Preparation and photocatalytic performance of TiO₂-RGO-CuO/Fe₂O₃ ternary composite photocatalyst by solvothermal method

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Abstract
In this work, an one-step solvothermal synthesis method is used to prepare TiO₂-reduced graphene oxide (RGO)-CuO/Fe₂O₃ ternary composite photocatalysts with TiO₂ and CuO/Fe₂O₃ nanoparticles coated RGO, while the structures and photocatalytic performance of these synthesized ternary composite photocatalysts are studied. It is found that Cu²⁺ and Fe³⁺ are substituted for Ti⁴⁺ into the crystal lattice of anatase TiO₂ in these prepared ternary composite photocatalysts. TiO₂ and CuO/Fe₂O₃ nanoparticles are uniformly coated on the surface of RGO and closely contact with each other. The Cu/Fe doping has obviously improved the absorption ability on the visible light, and the bandgap of the ternary composite can be reduced. Under visible light irradiation, by increasing the Cu/Fe doping amount, the photocatalytic performance can be improved until the Cu and Fe contents reached 0.075 wt.% and 0.1 wt.% respectively. The prepared products can be reused for eight cycles to degrade the methyl orange solution, and it retains over 93% photocatalytic efficiency.

1. Introduction
With the development of science and technology, the living standards of human beings are getting better and better, but while technology improves people’s lives, it also brings environmental pollution problems. Among various environmental pollution problems, water pollution is particularly serious, water is the source of human life, water pollution is also the most harmful to human health [1, 2]. In all directions of water pollution control, photocatalytic technology that achieves the purpose of water pollution control by using the energy of sunlight to degrade the pollutants in water has emerged, and this technology has been widely studied in the world [3].

As a green environmental protection technology with good application prospects in the treatment of environmental pollution, photocatalytic technology has developed rapidly in recent years. As a photocatalyst, TiO₂ is highly sought after due to its high catalytic activity, good stability, and low cost [4–6]. However, TiO₂ also has its own limitations such as low quantum yield, wide band gap, poor response to visible light, and easy recombination of photogenerated holes and electrons. These limitations affect its further applications [7–9].

Now researchers have developed many methods to improve the photocatalytic performance of TiO₂, such as non-metal ion doping [10–14], metal ion doping [15], semiconductor compound [16], etc.

In metal doping, the doping of metal elements Cu and Fe can form active sites by forming metal oxides like CuO and Fe₂O₃ on the surface of TiO₂ to change the electron-hole recombination and enhance the interface electron transfer speed [17–21], thereby improving the TiO₂ quantum yield and the separation efficiency of electrons and holes, and enhancing the photocatalytic performance. Non-metallic doping can increase the light absorption range of TiO₂ and enhance its ability to absorb visible light. The principle of visible light activity caused by non-metal doping is that the doping of anionic elements such as C, N, F, P, S, etc will replace the oxygen in TiO₂, forming an independent impurity band above the Ti⁴⁺ valence band. Ultraviolet light can excite electrons in the valence band and the energy band, and visible light can excite electrons in the conduction band of the energy band, so that TiO₂ has visible light catalytic activity [22, 23]. Among various non-metallic doping...
materials, carbon-containing semiconductors materials such as carbon nanotubes, graphene, carbon black, graphite, have been widely studied [24]. Among them, reduced graphene oxide (RGO) had attracted much attention due to its excellent electron transport capability, large specific surface area and other properties in recent years [25]. So far, scientists had prepared TiO2 photocatalyst doped with RGO by various methods [26–42] such as sol-gel method, hydrothermal synthesis method, electrospinning method and so on. For metal doping, metal ions can capture photogenerated electrons, thereby reducing the recombination of electron-hole pairs, the phase change increases the number of photo-generated hole-electron pairs on the surface of TiO2, and improves the photocatalytic activity of TiO2. Heperuma et al [15] found that as the semiconductor ions were doped with different valence metal ions, the catalytic properties will be changed. However, in the research of doping modification of TiO2, non-metallic doping and metal doping have certain limits to improve the photocatalytic performance of TiO2. Therefore, co-doping of TiO2 with metal and nonmetal has become a hot spot in the research of TiO2 doping modification. In the past, non-metal and metal co-doping mostly used two or more steps, and the preparation process was complicated. In this study, using RGO as non-metallic doping elements, Cu and Fe as metal doping elements, TiO2-RGO-CuO and TiO2-RGO-Fe2O3 ternary composite photocatalysts were prepared by one-step solvothermal synthesis. The effects of different amounts of Cu/Fe doping on the photocatalytic performance, structure and morphology of TiO2-RGO-CuO/Fe2O3 will be mainly studied.

