Enhanced Photodegradation of Paper-making Wastewater by Two-dimensional Heterojunction of Titania Plates with Exposed {001} Facets-Graphene Composite

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Abstract. As a typical industrial wastewater, paper-making wastewater contains a number of toxic compounds which is harmful to the environment. In this report, TiO2 plates/graphene composite based 2D–2D heterojunctions were synthesized via one-step solvothermal method. The structure and morphology of the as-prepared composite were characterized by Transmission electron microscope (TEM), X-ray diffraction (XRD), and Raman spectra. The results indicated that sheet-like anatase TiO2 with exposed {001} facets was anchored on the graphene nanosheet. In the degradation of papermaking wastewater under UV irradiation, the as synthesized TiO2 plates/graphene composite exhibited higher photocatalytic performance than the commercial Degussa P25. The effects of the amount of catalyst, H2O2 dosage, pH and the time of light irradiation on the photocatalytic efficiency were also discussed. At the optimum condition of 1.0 g L-1 RGO/TiO2 with the dosage of 0.3% H2O2 at pH=3, the removal rate of CODC and chroma could reach 86% and 100%, respectively in 8 h. This work could provide new insights into the wastewater treatment with a well-defined nanocomposite.

1. Introduction
Semiconductor photocatalysis has been receiving extensive attention on account of its good application in application of solar energy and environmental pollutant treatment [1-3]. The potential of TiO2 as a photocatalyst is well recognized because of its good biological non-toxic, low price and chemical stability [4]. It is very attractive for industrial water treatment and the degradation of Persistent Organic Pollutants. However, there are still two serious problems in pure TiO2, which affect its photocatalytic efficiency in practical application. The first is that TiO2 photocatalysts can only be excited under UV light due to its large band gap energy (3.2 eV); the second is the higher recombination rate of photogenerated electron-hole pairs, which seriously affected the photocatalytic reactions efficiency [5, 6].

Last several years, the photocatalytic activity of TiO2 with exposed {001} facets has been extensively studied [3, 7, 8]. It is generally known that the performance of the photocatalytic materials was closely related to the crystal structure and crystallinity. It has been reported that anatase TiO2
nanomaterials with exposed \{001\} facets showed higher photocatalytic performance than commercial Degussa P25, because of its higher surface energy. But simply changing the crystal structure of the catalyst to improve the catalytic properties is limited [9, 10].

The researchers adopted a variety of methods to improve the titanium dioxide photocatalysis. Carbon/TiO$_2$ composites have been proved that the photocalytic activity can be improved effectively [11, 12]. The heterojunctions between carbon materials and TiO$_2$ improved the separation efficiency of electron-hole pairs. Carbon doping can effectively transfer photogenerated electrons, which is an effective method to solve the recombination problem of photogenerated electron-hole pairs.

Compared with traditional carbon materials, graphene as a new material has been extensively concerned. Because of its excellent chemical stability, high electron transfer properties ($2\times10^7$ cm$^2$/Vs) and adsorption capacity for organic pollutants [13]. It is a simple and effective method to improve the photocatalytic activity by combining graphene with conventional photocatalyst. It is reported that the composite materials of graphene and photocatalytic materials can not only reduce the composite of electron-hole pairs, but also make the absorption wavelength red shift of the composite material [14, 15]. Thus, the improvement of the interfacial charge transfer processes between graphene and TiO$_2$ is important both theoretically and in practical applications.

Papermaking wastewater is mainly produced by pulp and paper making industry [16]. A major feature of wastewater discharge is containing a number of toxic compounds, such as chlorinated lignins, dyes and organic sulfur compounds [17, 18]. These organics cannot be completely removed by traditional coagulation/flocculation and sedimentation process or anaerobic/aerobic reaction [16]. Once discharged, it may cause slime growth, color problems and an increasing environmental risk. Previous researchers demonstrated that advanced oxidation technologies, especially semiconductor photocatalysis have been successfully applied to the complete mineralization of refractory organics derived from the lignin degradation [19, 20]. Among them, TiO$_2$ has been extensively investigated because of its stability and high efficiency in oxidizing various pollutants in papermaking wastewater.

In this paper, a Graphene/TiO$_2$ system with 2D-2D heterojunction interface by a solvothermal reaction was constructed. The photocatalytic properties of composite photocatalyst materials were investigated by the degradation of papermaking wastewater under UV irradiation. The affecting factors of the synthesized materials were also discussed in detail.

2. Experimental

All materials were analyzed and without further purification. Graphite powder was purchased from Bodi Chemical Co. Ltd (Tianjin, China). Sulfuric acid(H$_2$SO$_4$), hydrochloric acid (HCl), hydrogen peroxide (30 wt%), potassium permanganate(KMnO$_4$), ethanol(C$_2$H$_6$O) and tetrabutyl titanate were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), Degussa P25 and hydrofluoric acid were purchased from Sigma-Aldrich (St.Louis, MO, USA). Paper-making wastewater was obtained from the Key Laboratory of Pulp and Paper Science & Technology of the Ministry of Education in Qilu University of Technology. Deionized water used in the experiment was prepared by pure water meter.

