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A F-ion Assisted Preparation Route to Improve the Photodegradation Performance of TiO$_2$@rGO System-How to Efficiently Utilize the Photogenerated Electrons in the Target Organic Pollutants

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The comparison of the work function of reduced graphene oxide (rGO) and the conduction band position of TiO$_2$ reveals that the density of TiO$_2$ particles grown on rGO could affect the photodegradation efficiency of a TiO$_2$@rGO heterojunction. Herein, with the introduction of F-ion into the preparation route, F-doped shaped TiO$_2$ nanocrystals are densely and uniformly decorated on rGO sheets via the ice bath hydrolyzation method. Thus, more dye molecules are adsorbed on the surface of TiO$_2$ and the photogenerated electrons in the excited dye molecules could be efficiently utilized to improve the overall photodegradation efficiency. The as-prepared F-doped TiO$_2$@rGO heterojunction showed extremely high photocatalytic efficiency under UV-vis light irradiation compared with that of the commercial P25 and the mixture of F-TiO$_2$ and rGO. It is proved that the ice bath hydrolyzation preparation route is crucial to improve the photodegradation efficiency of the final product since the pure TiO$_2$@rGO heterojunction is also much more efficient than the mixture of F-TiO$_2$ and rGO. The present work provides new insights into efficiently utilizing the photogenerated electrons in the target organic pollutants.

1. Introduction

Photodegradation of organic pollutants has attracted extensive attention during the past decades due to its great potential in confronting energy and environmental challenges. To the authors’ knowledge, TiO$_2$ is regarded as one of the most promising candidate materials in the field of photocatalysis for its low toxicity, strong ultraviolet (UV) light absorption, excellent chemical and thermal stability and resistance to photocorrosion. Up to now, a series of TiO$_2$ and TiO$_2$-based materials have been widely applied in the photodegradation and detection of pollutants in air or water. Especially, the composites of TiO$_2$ and carbon (TiO$_2$-C) are currently being considered as potential photocatalysts in the purification of air and water.

RGO, owing to the large specific surface area, excellent conductivity, mechanical and chemical stability, has received considerable attention in many potential applications. Moreover, the functional groups of rGO could provide reactive sites for surface chemical modification, which facilitates its use in composites materials. Therefore, the combination of TiO$_2$ and rGO (TiO$_2$@rGO) could be much more promising to improve the photocatalytic performance of TiO$_2$ due to the vectorial transfer of photogenerated electrons from TiO$_2$ to rGO sheets which effectively suppresses the charge recombination, leaving more hole carriers and promoting the degradation of dyes. Though the photocatalytic activity has been greatly enhanced compared with pure TiO$_2$, the photodegradation is generally realized by utilizing the photogenerated electron-hole pairs in TiO$_2$. Thus, the importance of efficient utilization of the photogenerated electrons in the target degradation dye molecules is always ignored. It is known that the work function of rGO (~4.42 eV) is larger than the conduction band position of TiO$_2$ (~4.40 eV), and the injection rate of the electrons from the excited dyes* into the rGO sheets is even faster than that into TiO$_2$. However, the injected electrons in rGO could hardly promote the subsequent degradation efficiency. Only those excited dyes adsorbed on the surface of TiO$_2$ could directly inject electrons into TiO$_2$, forming reactive oxygen species (ROSs) on TiO$_2$. The dyes which lost electrons are subsequently degraded by these ROSs, thus greatly enhancing the degradation efficiency. Rhodamine B (RhB) is a typical simulating organic pollutant molecule frequently used for evaluating the photodegradation efficiency of a photocatalyst. The work function of RhB and excited RhB* are ~5.45 and ~3.08 eV, respectively. When RhB is used to evaluate the...
photodegradation efficiency of a TiO$_2$@rGO system, the energy band diagram can be expressed by Scheme 1. It is shown that if the surface of rGO sheets is not fully covered with TiO$_2$ nanoparticles, most of the RhB molecules will be adsorbed on rGO, the photogenerated electrons in the excited RhB* cannot flow to TiO$_2$ (line 1 in Scheme 1) and have little contribution to the photocatalytic activity. On the contrary, if most of the RhB molecules are adsorbed on TiO$_2$ nanoparticles, the excited RhB* could directly inject electrons into TiO$_2$ (line 2 in Scheme 1), thus the photogenerated electrons in RhB* could be efficiently utilized. Therefore, the dense and uniform growth of TiO$_2$ on rGO sheets, which is beneficial for the adsorption of the majority of dyes on the surface of TiO$_2$, is crucial to improve the photodegradation efficiency of the TiO$_2$@rGO system. However, this critical issue has been ignored for a long time and the realization and control of dense and uniform growth of TiO$_2$ on rGO sheet is still a great challenge.