2. Experimental

2.1. Materials

The graphene oxide (GO) aqueous suspension was bought from Nanjing Pioneer Nanomaterials Co., Ltd Ti(SO4)2, Cetyltrimethylammonium bromide (CTAB), Cu(NO3)2·3H2O, Fe(NO3)3·9H2O and methyl orange (MO) were bought from Sinopharm Group Chemical Reagent Co., Ltd. All the reagents were at analytical grade and used without further purification. The deionized water was obtained from a Yi Chang deionized water machine.

2.2. Synthesis of TiO2-RGO-CuO and TiO2-RGO-Fe2O3 ternary composite photocatalysts

In figure 1, TiO2-RGO-CuO and TiO2-RGO-Fe2O3 ternary composite photocatalysts were produced by a solvothermal method using GO aqueous suspension, CTAB ethanol solution, Cu(NO3)2·3H2O aqueous solution, Fe(NO3)3·9H2O aqueous solution and Ti(SO4)2 ethanol solution through the following steps. **Step-1:** 1 g Ti(SO4)2 was dissolved into 25 ml anhydrous ethanol and stirred for 1 h to form solution A, 0.48 g CTAB was dissolved into 25 ml anhydrous ethanol and stirred for 1 h to obtain solution B, then solution B was dropped into solution A and stirred for 0.5 h to form solution C. **Step-2:** 0.0005 g GO were dissolved into 10 ml deionized water and stirred for 1 h then ultrasonically dispersed for 0.5 h to form solution D, meanwhile x g Cu(NO3)2·3H2O (or Fe(NO3)3·9H2O) were dissolved into 10 ml deionized water and stirred for 1.5 h to obtain solution E, then solution D and E were sequentially dropped into solution C and stirred for 1 h to form solution F. **Step-3:** the suspension F was transferred into a 100 ml Teflon–sealed autoclave and maintained at the reaction temperature of 150 °C for 10 h in a furnace, after the reactor was cooled to room temperature, the products were taken out. Subsequently, the obtained products were centrifugally washed four times with deionized water and alcohol at a ratio of 1:1, and then centrifugally washed four times with anhydrous ethanol to remove impurities formed in the reactions. Finally the washed products were dried at a temperature of 80 °C for 12 h to form TiO2-RGO-CuO or TiO2-RGO-Fe2O3 ternary composite photocatalysts. According to the different amounts of Cu(NO3)2·3H2O...
and Fe(NO₃)₃·9H₂O added in the reactions, the prepared ternary composite photocatalysts were denoted as TiO₂-RGO-XCuO (X = 0.05%, 0.75%, 0.1%, 0.3%, 0.5%) and TiO₂-RGO-YFe₂O₃ (Y = 0.05%, 0.1%, 0.3%, 0.5%, 1%), where X, Y represent the mass percentage content of Cu and Fe elements in the ternary composite photocatalysts, respectively. In order to make comparative experiments, TiO₂-RGO binary composite photocatalyst and pure TiO₂ photocatalyst were also prepared under the same conditions.

2.3. Characterization

The crystal structure of these materials was detected by x-ray diffraction (XRD) using a D8 Advance polycrystalline x-ray diffractometer, Cu target (λ = 0.154 056 nm) was used, the voltage and current were set at 40 kV and 40 mA, respectively. Scan rate as low as 2° min⁻¹ was used throughout the experiment. Transmission electron microscope (TEM) was applied using a Tecnai G2 F30 S-TWIN (FEI, US) at an accelerating voltage of 300 kV to obtain further detailed observation of the products. UV-visible diffuse reflectance spectra (DRS) were recorded on a Cary 5000 spectrophotometer (Varian, US) in diffuse reflection mode.

