Photocatalytic reduction of CO$_2$ under visible light over Fe/TiO$_2$/rGO Nanocomposites by one-step Hydrothermal Synthesis

Wei Feng, Jiang Wu*

College of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai 200090, China

*Corresponding Author: E-mail Address: wjcfd2002@163.com
Mobile: +86-13761615154

Abstract. Hydrocarbon fuels production from photocatalytic CO$_2$ reduction reaction is a promising route for the energy crisis and climate change, but its industrialized application is limit by lacking of photocatalytic activity, poor selectivity and unsatisfied stability of photocatalysis. In this work, we describe the design and fabrication of Fe/TiO$_2$/rGO nanocomposites to promote the separation and transfer of photogenerated electrons. Due to the doping of Fe, Fe ions form a doping level near the conduction band of TiO$_2$, the composite material can absorb visible light, some photogenerated electrons are transferred to the surface of graphene, which further reduces the electron-hole recombination rate. This work provides some references for the field of photocatalytic decarburization.

1. Introduction

One of the most promising ways to tackle both the energy crisis and the ever-increasing climate change triggered by carbon dioxide is to convert it into renewable hydrocarbon fuels by photocatalysts.[1] Among the photocatalysts semiconductors that have been studied as photocatalysts for CO$_2$ reduction, titanium dioxide (TiO$_2$) is considered to be the most feasible due to its advantages of cheap, non-toxic and high redox potential.[2-4] However, the application of unmodified pure TiO$_2$ as photocatalyst has some limitations. For example, anatase phase TiO$_2$ has a wide bandgap width (3.2 eV) and a high electron hole recombination rate under ultraviolet irradiation. TiO$_2$ doping metal (Cs, Cr, Fe, Au, Cu) is a method to improve the light adsorption, which can make TiO$_2$ active under visible light irradiation.[5] It can be seen from the literature that, at the optimal concentration, Fe ion can increase the number of surface active sites of TiO$_2$, reduce the recombination rate of electron holes and narrow the band gap of TiO$_2$, so it is considered as a good TiO$_2$ dopant.[6]

In order to further improve the photocatalytic performance of TiO$_2$, researchers proposed to fix TiO$_2$ particles on carbon-based materials. Carbon materials such as fullerenes, activated carbon, graphene and carbon nanotubes have been widely studied for their unique structure, high adsorption capacity, electronic and thermal properties.[7-9] Graphene can improve the photocatalytic activity of semiconductor due to its high carrier mobility, large surface area, thermal conductivity and electrical conductivity. However, the graphene layer is hydrophobic, so it is difficult to ensure that graphene is evenly dispersed in an aqueous solution. Because GO has large oxygen-containing functional groups (such as -OH and -COOH), it can be dispersed evenly in aqueous media. Therefore, GO is a common material for the synthesis of composites. Reduced GÖ (rGO) is more stable than GO, especially with
graphene-like properties, as the hydrophobic groups of GO impede the transfer of charge[10]. Therefore, in this article, during the facile hydrothermal process, GO was reduced to rGO and Fe/TiO$_2$ were anchored on the rGO. The surface morphology, structural properties, optical and photoelectrochemical characteristics of the Fe/TiO$_2$/rGO nanocomposites were studied. Moreover, the mechanism of enhanced production activity was discussed in detail.

2. Experimental Section

2.1 Preparation of Fe/TiO$_2$/rGO

The chemicals were all analytic grade reagents and without further purification. Graphite oxide (GO) was prepared by the modified Hummers method from graphite power. A one-step hydrothermal method was used to prepare Fe/TiO$_2$/rGO. 4.8 g of the Ti(SO$_4$)$_2$ and mole ratio of 2 to Fe (NO$_3$)$_3$·9H$_2$O dissolves in 300 ml deionized water and 150 ml ethanol, after being fully dissolved, graphene oxide was added different mole ratio of 1%, 3%, 5% and 10% respectively, and then transfer the mixture to 100 ml Teflon lined stainless autoclave and heated at 180 $^\circ$C for 24 h. Finally, the products were washed with deionized water and anhydrous ethanol for three times respectively. The as-prepared samples with different molar ratios were denoted as 1#, 2#, 3# and 4#.

2.2 Material characterizations

The crystal phase of the samples were checked by X-ray diffraction (XRD, Bruker D8 Advance Diffractometer, Germany) with Cu K$_\alpha$, which scanning range was 10-80$^\circ$ (scan rate 2$^\circ$ min$^{-1}$). Fourier transform infrared (FTIR) was utilized to detect the local construction and the composition of the material related to the bonding states of the compounds with the range 4000-400 cm$^{-1}$. The microstructure and morphology of the catalyst was detected using a scanning electron microscope (SEM, Phillips XL-30 FEG/NEW). UV-vis diffuse reflectance spectra (UV-vis DRS) (SHIMADZU UV-3600, Japan) was used to obtain the optical absorption properties recorded over the range 250-1200 nm. Barium sulfate (BaSO$_4$) was used as a reference standard.