Herein, the ice bath hydrolysis method is adopted to achieve the dense and uniform growth of anatase TiO$_2$ nanoparticles on rGO sheets. Furthermore, F-ions are introduced to further improve the crystallinity of TiO$_2$ nanoparticles. The F-doped TiO$_2$@rGO can completely photodegrade the RhB solution with a concentration of 30 mg/L within 6 min under UV-vis light irradiation, which is in sharp contrast with the F-doped TiO$_2$-rGO mixture, which can only degrade 60% of the RhB. It is proved that the dense cover of TiO$_2$ nanoparticles on rGO sheets, no matter with or without the doping of F-ion, can help to efficiently utilize the photogenerated electrons in the target RhB molecules to enhance the final photodegradation efficiency.

2. Experimental
2.1. Catalyst Preparation
Graphene oxide (GO) was prepared using a modified Hummers’ method.$^{46,47}$ 0.55 mL of TiCl$_4$ kept in a refrigerator was extracted using a 1 mL syringe and rapidly injected into the bottom of a parafilm sealed 100 mL bottle with 50 mL of Deionized (DI) water in the form of ice. After that, the bottle was firmly covered with the bottle cap and shaken continuously until the ice was dissolved. In the whole process, no white precipitation was observed. Then 9.57 mL of GO solution (4.6 mg/mL) was injected into the above bottle under stirring to disperse it well. After that, 0.21 g of NaF was added to the above TiO$_2$/GO solution to prepare the F-doped rGO@TiO$_2$ heterojunction. Then the solution was kept stirring in a water bath at 50 °C for 48 h. The color of the solution turned from transparent to gray slowly. The precipitate was collected by centrifugation after being washed with DI water and ethanol several times and then was dried completely at 70 °C. Finally, the product was kept in a ceramic crucible and annealed in a tubular oven at 500 °C for 120 min with nitrogen gas protection. For the preparation of pure TiO$_2$@rGO heterojunction: all the procedures were the same with that of F-doped TiO$_2$@rGO heterojunction without the addition of NaF in the precursor solution. The weight ratio of rGO in these two samples is 11%. The other TiO$_2$@rGO heterojunctions with different weight ratios of rGO were obtained by tuning the volume of the GO solution.

2.2. Catalyst Characterization
X-ray diffraction (XRD) measurement was carried out using powder XRD (Bruker D8 Advance, with Cu K$_\alpha$ radiation operating at 40 kV and 40 mA, scanning from 2θ = 10° to 80°). Transmission electron microscope (JEM-2011 TEM, 200 kV) and Raman spectroscopy (LabRAM HR Evolution, 532 nm) were used to characterize the samples. The X-ray photoelectron spectroscopy (XPS) measurement was conducted on a Escalab 250Xi spectrometer (Thermo Scientific) using monochromatic Al K$_\alpha$ X-ray source (anode HT = 15 kV) operating at a vacuum higher than 2*10$^{-9}$ mbar. Nitrogen adsorption-desorption isotherms were measured on the system (Quantachrome, USA) at -196 °C. The specific surface area and porosity property analysis was calculated by the Brunauer-Emmett-Teller (BET) method. The optical property of the present nanocomposites was measured with diffuse reflectance UV-vis spectrometer (Shimadzu, SolidSpec-
3700DUV) using an integrating sphere and adopting BaSO₄ as a reference.

2.3. Photocatalytic measurement

The photodegradation of RhB was measured under UV-vis light irradiation (300 ≤ λ ≤ 2500 nm) at room temperature. The light source is a 300 W Xe-arc lamp (PLS-SXE300, Beijing). In a typical process, 30 mg of catalyst was firstly dispersed in 42 mL DI water, and then mixed with 18 mL of 100 mg/L RhB solution. Thus, the concentration of the final RhB solution is 30 mg/L. Before irradiation, the suspension was stirred in dark for 40 min to ensure the adsorption-desorption equilibrium. At a given time interval of 1 min, 2 mL solution was taken out and immediately centrifuged to remove the catalyst completely. In the durability test of the F-doped TiO₂@rGO heterojunction in the photodegradation of RhB under UV-vis light, three consecutive cycles were tested. After each cycle, the F-doped TiO₂@rGO heterojunction was filtered, washed thoroughly with water and annealed at 400 °C for 2 h. The concentration of the RhB solution was analyzed on a UV-vis spectrophotometer (UV-1800, Shimadzu). The pH value of the RhB solution was measured by a pH-meter (METTLER TOLEDO, PE20k) after completely removing the catalyst from solution (5 mL) by centrifugation.

