml water and 10 ml methanol. 2.5 \textmu L chloroplatinic acid solution (10 mg/L), as the assistant catalyst, was added into the solution. Under the 300 W xenon lamp (with cutoff filter) irradiation, the hydrogen amount was analyzed by gas chromatography (GC 7900).

### 3. Results and Discussion

Figures 1(a) and 1(b) are Raman and SEM images of biomass carbon fiber. Figure 1(a) shows that D peak and G peak of the biomass fiber were located at around 1360 cm\(^{-1}\) and 1580 cm\(^{-1}\), which are consistent with the Raman shift peaks of carbon [19]. This indicates that natural bast fiber has been transformed into inorganic carbon fiber after 300°C carbonization process in hydrogen ambience. Figure 1(b) shows that the surface of carbon fiber is much rough. There is a lot of hollow structure on the surface of biomass carbon fiber (the inset), which is in favor of enhancing the adhesion and loading amount of TiO\(_2\) nanoparticles on carbon fiber. In addition, during the measurement process of SEM images, we find that the electrical conduction of the biomass carbon fiber is obviously good,
which facilitates the photocatalytic activity of TiO$_2$/carbon fiber composite.

Figure 2 is XRD patterns and Raman spectra of TCF05, TCF10, TCF15, and TCF20 samples. In Figure 2(a), the peaks sited at approximately 25.21, 37.81, 47.81, 53.91, 55.11, 62.81, 68.81, 70.51, 75.31, and 27.48° are corresponding to the crystal plane (101), (004), (200), (105), (211), (204), (116), (220), and (215) of anatase TiO$_2$ and (110) of rutile TiO$_2$, respectively. The broad diffraction peak located at around 20° is related to amorphous carbon, and the peak gradually decreases due to the increase of TiO$_2$ load amount from TCF05 to TCF20. These results indicate that the loaded photocatalyst on the biomass carbon fiber is a mixture of anatase and rutile TiO$_2$. Figure 2(b) shows the Raman spectra of TiO$_2$/carbon fiber composites. Besides the peaks of carbon fiber, the Raman shift peaks located at 144, 400, 518, and 640 cm$^{-1}$ are related to the Eg, B1g, A1g, and Eg Raman vibrations of anatase TiO$_2$. It illustrates that there are a large number of TiO$_2$ nanoparticles on the biomass carbon fiber, which is consistent with XRD results.
We can believe that TCF15 might be better in the four different TiO$_2$/carbon fiber composites based on the XRD and Raman spectra.

Figure 3 shows the SEM images of TCF05, TCF10, TCF15, and TCF20. For the TCF05 (Figure 3(a)) and TCF10 (Figure 3(b)), TiO$_2$ nanoparticles are locally adhered on the surface of biomass carbon fiber. After increasing TiO$_2$ dispersion concentration, the load amount of TiO$_2$ nanoparticles has been greatly improved for the TCF15 (Figure 3(c)). However, the exceeded dispersion concentration leads to the aggregation of TiO$_2$ nanoparticles on the biomass carbon fiber (Figure 3(d)). Due to the weak adhesion between TiO$_2$ nanoparticles, the aggregated nanoparticles will break off during the following photocatalysis experiment. Therefore, it is obvious that the optimal TiO$_2$/carbon fiber composite is TCF15 due to the suitable load amount and uniformity of TiO$_2$ nanoparticles.

Figure 4 shows the photocatalytic degradation of RhB molecules operated by TiO$_2$/carbon fiber composite under UV light irradiation. It can be seen that the TCF15 has the optimal photocatalytic efficiency from Figure 4(a). Photocatalytic reaction kinetic process should conform to the Langmuir-Hinshelwood model [20]:

\[- \frac{dC}{dt} = v = kH = kK[C](1 + K[C]). \tag{1} \]

Here, C is the concentration of RhB and K is a constant. When the initial concentration of reactants is low, the formula can make the appropriate mathematical transform:

\[ \ln \left( \frac{C_0}{C} \right) = Kt. \tag{2} \]

Here, $C_0$ represents the initial concentration of RhB and C is the concentration of RhB after irradiation t min. This formula is a reaction kinetic equation. It is found that TiO$_2$ photocatalytic degradation reactions abide by the first-order reaction kinetic equation [21, 22]. Based on the kinetic data in Figures 4(c) and 4(d), we can get the optimum load amount of TiO$_2$ nanoparticles on the TiO$_2$/carbon composite by comparing the degradation rate K value. It is obviously seen that TCF15 is the optimal composites in our research range. TiO$_2$ nanoparticles are uniformly loaded on the TCF15 surface, and an ideal photocatalytic efficiency can be expected. The higher concentration will lead to the aggregation of TiO$_2$ nanoparticles and the exfoliation in the photocatalyst experiment process.