2.4. Photocatalytic activity test

The GHX-3 photocatalytic reactor prepared by Yangzhou University City Science and Education Instrument Company and the UV 752 ultraviolet-visible branch spectrophotometer (Shanghai Yidian Analysis Co., Ltd, Shanghai) were used to test the photocatalytic performance for the prepared samples. 100 ml of MO deionized water solution (20 ppm) and 20 mg of photocatalyst were added into a 400 ml quartz beaker, then the beaker was put into the photocatalytic reactor at room temperature and atmospheric pressure. The suspension of MO and photocatalyst was first magnetically stirred in the dark for 30 min to achieve adsorption-desorption equilibrium, and then the suspension was placed under a 250 W neon lamp and a 300 W medium pressure mercury lamp to simulate visible light and ultraviolet light irradiation environment, respectively. During the irradiation period, water circulation was performed through an external cooling water pipe to maintain the temperature of the suspension at about 25°C, while 5 ml suspension samples were taken out at 15 min intervals under ultraviolet light irradiation and 30 min intervals under visible light irradiation. The MO concentration of all samples was estimated by measuring the absorbance at the maximum peak (464 nm) of the MO solution using an ultraviolet-visible spectrophotometer. The repeatability of photocatalytic performance for all prepared photocatalysts was tested in eight consecutive cycles, after each cycle, the catalyst was recovered by centrifugation, washing with deionized water and absolute ethanol, then dried at 80°C for 12 h. Cᵣ/C₀ was used to describe the results of photocatalytic degradation of MO in solution and showed the photocatalytic performance of these photocatalysts, where Cᵣ refers to the concentration of MO measured at time t, and C₀ refers to the initial concentration of MO after adsorption-desorption equilibrium without irradiation.

3. Results and discussion

3.1. Crystallization and morphology

Figure 2 shows the XRD patterns of TiO₂-RGO, TiO₂-RGO-XCuO and TiO₂-RGO-YFe₂O₃ composite photocatalyst. In figures 2(a) and (c), the peaks appear at 25.3°, 37.9°, 48.2°, 54.1°, 55.2°, 62.7°, 68.8°, 70.2° and 75.1° corresponding to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) crystal plane of the anatase TiO₂, which indicates that the anatase TiO₂ was produced by hydrothermal synthesis. However, the diffraction peaks of RGO, Cu and Fe can not be observed in the XRD results, because the content of RGO, Cu and Fe is too low. In Figure 2(b), Cu²⁺ and Ti⁴⁺ may entered the TiO₂ lattice in the form of a solid solution instead of Ti³⁺. Moreover, figure 2(b) shows the XRD patterns of TiO₂-RGO-XCuO in the range of 24 ~ 26.5°, it is found that the characteristic peak of TiO₂-RGO-XCuO corresponding to the (101) crystal plane has a certain offset to a small angle with the increase of Cu doping content, this is because Cu²⁺ has a slightly larger ion radius than Ti⁴⁺. However, the addition of Fe element in the TiO₂-RGO composite has no influence on the anatase peak intensity. Moreover, the detailed observation of TiO₂-RGO-YFe₂O₃ in the range of 24 ~ 26.5° shows that the characteristic peak of TiO₂-RGO-YFe₂O₃ corresponding to the (101) crystal plane has a certain offset to a large angle with the increase of Fe doping content, this is because Fe³⁺ has a slightly smaller ion radius than Ti⁴⁺. The crystallite size of these composites can be obtained from Scherrer’s formula, the calculated results indicate that the grain size of pure TiO₂ and TiO₂-RGO are 11.75 nm and 10.5 nm, respectively. The increase of Cu/Fe doping amount can hinder the grain growth which leads to the decrease of the grain size, it has been reduced to 7.3 nm or 7.6 nm for TiO₂-RGO-0.5%CuO and TiO₂-RGO-1%Fe₂O₃, respectively.
Figure 3 shows the TEM and HRTEM images of the TiO$_2$-RGO-$0.075\%$CuO and TiO$_2$-RGO-$0.1\%$Fe$_2$O$_3$ ternary composite photocatalysts. It can be seen from figures 3(a), (b), (c), (d), (e), (f) that the surface of RGO was uniformly and densely distributed with nanoparticles with a grain size between 5 and 10 nm. It is found that most of the nanoparticles on the surface of the RGO are TiO$_2$, and a small amount of CuO/Fe$_2$O$_3$ can also be detected in figures 3(c), (g). In the diffraction images (figures 3(d), (h)), the lattice spacing of 0.352 nm belongs to the TiO$_2$ (101) crystal plane, CuO (110) and Fe$_2$O$_3$ (110) can be identified at the lattice spacing of 0.272 nm and 0.204 nm, respectively. TEM and HRTEM results imply that TiO$_2$, CuO and Fe$_2$O$_3$ nanoparticles are in close contact with the surface of RGO, which means that TiO$_2$-RGO-XCuO and TiO$_2$-RGO-YFe$_2$O$_3$ ternary composite photocatalysts had been well prepared.