3. Results and discussion

The preparation route of the F-doped TiO₂@rGO heterojunction is illustrated in Scheme 2. Generally, ice bath is adopted to ensure a slow hydrolyzation of TiCl₄ to form TiO₂ nanocrystal seeds with extremely small size on rGO sheets. The low temperature (50 °C) growth method could retard the rapid growth of TiO₂ nanocrystals in the solution. Thus, the further growth of TiO₂ on the seeds is expected to result in the dense and uniform growth of TiO₂ nanoparticles on rGO sheets. Moreover, the introduction of F- ion could enhance the photocatalytic activity of TiO₂ by improving the crystallinity of TiO₂.
Figure 2 (a) The liquid-phase photodegradation performances of rGO, F-doped TiO$_2$, the physical mixture (F-doped TiO$_2$ and rGO) and F-doped TiO$_2$@rGO heterojunction towards RhB with time under UV-vis light irradiation (300 ≤ λ ≤ 2500 nm); (b) The liquid-phase photodegradation performance of the F-doped TiO$_2$, mixture, F-doped TiO$_2$@rGO towards RhB with time under visible light irradiation (400 ≤ λ ≤ 2500 nm); (c) Cycling photodegradation towards RhB; (d) The liquid-phase photodegradation performance of F-doped TiO$_2$@rGO heterojunction towards RhB (40 and 50 mg/L) with time under UV-vis light irradiation.

To investigate the crystal phases of the F-doped TiO$_2$@rGO heterojunction, X-ray diffraction (XRD) analysis was performed (Figure 1a). All the diffraction peaks are sharp, and can be indexed to anatase TiO$_2$ (JCPDS, 84-1286), suggesting a good crystallinity of TiO$_2$ nanoparticles. According to the Scherrer formula:

$$D = \frac{0.89 \lambda}{\beta \cos(\theta)}$$  

(1)

where D is average grain size, $\lambda$ is the X-ray wavelength employed, $\theta$ is the diffraction angle, and $\beta$ is the line broadening at half the maximum intensity after subtracting the instrumental broadening. The particle size of the decorated TiO$_2$ nanoparticles could be calculated by typical XRD peaks (Table S1). Taking the (101) diffraction peak as an example, the size of the TiO$_2$ nanoparticles in the F-doped TiO$_2$@rGO heterojunction is around 12 nm. From the Raman spectra (Figure 1b), the graphitized structures (D band (~ 1341 cm$^{-1}$) and G band (~ 1580 cm$^{-1}$)) were observed in both the F-doped TiO$_2$@rGO heterojunction and GO. It is shown that there is no peak position shift of the F-doped TiO$_2$@rGO heterojunction compared with that of GO. Furthermore, the intensity ratio of D band over G band ($I_D/I_G$) increases from 1.05 to 1.09, indicating the reduction of GO with the hydrothermal treatment.  

Owing to the small particle size, the supported TiO$_2$ nanoparticles can be hardly observed in the scanning electron microscopy (SEM) image (Figure S2). Here, the TEM image of the F-doped TiO$_2$@rGO heterojunction confirms that the TiO$_2$ nanoparticles were densely and uniformly decorated on rGO sheets (Figure 1d). Compared with the previously reported TiO$_2$@rGO systems, the decorated TiO$_2$ nanoparticles are much more dense and uniform in the present system. It is supposed that the formation of seeds in ice bath method greatly helps the in-situ growth of the TiO$_2$ nanoparticles on rGO sheets, favouring the photoinduced electron transfer from TiO$_2$ to rGO. Both the edge of rGO and the structure of the TiO$_2$ nanoparticles were shown in an enlarged TEM image (Figure 1e). RGO sheet behaves as a support for TiO$_2$ nanoparticles, and the TiO$_2$ nanoparticles are shaped due to the introduction of F-ion. The average size of the TiO$_2$ nanoparticles in F-doped TiO$_2$@rGO heterojunction is 13 nm (Figure S3), which is very consistent with the above calculated crystal size along (101) diffraction peak. All the observed
Figure 3 (a) The TEM image, (b) HRTEM image and (c) XRD pattern of the pure TiO$_2$@rGO heterojunction; (d) The liquid-phase photodegradation performance towards RhB.

lattice fringes of the shaped TiO$_2$ nanoparticles show a d-spacing of 0.357 to 0.360 nm (Figure 1f), which can be well assigned to the (101) lattice fringes of anatase TiO$_2$.