To characterize the stabilization of the photocatalysis properties, TCF15 is done in the cycle test for photocatalytic degradation of RhB molecules (Figure 5). It can be seen that the photocatalyst efficiency of TCF15 has no obvious decrease after three cycles. The degradation of RhB molecules was more than 90% within 60 min. Therefore, the composite maintains the high photocatalytic degradation performance. It indicates that the TiO$_2$/carbon fiber composite has the reusability without the decrease of photocatalysis efficiency.

Besides the photocatalytic degradation of organic molecules, water splitting for hydrogen production is another excellent property of photocatalyst. The TiO$_2$/carbon fiber composite can also be used to produce hydrogen energy. Figure 6 shows the photocatalytic hydrogen production under UV light irradiation with TCF15. It is found that the amount of production hydrogen with TCF15 photocatalyst linearly increases with the increase of irradiation time. The average hydrogen production rate reaches to 338.51 µmol/h. Therefore, we believe that the TiO$_2$/carbon fiber composite not only has superior photocatalytic degradation reusability, but also exhibits excellent photocatalytic hydrogen production performance.

The above-depicted results indicate that TiO$_2$/carbon fiber composite has the superior photocatalytic degradation of RhB molecules and water splitting for hydrogen production. To check the reliability of the composite, XRD and SEM are carried out on the TCF15 sample after performing the photocatalysis experiments. In Figure 7(a), the XRD peaks of TiO$_2$ are still very obvious, which indicate that TiO$_2$ nanoparticles existed after photocatalytic reaction. SEM image (Figure 7(b)) also proves that the TiO$_2$ nanoparticles are still uniformly loaded on the surface of carbon fibers, which indicates that the exfoliation of TiO$_2$ nanoparticles is not obvious.

Based on the above experimental results, a model is proposed to explain the photocatalytic mechanism of TiO$_2$/biomass carbon fiber composite. Figure 7(c) shows the schematic diagram of the photocatalysis. The biomass carbon fiber surface is very rough, and there is a large number of hollow structures with robust physical adsorption characteristics. After loading TiO$_2$ nanoparticles, the roughness of the fibers is further increased, which is beneficial to the absorption of RhB molecules. As seen from Figure 2(a), TiO$_2$ nanoparticles are made of anatase and rutile phases with 80:20 ratio, which formed the heterojunctions (the schematic diagram in Figure 7(d)) [23]. Under the UV light irradiation, the electrons are excited from the valance band (E$_v$) into the conduction band (E$_c$) in TiO$_2$, leaving the holes in the valance band. Due to the separation effect of TiO$_2$ heterojunctions for the photogenerated electron-hole pairs, the
photogenerated electrons would transfer from the excited rutile TiO$_2$ phase to the E$_c$ band of anatase TiO$_2$ phase. At the same time, the photogenerated holes would collect in the E$_v$ band of rutile TiO$_2$ phase. It is noted that TiO$_2$ heterojunctions are loaded on the surface of carbon fibers. The carbon fibers have the ability of electron capture since they show high electron storage capacity and electrical conductivity [24]. Due to lower Fermi level of carbon fibers than that of anatase TiO$_2$ phase, electrons transferred from anatase TiO$_2$ phase to carbon fibers can be prompted. The above-depicted two processes can minimize the recombination chance of the photogenerated electron-hole pairs, which improves the efficiency of the photocatalytic activity. After being separated, the photogenerated holes combine with water molecules to form hydroxyl radicals. Meanwhile, superoxide radicals can be formed by combining the photogenerated electrons with oxygen molecules. These radicals possess the potential to oxidize the adsorbed RhB molecules on the photocatalyst surfaces [25]. Photocatalytic degradation process of RhB molecules is dominated by the oxidation of chemical reaction under the UV light irradiation. In addition, the strong adsorption ability of carbon fibers increases the contact opportunities of RhB molecules with the composites, which are also beneficial to the enhancement of photocatalytic properties. Photocatalytic hydrogen production is a dominant reduction reaction of water splitting. Methanol is used to consume the photogenerated hole carriers. The electrons reduce water molecules to produce hydrogen. Therefore, through the design of micronanostructure, we have achieved the recycled, high-efficient TiO$_2$/biomass carbon fiber composite photocatalyst.

4. Conclusions

As the raw material, natural bast fiber is carbonized to get biomass carbon fiber. TiO$_2$/carbon fiber composites are achieved by combining biomass carbon fiber and TiO$_2$ nanoparticles with anatase and rutile mixed phase. Based on the superior adsorbability and electrical conduction of the biomass carbon fiber, the composites show the excellent catalytic activities on photocatalytic degradation and water splitting for hydrogen production. The rate of photocatalytic hydrogen production can reach 338.51 μmol/h. The very favorable feature for TiO$_2$/carbon fiber composite is easy to recycle as the photocatalyst.
Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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