3.2. Optical properties

Figure 4 shows the UV–vis spectra and corresponding conversion curves of ternary composite photocatalysts of TiO$_2$-RGO-XCuO and TiO$_2$-RGO-YFe$_2$O$_3$ ternary composite photocatalysts in the range of 200–800 nm. It can be seen from figure 4(a) that as the amount of Cu doping increased, the absorption edge of the sample moved toward the visible wavelength, and the absorption intensity increased in the visible wavelength range. When $X = 0.075\%$, the red shift of the absorption edge was the largest and the absorption intensity was the strongest in the visible wavelength range. As the Cu doping amount continues to increase ($>0.075\%$), the red shift of the absorption edge and the absorption intensity in the visible light wavelength range began to decrease. These phenomena indicate that Cu doping can expand the absorption range of TiO$_2$-RGO-XCuO in the visible light region and improve its absorption of visible light, but the doping amount has a maximum value for the above trend, after exceeding this value ($0.075\%$), the range of TiO$_2$-RGO-XCuO absorption region of visible light will be reduced, and the absorption intensity will also be weakened. Cu doping has almost no effect on the absorption of ultraviolet light by TiO$_2$-RGO-XCuO. Figure 4(b) shows the corresponding conversion curves, the band gap value of TiO$_2$-RGO-XCuO can be obtained by fitting the curves. It is found that the band gap value of TiO$_2$-RGO is about 3.12 eV which has been decreased to about 3.0 eV for TiO$_2$-RGO-$0.075\%$CuO, but as the Cu doping content was further increased at $X = 0.5\%$, the band gap value was increased to about 3.15 eV, which also corresponds to the UV–vis absorption spectra. This seems to be related to the introduction of Cu$^+/Cu^{2+}$ species.
into the new energy level in the TiO₂ band gap. Since there are two Cu ions with different valences, as the amount of Cu doping increases, there will be a certain limit between them, which brings about a special change in the band gap [43].

Figure 3. TEM images of TiO₂-RGO-0.075%CuO (a)–(d) and TiO₂-RGO-0.1%Fe₂O₃ (e)–(h).
In figure 4(c), as the amount of Fe doping increased from 0.05% to 1%, the light absorption edge of TiO$_2$-RGO-YFe$_2$O$_3$ also produces a certain degree of red shift, and its light absorption intensity in the visible light region also increased, the absorption intensity of TiO$_2$-RGO-YFe$_2$O$_3$ in the ultraviolet region changed also very little. Figure 4(d) shows the conversion curves corresponding to the ultraviolet-visible spectra, with the increase of Fe content, the band gap of TiO$_2$-RGO-YFe$_2$O$_3$ shows a downward trend, it has been reduced to about 2.95 eV for TiO$_2$-RGO-1%Fe$_2$O$_3$. Such decrease in the band gap energy is attributed to the interaction of the 3d orbital of Ti and d orbital of Fe introducing intra-band gap states [44, 45].