Figure 2a shows the photodegradation performance of the F-doped TiO$_2$@rGO heterojunction towards RhB with time under UV-vis light irradiation as a function of time. Here, C and $C_0$ represent the remaining concentration of dye solution with certain degradation time and after dark adsorption. And for comparison, the photodegradation performances of rGO, F-TiO$_2$, the mixture of F-TiO$_2$ and rGO, and P25 under the same condition are also shown. Before light irradiation, the RhB solutions with catalysts were maintained in dark for 40 min under stirring, this time period is proved to be long enough to reach the adsorption equilibrium as shown in Figure S4. And the remaining concentration of RhB was calibrated via the fitting curve (Figure S5). It is clearly shown that the F-doped TiO$_2$@rGO heterojunction possesses much better adsorption ability towards RhB compared with F-TiO$_2$, the mixture (F-TiO$_2$ and rGO), or P25 due to the present preparation route induced large surface area (Figure S6, S7 and Table S2), which can be attributed to the dense and uniform growth of TiO$_2$ on rGO and the little ratio of bare rGO between covered TiO$_2$ nanocrystals. The F-doped TiO$_2$@rGO heterojunction shows much better photocatalytic efficiency than F-doped TiO$_2$, suggesting the formation of heterojunction between F-doped TiO$_2$ and rGO. The photodegradation efficiency of F-doped TiO$_2$ increased from 25% to 100% with the formation of the heterojunction structure since it can greatly suppress the electron-hole recombination. Similarly, the performance of the F-doped TiO$_2$@rGO heterojunction is more efficient than P25 for the same reason. Moreover, the performance of the mixture of the same amount of F-doped TiO$_2$ and rGO was much lower than that of the F-doped TiO$_2$@rGO heterojunction. The remaining amount of RhB at 6 min was still 44.9% when the mixture was used as the photocatalyst. It should be noted that in the whole adsorption and degradation process, the pH value maintains at a constant value of around 5.8 (Figure S8), thus, the pH value has no effect on the RhB degradation rate during the whole process. Moreover, there is no obvious change in band gap of TiO$_2$ by the introduction of F-ion (Figure S9), confirming that the influence of light absorption by TiO$_2$ can be ignored. Thus, it is considered that the dense and uniform growth of TiO$_2$ nanocrystals on rGO greatly favours the adsorption of the majority of dyes on the surface of TiO$_2$. As a result, the final photodegradation efficiency of the F-doped TiO$_2$@rGO heterojunction is much higher than the simple mixture. This conclusion could be further supported by the much better photocatalytic performance of F-doped TiO$_2$@rGO heterojunction than those of F-TiO$_2$ and the mixture under visible light (Figure 2b). The photodegradation efficiencies of F-doped TiO$_2$@rGO and the mixture under visible light are 45% and 6% at 30 min, respectively. Considering that RhB solution is stable even under UV-vis light illumination (Figure S10), and holes in TiO$_2$ could not be generated, the efficient utilization of the photogenerated electrons in RhB molecules by the present F-doped TiO$_2$@rGO catalyst can be well confirmed. One should
note that the photodegradation efficiency of F-doped TiO$_2$@rGO under visible light is only 7.2% at 6 min, which falls far behind that under UV-vis light illumination (100%), indicating that holes produced by the band-gap excitation of TiO$_2$ still play a dominant role in the photodegradation process, while the dense and uniform growth of F-doped TiO$_2$ nanocrystals on rGO further enhances the photocatalytic efficiency by the efficient utilization of the photogenerated electrons in the target RhB molecules. Recyclability is another key factor for photocatalysts. Figure 2c shows 3 cycles of photodegradation of the F-doped TiO$_2$@rGO heterojunction towards RhB. It is proved that the good photocatalytic activity could be maintained perfectly after 3 cycles, implying the promising practical application potential of the F-doped TiO$_2$@rGO heterojunction. RhB solutions with high concentrations (40 and 50 mg/L) can also be photodegraded in 12 and 16 min with 30 mg F-doped TiO$_2$@rGO heterojunctions under UV-vis light irradiation (Figure 2d), which further confirms the practical application capability of the present F-doped TiO$_2$@rGO heterojunctions.