2.3 Photocatalytic activity for the reduction of CO$_2$

The activity of photocatalytic CO$_2$ reductions tests were carried out in a gas-closed circulation system with a 500 ml reactor, containing 50 mg catalyst, 100 ml deionized water stirred continuously, without the sacrificial agent. The reaction was performed with a 300 W Xe lamp as a light source by using a 420 nm cut filter for 4 h. Before light illumination, the glass reactor was bubbled with the CO$_2$ gas for 200 ml, then the experiment was started when the light was on. The reactor temperature were maintained at 6 $^\circ$C via a cooling circulating water device. During the reaction, the gas product of the CO$_2$ photoreduction was detected by gas chromatograph with FID and TCD detector.

3. Results and Discussion

To determine composition and structure of the different content of graphene on photocatalyst, Figure 1 shows the XRD patterns of the as-prepared samples synthesized via hydrothermal process in different molar ratios of graphene, the characteristic peak (101), (004), (200), (105), (211), (213), (201) corresponding to the 2θ=25.3$^\circ$, 37.8$^\circ$, 48.0$^\circ$, 53.9$^\circ$, 55.1$^\circ$, 62.1$^\circ$ and 62.7$^\circ$, the XRD peaks could be readily indexed to pure anatase phase of TiO$_2$ (JCPDS No. 21-1272)[11]. However, nearly no obvious characteristic peaks of rGO could be observed in the pattern of samples, which could be attributed to the low content and high dispersion of rGO[12]. FT-IR analysis was further carried out to verify bond characteristics of functional groups in the nanocomposites. As shown in Figure 1, the peaks at 420 cm$^{-1}$ and 1640 cm$^{-1}$ could be ascribed to the bending vibration of O-H groups and H-O-H groups, shows that the composite containing oxygen functional groups and water molecules[13]. The wide peaks at 2970 cm$^{-1}$ and 2924 cm$^{-1}$ came from the stretching vibration of the C-H bond of graphene, and the peaks at 1640 cm$^{-1}$ came from the stretching vibration peak of the C=C bond of the graphene, which indicates that the GO was reduced to rGO by one-step hydrothermal reaction[14]. The
absorption peak at 656 cm\(^{-1}\) is related to the stretching vibration of O-Ti-O bond, Ti-O bond and possible Ti-O-C bond in TiO\(_2\) \cite{15}. It is noteworthy that the absorption peak at 571 cm\(^{-1}\) is from Fe-O bond, which proves that Fe is also doped into the composite material\cite{16}.

As indicated in Figure 2, the SEM image of the as-prepared Fe/TiO\(_2\)/rGO showed that compared to graphene large amount of particle agglomerates can be observed uniformly distributed on the 2D rGO nanosheets. This allows the direct interaction between Fe/TiO\(_2\) and rGO to effectively inhibit the recombination of photogenerated electron-hole pairs, thus enhancing the photocatalytic activity. The size of the particles decreases with the increase of the content of graphene oxide, the reason is that in the hydrothermal reaction the increase of the content of graphene oxide can provide more surface area to make more particles adhere to the above, there are also more containing oxygen functional groups to participate in the hydrothermal reaction, so the particles on the surface of graphene becomes more uniform distribution and fine particulate.

As shown in Figure 3, the bandgaps of Fe/TiO\(_2\)/rGO were determined by the UV–vis DRS in ambient temperature. Pure TiO\(_2\) can not adsorb the visible light (400-700 nm), as a result of the Fe doping, Fe/TiO\(_2\) composite materials can absorb visible light. The adsorption edges of Fe/TiO\(_2\) and Fe/TiO\(_2\)/rGO nanocomposites moved in the direction of higher wave, resulting in a decrease in band

![Figure 1. XRD patterns and FTIR spectra of 1#, 2#, 3#, 4#, Fe/TiO\(_2\) and TiO\(_2\), respectively.](image1)

![Figure 2. a-d. SEM images of 1#, 2#, 3#, 4# , graphene and GO, respectively.](image2)

![Figure 3. a-d. SEM images of 1#, 2#, 3#, 4# ,graphene and GO, respectively.](image3)
gap. This change of adsorption edge can be explained as that Fe ions formed doping levels near the conduction band (CB) of TiO$_2$, thereby enabling electrons to absorb visible light and excite from valence band (VB) to the intermediate state. After calculation, the bandgap width of pure TiO$_2$ was 3.18 ev, while the bandgap of Fe/TiO$_2$ composite material was reduced to 2.94 ev. After the addition of Go, the bandgap of 1#, 2#, 3# and 4# samples of Fe/TiO$_2$/rGO composites were 2.91eV, 2.74 eV, 2.69 eV and 2.57 eV, respectively.