3.3. Photocatalytic activity

In figure 5, the photocatalytic performance of the prepared samples was evaluated through the residual ratio of the corresponding methyl orange solution ($A_m$) by TiO$_2$-RGO-XCuO and TiO$_2$-RGO-YFe$_2$O$_3$ ternary composite photocatalysts under ultraviolet and visible light illumination, respectively. The photocatalytic performance of TiO$_2$-RGO-XCuO has been obviously improved compared with TiO$_2$-RGO, and the maximum photocatalytic activity was obtained at $X = 0.075\%$, as the Cu doping content was further increased more than 0.075%, the photocatalytic activity of TiO$_2$-RGO-XCuO began to decrease, even lower than that of TiO$_2$-RGO for TiO$_2$-RGO-0.5%CuO.

In the case of Fe doping, it can be seen from figures 5(c), (d) that the photocatalytic performance of TiO$_2$-RGO-YFe$_2$O$_3$ ($Y < 1\%$) was also improved compared with TiO$_2$-RGO under UV or visible light irradiation. Moreover, with the further increase of Fe$_2$O$_3$ content ($Y = 1\%$), an amorphous layer (i.e. iron oxide) will be formed on the surface of TiO$_2$ nanoparticles, which limits the photocatalytic activity of TiO$_2$-RGO-YFe$_2$O$_3$. Therefore, the residual degradation rate of TiO$_2$-RGO-YFe$_2$O$_3$ is less than that of TiO$_2$-RGO [46].

However, the effect of improving the photocatalytic performance by Cu-doped TiO$_2$-RGO was better than that of Fe-doped TiO$_2$-RGO through comparison, which may be related to the different ability of CuO and Fe$_2$O$_3$ to transfer electrons.

Reuse is very important for the practical application of photocatalysts. In figure 6, the recycling efficiencies of TiO$_2$-RGO-0.075%CuO and TiO$_2$-RGO-0.1%Fe$_2$O$_3$ were evaluated under eight consecutive cycles of methyl
orange solution degradation. After eight continuous cycle tests, the photocatalytic efficiencies of TiO$_2$-RGO-0.075%CuO and TiO$_2$-RGO-0.1%Fe$_2$O$_3$ under visible light conditions were still higher than 94.8% and 93%, respectively.

### 3.4. Enhancement mechanism

TiO$_2$-RGO-XCuO (or TiO$_2$-RGO-YFe$_2$O$_3$) ternary composite photocatalyst with TiO$_2$ and CuO (or Fe$_2$O$_3$) nanoparticles coated RGO has high photocatalytic performance, and the main enhancement mechanism of the photocatalytic performance is shown in figure 7. The presence of Cu$^{2+}$ and Fe$^{3+}$ metal ions on the surface of TiO$_2$ can act as photoactive species, which is conducive to electron transfer to the surface and avoids electron-hole recombination. In addition, the presence of coated graphene can improve the conductivity and quickly
transfer electrons generated by the semiconductor, thereby reducing the recombination probability of electron-hole pairs. The faster electron transfer rate and lower electron-hole recombination rate may make it have a significantly enhanced photocatalytic performance.

4. Conclusion

In this work, an one-step solvothermal synthesis method was used to prepare TiO2-RGO-XCuO and TiO2-RGO-YFe2O3 ternary composite photocatalysts with high photocatalytic performance. Both Cu and Fe doping inhibited the crystallization of TiO2 and reduced its grain size, Cu$^{2+}$ and Fe$^{3+}$ were partially incorporated into the crystal lattice of TiO2 instead of Ti$^{4+}$. TiO2 and CuO/Fe2O3 nanoparticles were uniformly and densely attached to the surface of RGO, which helps the transfer of photogenerated electrons and has a certain influence on the improvement of photocatalytic performance. The optical bandgap of TiO2-RGO-XCuO and TiO2-RGO-YFe2O3 were decreased by Cu/Fe doping. The maximum photocatalytic activities of TiO2-RGO-XCuO and TiO2-RGO-YFe2O3 ternary composites were obtained at $X = 0.075\%$ and $Y = 0.1\%$, respectively. Meanwhile, the TiO2-RGO-0.075%CuO and TiO2-RGO-0.1%Fe2O3 ternary composites still had quite high photocatalytic activities after the repetitive use of eight cycles. Therefore, it is expected that the TiO2-RGO-XCuO and TiO2-RGO-YFe2O3 ternary composites prepared by this simple solvothermal method supply promising photocatalytic materials with excellent potential for pollutant purification.

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