2.1. Synthesis of graphene oxide (GO)

Graphite oxide was prepared by modified Hummers’ method [10]. In a typical reaction, 1.0 g of graphite and 1.0 g of NaNO$_3$ were added into 23.0 mL of H$_2$SO$_4$, stirred in the ice water bath. Then, 3.0 g of KMnO$_4$ was added into the above solution slowly. The mixed solution was sonicated for 5 h to form a thick paste. Then 46 mL of ultrapure water was added gradually and stirred for 10 min. Finally, another 140 mL of ultrapure water and 10 mL of H$_2$O$_2$ (30 %) was added into the mixture solution. The above solution was filtered and washed by 5% HCl solution and ultrapure water for several times. The final sediment was dried by vacuum freeze drying.

2.2. Synthesis of TiO$_2$ with exposed \{001\} facets
In a typical experimental procedure, 2.5 mL of HF (40 wt%) was added into 55 mL methanol solution under stirring. Then 8.5 mL of Ti(OBu)$_4$ was added dropwise. Finally, the viscous solution was transferred into a dried 100 mL polytetrafluoroethylene autoclave and kept at 180 °C for 24 h [3, 21]. After let the reactor natural cooling, open the reaction vessel to collect the samples and washed with ethanol and deionized water several times, then freeze-drying.

2.3. Synthesis of RGO/TiO$_2$ nanocomposites.
A certain amount of GO was mixed with methanol solution, ultrasonicated for 60 min to form a homogeneous GO (1 g·L$^{-1}$) solution. Then, 8.5 mL of Ti(OBu)$_4$ and 2.5 mL of HF (40 wt%) were added into 55 mL the above solution slowly drop by drop under stirring. Continue stirring the above solution for 1 h. Finally, the mixed solution was transferred to a 100 mL polytetrafluoroethylene autoclave and kept at 180 °C for 24 h. After let the reactor natural cooling, open the reaction vessel to collect the gray-white samples and washed with ethanol and deionized water several times, then freeze-drying. With the same preparation method, a series of composite photocatalytic materials were prepared by changing the amount of GO, which are marked as 0.125%, 0.25%, 0.5%, and 1%, respectively.

2.4. Characterization
The samples structure was characterized by powder X-ray diffraction (XRD) using a scanning rate of 0.05 °/s within a 2θ range of 10° − 80° (Bruker D8 Advance; Cu Kα = 1.5404 Å). The microstructure of the samples was observed by high transmission electron microscopy (HRTEM, JEM-2100) with an acceleration voltage of 200 kV. The samples were tested by loading on the microgrid copper network.

2.5. Photocatalytic activity measurements
The photocatalytic activity was verified by photocatalytic of a certain concentration of papermaking wastewater in a photocatalytic reactor. The experiments were used the internal irradiation type of 300 W high-pressure mercury lamp as a light source. The light source was placed in the center of the quartz cold trap, and a 250 mL glass bottle was nested as a reactor to load reaction solution. The distance between the center of the light source and the inner wall of the reaction bottle was about 4 cm. The experiment was carried out by loading a magnetic stirrer at the bottom of the reactor to ensure that the reaction solution and the catalyst were mixed homogeneous during the experiment. The experiment by opening the flow of water to control the reaction solution temperature at 30 ± 0.5 °C. 0.15 g photocatalyst was added into 150 mL of paper wastewater to form suspension and homogenized by sonication. Before the photocatalytic experiment, the mixed solution was stirred under the condition of no light for 30 min, in order to make the mixed solution reach the adsorption equilibrium. After adding a certain amount of hydrogen peroxide to the solution and starting the UV irradiation, and 10 mL of the mixed solution was sampled at regular intervals to measure the absorbance at 350 nm after filtration with a microporous filter. COD$_{cr}$ was detected by potassium dichromate method.

3. Results and discussion

3.1. Characterization of the TiO$_2$ nanosheet/graphene composite.
Transmission electron microscopy (TEM) has been used to analyze the morphology and structure of 0.25% RGO/TiO$_2$. It can be clearly observed from the picture (Figure 1a) that RGO has a thin lamellar folds and exhibits 2D shape. It is seen obviously that 2D TiO$_2$ nanosheets evenly covering on the surface of RGO. According to the measurement of the lattice fringes of the HRTEM image (Figure 1b) shows that the lattice fringe width is about 0.235 nm, which proves that the sample is (001) exposed planes of anatase phase [9, 21]. These atomic planes prove that the TiO$_2$ crystals exhibit anatase facets exposed with [001]. It also further confirms the 2D-2D interface heterojunction between RGO and TiO$_2$ is successfully constructed.