Figure 3. UV–vis DRS spectra of 1#, 2#, 3#, 4#, Fe/TiO$_2$ and TiO$_2$, respectively.

For evaluating the photocatalytic activity of the as-prepared samples, the CO$_2$ photoreduction experiments were performed under a 300W Xe lamp ($\lambda>$420 nm). Control experiments were also conducted in the dark and in the absence of photocatalyst, and no hydrocarbon products were detected in the control experiments, which suggests that the CO$_2$ photocatalytic reduction process is not substitutable owing to above factors. Figure 3 exhibited the amount of CH$_4$, O$_2$ and H$_2$ generation on the photocatalyst without sacrifice agent. Compared with Fe/TiO$_2$ composite materials, the photocatalytic reduce CO$_2$ activity of Fe/TiO$_2$/rGO composite materials was significantly improved, indicating that the interaction between Fe/TiO$_2$ and rGO improved the photocatalytic performance. In addition, when the content of rGO in Fe/TiO$_2$/rGO composite increased from 3% to 5%, the yield of CO$_2$ products of photocatalytic reduction increased, the yield of methane increased from 2.466 mol g$^{-1}$ h$^{-1}$ to 4.076 mol g$^{-1}$ h$^{-1}$, and the yield of oxygen increased from 3.45 mol g$^{-1}$ h$^{-1}$ to mol g$^{-1}$ h$^{-1}$. However, when the content of rGO increased from 5% to 10%, the yield of CO$_2$ products from photocatalytic reduction did not significantly improve. The yield of methane slightly decreased from 4.076 mol g$^{-1}$ h$^{-1}$ to 3.046 mol g$^{-1}$ h$^{-1}$, and the yield of oxygen slightly decreased from 3.45 mol g$^{-1}$ h$^{-1}$ to 4.32 mol g$^{-1}$ h$^{-1}$. These results show that with the content of rGO increasing, more photogenerated electrons are transferred to the surface of rGO and the charge separation impedes the recombination of carriers. In addition, rGO flakes can adsorb CO$_2$ molecules, further enhancing the photocatalytic performance of Fe/TiO$_2$/rGO. But when rGO content higher than 5%, photocatalytic performance degradation, this may be due to Fe/TiO$_2$ nanoparticles on the surface of the graphene gathered together, wrapped in the reduction of graphene oxide surface, even though the reduction oxidation graphene can absorb more CO$_2$ molecules, but lower Fe/TiO$_2$ nanoparticles with light contact, so as to reduce the photocatalytic performance. More importantly, the CH$_4$ evolution of the Fe/TiO$_2$/rGO were not passivated during 24 h reaction in the aggregate at least 6 cycles, showing the high stability of the photocatalyst.
Figure 4. a-c. CH4, H2 and O2 evolution on the photocatalysts Fe/TiO2/rGO and Fe/TiO2 for 5 h reaction. d. Stability test of 3# Fe/TiO2/rGO during six photocatalytic cycles of CO2 photoreduction under visible light irradiation.

The mechanism of photocatalytic reduce CO2 by Fe/TiO2/rGO photocatalyst under simulated sunlight is shown in Figure 4, Fe/TiO2 nanoparticles adhered to the rGO. The introduction of iron into titanium dioxide effectively reduced the band gap, meaning that the iron ions actually acted as an electron/hole trap by introducing a subband gap around the CB of TiO2. Thus, the charge separation is improved and the lifetime of photogenerated electrons and holes is increased. Graphene has an excellent ability to absorb CO2 molecules and a large specific surface area. The photocatalytic activity can be enhanced through the π-π conjugated bonds and the interaction between Fe/TiO2 nanoparticles and graphene. As shown in the Figure 4, CO2 molecules adsorbed on the graphene sheet generate photogenerated electrons and holes on the catalyst surface under sunlight. Fe doping formed a new surface energy level below the CB of TiO2 and reduced the band gap. Therefore, the electron is transferred from VB to the impurity level below CB. Some photogenerated electrons are transferred to the graphene surface, which further reduces the electron hole recombination rate.

Figure 5. Schematic diagram of mechanism of photocatalytic process.