To confirm that the dense and uniform growth of TiO$_2$ nanocrystals on rGO can efficiently utilize the photogenerated electrons in the target RhB molecules, pure TiO$_2$@rGO heterojunction was also prepared to exclude the influence of F-ion on the crystallinity and morphology of TiO$_2$. The TEM and HRTEM images of the pure TiO$_2$@rGO heterojunction were shown in Figure 3a and 3b, respectively. From the Figure 3a, it can be found that TiO$_2$ nanoparticles were densely and uniformly decorated on rGO sheets, suggesting the crucial role of the present preparation route to the dense growth of TiO$_2$ on rGO. And TiO$_2$ nanoparticles are spherical (compared with the shaped TiO$_2$ nanocrystals in Figure 1e). From the HRTEM image of the pure TiO$_2$@rGO heterojunction (Figure 3b), it can be found that the lattice fringes of TiO$_2$ show a d-spacing of 0.358 to 0.364 nm, which also can be well assigned to the (101) lattice fringes of TiO$_2$. It can be concluded that the introduction of F-ion could modulate the morphology of TiO$_2$. The corresponding average size of the spherical TiO$_2$ nanoparticles in the pure TiO$_2$@rGO heterojunction is 7 nm (Figure S11a), which agrees well with the surface and pore measurement results (Figure S11b and Table S2). All the diffraction peaks (Figure 3c) can also be indexed to anatase TiO$_2$ (JCPDS, 84-1286). However, the diffraction peaks are not as sharp as those of the F-doped TiO$_2$@rGO heterojunction, suggesting the crucial role of F-ion in improving the crystallinity of TiO$_2$ nanocrystals. The Figure 3d shows the photodegradation performance of the pure TiO$_2$@rGO heterojunction towards RhB under UV-vis light irradiation. When the photodegradation time is 6 min, the remaining amount of RhB is 19%, which is still more efficient than the mixture. It is further proved that the dense cover of TiO$_2$ nanocrystals on rGO sheets, no matter with or without the doping of F-ion, can help to efficiently utilize the photogenerated electrons in RhB and enhance the final photodegradation efficiency. However, with the help of F-ion, the photodegradation efficiency is even better considering the higher surface area of the pure TiO$_2$@rGO heterojunction (263 m$^2$/g, Table S2).

To further confirm the influence of the density and uniformity of TiO$_2$ on the photocatalytic performance, F-doped TiO$_2$@rGO heterojunctions with different weight ratios of rGO (1, 5, 13 and 15%) were prepared, and the surface areas of them are 53, 101, 203 and 182 m$^2$/g (Figure S12 and Table S2), respectively. It is found that these samples could degrade 64%, 29%, 95% and 88% of RhB within 6 min as shown in Figure 4, respectively. Although all these samples are much more efficient than the mixture (Figure 2a), the content of rGO can affect the photocatalytic activity of F-TiO$_2$@rGO remarkably. A lower content of rGO would not favour the growth of TiO$_2$ on rGO and there is free TiO$_2$ nanocrystals in the catalyst, thus, the photodegradation efficiency is low due to the inefficient separation of the electron-hole pairs. The excessive content of rGO would induce more RhB molecules adsorbed on rGO rather than on the surface of TiO$_2$, which would not benefit the efficient utilization of the photogenerated electrons in RhB molecules. Thus, it is considered that a proper content of rGO could realize the dense and uniform growth of TiO$_2$ on rGO sheets and to ensure the efficient separation of the electron-hole pairs and the sufficient adsorption of RhB molecules on TiO$_2$.

4. Conclusions

In conclusion, an ice bath hydrolyzation method is adopted to grow dense and uniform F-doped TiO$_2$ nanocrystals on rGO sheets. The as-prepared F-doped TiO$_2$@rGO heterojunction showed extremely high photocatalytic efficiency under UV-vis light irradiation compared with that of the commercial P25 and the mixture of F-TiO$_2$ and rGO. It is proved that the dense and uniform growth of TiO$_2$ nanocrystals on rGO greatly favors to utilize the photogenerated electrons in RhB. The pure TiO$_2$@rGO heterojunction is also much more efficient than the mixture of F-TiO$_2$ and rGO, proving that the ice bath hydrolyzation preparation route is crucial to ensure the dense and uniform growth of TiO$_2$ nanocrystals on rGO and improve the
photodegradation efficiency of the final product. The present work presents a new idea on how to efficiently utilize the photogenerated electrons in the target organic pollutants.

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Notes and references

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The F-doped TiO$_2$ densely and uniformly decorated on rGO sheet could adsorb more RhB on TiO$_2$ and efficiently utilize the photogenerated electrons of excited RhB to improve the photodegradation efficiency.