In order to analyze the crystal shape and crystallinity of the prepared samples, the samples were scanned by XRD. XRD patterns of GO, pure TiO$_2$, 0.125% RGO/TiO$_2$, 0.25% RGO/TiO$_2$, 0.5% RGO/TiO$_2$ and 1% RGO/TiO$_2$ composite catalysts are shown in Figure 2. Notably, in Figure 2a, the peak at 2θ = 9.8° corresponds to the (002) reflection of stacked GO sheets. However, in the composites in Figure 2b, no diffraction peak at the same angle, confirming the graphene oxide has been completely reduced [22]. The distinctive peaks at 2θ =25.6°, 38.8°, 48.1°, 53.9°, 55.0°, 62.8°, 69.4°, 70.5° and 75.1° can be indexed to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of pure anatase phase of TiO$_2$, respectively. It is obviously showed that the as prepared TiO$_2$ in the compositions was anatase phase (JCPDS card No: 73-1764). Sharpness of all the peaks indicates that TiO$_2$ is highly crystalline.

The prepared catalysts were characterized by Raman spectroscopy (Figure 2c). The typical Raman bands at 153 cm$^{-1}$(E$_{g}$), 400 cm$^{-1}$ (B$_{1g}$), 517 cm$^{-1}$ (A$_{1g}$), and 640 cm$^{-1}$ (E$_{g}$) further confirm the presence of anatase phase of TiO$_2$ in the composites. In addition, the D band centered at 1320 cm$^{-1}$ (disorder band) and the G band at 1594 cm$^{-1}$ (tangential vibration band) attributed to the graphene substrate are also present, which further proves that the catalyst is successfully combined with RGO [10]. The observed TEM pictures, XRD patterns and Raman spectra demonstrated that the sheet-like anatase TiO$_2$ with exposed {001} facets are successfully anchored on the graphene nanosheet.
3.2. Photocatalytic activity and reaction mechanism.

The photocatalytic activity of the catalyst was verified by photocatalytic degradation of paper-making wastewater. Degussa P25 and pure TiO2 were examined as a reference for photocatalytic performance. Figure 3a displays the trend of CODcr concentration of paper-making wastewater with the change of illumination time. The control experiment displayed that CODcr were scarcely removed under UV light without photocatalyst or with pure H2O2. Upon UV irradiation, the highest photocatalytic activity was observed on 0.5% RGO/TiO2 samples, and approximately 86% of CODcr were degraded within 8 h. It is noted that the photocatalytic performance of titania with different G doping ratio is better than that of pure titania. It can be demonstrated that the 2D-2D heterojunction interface between graphene and TiO2 nanosheet contributed significantly to the photocatalytic degradation of CODcr due to the constructive to the carrier transfer. Moreover, TiO2 nanosheets with exposed of {001} facets in papermaking wastewater showed a better effect than the commercial P25. Figure 3b displays the removal rate of chroma for three hours irradiation under different catalysts, consistent with the tendency of CODcr elimination.

![Figure 3.](image_url)

Figure 3. (a) Photocatalytic activities of different samples for paper-making wastewater degradation under UV light and (b) the removal rate of chroma for three hours irradiation.

The effects of the amount of catalyst, H2O2 dosage and pH on the photocatalytic degradation efficiency were studied in detail in Figure 4. The amount of the catalyst is closely related to the surface active site of the catalyst system, and the amount of the catalyst directly affects the optical transmittance of the reaction system. Although the number of active sites or the free radicals increases with the catalyst dosage, the penetration rate of light decreases and further influence CODcr removal rate because of shielding effects. In Figure 4a, the optimal catalyst concentration is 1.0 g·L⁻¹.

In Figure 4b, with the increase of H2O2 dosage, CODcr removal rate also has a tendency to increase first and then decrease. The possible reason is the hydrogen peroxide can well capture electrons and then produce hydroxyl radicals. So adding hydrogen peroxide can enhance the oxidation ability of the system, and then improve the removal rate of CODcr. However, when the hydrogen peroxide concentration continues to rise, the hydrogen peroxide will inhibit the adsorption of organic compounds on the surface of titanium dioxide, resulting in the reduction of CODcr removal rate.

Generally, the pH of the suspension exhibits dissimilar effects on the CODcr removal rate of wastewater because of the different hydroxyl radical amount under various pH values [23]. At pH=3, the removal rate of CODcr reached the highest level in Figure 4c. The removal rate of CODcr is clearly lower at higher pH (pH>3) and lower pH (pH=2). The possible reason is that, in higher pH condition, alkaline solutions are disadvantageous at the lignin molecules adsorbing on the surface of TiO2. Meanwhile, too strong acidity of the solution is not conducive to •OH production.
4. Conclusions
2D-2D heterojunctions interface composed of anatase TiO$_2$ plates with exposed {001} facets and graphene nanosheets were constructed by a simple one-step solvothermal method. Due to the heterojunction interface nature of these hybrids, the as synthesized TiO$_2$ plates/graphene composite exhibited higher photocatalytic performance than the commercial Degussa P25 and pure TiO$_2$. The 2D-2D heterojunction system gives a new insight into the photocatalytic materials assembly. This work broadens the potential application of the photocatalytic system in wastewater treatment.

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Figure 4. Effects of (a) catalyst dosage, (b) H$_2$O$_2$ and (c) pH on the removal rate of COD$_{cr}$.