4. Conclusions
In summary, Using one-step hydrothermal prepared iron doped TiO2 and reduction graphene oxide composite photocatalyst, the preparation of the composite photocatalyst, TiO2 are anatase phase in the samples and after hydrothermal treatment the oxidized graphene is reducing as reduction graphene oxide (rGO). After the hydrothermal reaction, Fe-TiO2 was uniformly adhered to the lamellar structure surface of rGO. The size of agglomerated particles on the surface of the graphene sheet decreases as the content of GO increases, but excessive graphene can cause graphitization. Due to the doping of Fe, Fe ions form a doping level near the conduction band of TiO2, the composite material can absorb visible light. Graphene is a carrier for transferring and conducting electrons. Some photogenerated
electrons are transferred to the surface of graphene, which further reduces the electron-hole recombination rate. However, excessive doping of graphene will affect the active site of TiO₂ and inhibit the further improvement of photocatalytic effect. This strategy will provide inspiration for other photocatalytic systems for the utilization of CO₂.

References

[1] P. Pichat, Fundamentals of TiO₂ Photocatalysis. Consequences for Some Environmental Applications in Heterogeneous Photocatalysis: From Fundamentals to Green Applications. Springer Berlin Heidelberg, Berlin, Heidelberg, 2016, pp. 321-359.

[2] C. Peng, X. Yang, Y. Li, H. Yu, H. Wang, F. Peng, Hybrids of two-dimensional Ti₃C₂ and TiO₂ Exposing {001} facets toward enhanced photocatalytic activity. ACS Appl. Mater. Interfaces, 2016, 8, 6051-6060.

[3] G. Peng, J.E. Ellis, G. Xu, X. Xu, A. Star, In situ grown TiO₂ nanospindles facilitate the formation of holey reduced graphene oxide by photodegradation. ACS Appl. Mater. Interfaces, 2016, 8, 7403-7410.

[4] X. Liu, G. Dong, S. Li, G. Lu, Y. Bi, Direct observation of charge separation on anatase TiO₂ crystals with selectively etched {001} facets. J. Am. Chem. Soc. 2016,138, 2917-2920.

[5] S.N.R. Inturi, T. Boningari, M. Suidan, P.G. Smirniotis, Visible-light-induced photodegradation of gas phase acetonitrile using aerosol-made transition metal (V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce, and Zr) doped TiO₂. Applied Catalysis B: Environmental, 2014,144 ,333-342.

[6] C. Liu, L. Zhang, R. Liu, Z. Gao, X. Yang, Z. Tu, F. Yang, Z. Ye, L. Cui, C. Xu, Hydrothermal synthesis of N-doped TiO₂ nanowires and N-doped graphene heterostructures with enhanced photocatalytic properties. Journal of Alloys and Compounds, 2016,656,24-32.

[7] Novoselov, K. Nobel Lecture: Graphene: Materials in the Flatland. Reviews of Modern Physics, 2011, 83(3):837-849.

[8] Low J , Yu J , Ho W . Graphene-Based Photocatalysts for CO₂ Reduction to Solar Fuel. Journal of Physical Chemistry Letters, 2015, 6(21):4244-4251.

[9] T.L. Guo, J. G. Li, X. Sun, Y. Sakka, Photocatalytic growth of Ag nanocrystals on hydrothermally synthesized multiphasic TiO₂/reduced graphene oxide (rGO) nanocomposites and their SERS performance. Applied Surface Science, 2017, 423, 1-12.

[10] N. Farhangi, R.R. Chowdhury, Y. Medina-Gonzalez, M.B. Ray, P.A. Charpentier, Visible light active Fe doped TiO₂ nanowires grown on graphene using supercritical CO₂. Applied Catalysis B: Environmental, 2011, 110, 25-32.

[11] S. Sun, J. Ding, J. Bao, C. Gao, Z. Qi, X. Yang, B. He, C. Li, Photocatalytic degradation of gaseous toluene on Fe-TiO₂ under visible light irradiation: A study on the structure, activity and deactivation mechanism. Applied Surface Science, 2012, 258, 5031-5037.

[12] B. Bhanvase, T. Shende, S. Sonawane, A review on graphene-TiO₂ and doped graphene-TiO₂ nanocomposite photocatalyst for water and wastewater treatment. Environmental Technology Reviews, 2017, 6 , 1-14.

[13] S. Min, J. Hou, Y. Lei, X. Ma, G. Lu, Facile one-step hydrothermal synthesis toward strongly coupled TiO₂/graphene quantum dots photocatalysts for efficient hydrogen evolution. Applied Surface Science, 2017, 396, 1375-1382.

[14] M. Long, Y. Qin, C. Chen, X. Guo, B. Tan, W. Cai, Origin of visible light photoactivity of reduced graphene oxide/TiO₂ by in situ hydrothermal growth of undergrown TiO₂ with graphene oxide. The Journal of Physical Chemistry C, 2013, 117, 16734-16741.

[15] Y. Xu, Y. Mo, J. Tian, P. Wang, H. Yu, J. Yu, The synergistic effect of graphitic N and pyrrolic N for the enhanced photocatalytic performance of nitrogen-doped graphene/TiO₂ nanocomposites. Applied Catalysis B: Environmental, 2016, 181, 810-817.