A magnetically recoverable CaTiO3/reduced graphene oxide/NiFe2O4 nanocomposite for the dye degradation under simulated sunlight irradiation

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In this work, ternary CaTiO3/reduced graphene oxide (rGO)/NiFe2O4 nanocomposite was successfully prepared using polyacrylamide gel route followed by hydrothermal method. It is observed that NiFe2O4 and CaTiO3 nanoparticles are assembled on the surface of rGO. Furthermore, the formation of chemical bonding between the nanoparticles and rGO is confirmed. The photocatalytic activities of the samples were evaluated through the degradation of methylene blue and rhodamine B under the simulated sunlight irradiation. The results indicate that the ternary nanocomposite exhibits remarkable enhanced photocatalytic activity compared with bare CaTiO3 and NiFe2O4. In this nanocomposite, the photogenerated electrons of CaTiO3 and NiFe2O4 can be captured by rGO, leading to an increased separation and availability of electrons and holes for the photocatalytic reaction. Moreover, this nanocomposite exhibits obvious ferromagnetism and can be readily recovered by external magnetic field. The recycling photocatalytic experiment demonstrates that the nanocomposite possesses good photocatalytic reusability.

Key-words : CaTiO3, NiFe2O4, Graphene, Photocatalysis, Nanocomposite

1. Introduction

With the rapid development of global industrialization, the environmental pollution and energy shortage have become two serious worldwide problems. Semiconductor-based photocatalysis is regarded as an ideal “green” technology to solve environmental and energy problems.11–12) Titanium dioxide and titanium-based perovskite-type oxide semiconductors are famously known to be an important class of photocatalysts owing to their excellent photocatalytic performance for degrading organic pollutants and splitting water into hydrogen and oxygen.63–10) Among titanium-based perovskite-type oxide photocatalysts, CaTiO3 has attracted increasing attentions because of its suitable energy band position.10) The conduction band (CB) potential of CaTiO3 is more negative than that of the most famous photocatalyst TiO2, thus making it possess powerful capability to photocatalytically split water into H2. However, CaTiO3 can only absorb ultraviolet (UV) light (about 5% of sunlight) due to its wide bandgap energy (~3.6 eV).11) In addition, the separation and recycling of the photocatalyst from treated wastewater is a big challenge, and thus could lead to the secondary pollution of the treated water.

Recently, construction of heterostructured composites from titanium oxide semiconductors and other narrow-bandgap semiconductors (particularly magnetic semiconductors) has been widely used as a convenient way to extend the light response region and separate catalysts particles by using an external magnetic field.17)–21) NiFe2O4, a well-known spinel-type metal oxide with a bandgap energy of ~1.8 eV, has been frequently employed as a magnetic component to combine with semiconductor photocatalysts owing to its strong magnetism and visible-light-responsive photocatalytic activity.22)–25) Graphene, being a two-dimensional (2D) sheet of sp²-hybridized carbon atoms, possesses outstanding properties including high electrical conductivity, electron mobility, thermal conductivity, mechanical strength, chemical stability, and so forth.50)–27) The unique structure and remarkable properties make graphene an ideal 2D support material for assembling functional nanocomposites with improved performance in fields of photocatalysts, microsupercapacitors, fuel cells and surface plasmon resonance sensors.28)–32) In particular, due to its excellent electron capture and transport properties, the combination of graphene with photocatalysts has been demonstrated to be an efficient way to promote the separation of photogenerated electron–hole pairs and then enhance their photocatalytic activity.32)–37) We put forward herein an idea to assemble CaTiO3,
NiFe₂O₄ and graphene into ternary nanocomposite. The assembled ternary nanocomposite is expected to exhibit some appealing advantages. For example, NiFe₂O₄ can provide strong ferromagnetism for the magnetic recycling of the composite photocatalyst, and it can also extend the photo-response of the composite photocatalyst to visible light region. Moreover, the photogenerated electrons on CaTiO₃ and NiFe₂O₄ can be readily captured by graphene, leading to an increased separation and availability of electrons and holes for the photocatalytic reaction. In this work, CaTiO₃ and NiFe₂O₄ nanoparticles were prepared via a polyacrylamide gel route, and then assembled onto the reduced graphene oxide (rGO) via a hydrothermal method. The photocatalytic activity of the obtained CaTiO₃/rGO/NiFe₂O₄ nanocomposite was evaluated by the degradation of methylene blue (MB) and rhodamine (RhB) under simulated sunlight irradiation and the possible photocatalytic mechanism was discussed.

2. Experimental

CaTiO₃ and NiFe₂O₄ nanoparticles were fabricated via a polyacrylamide gel route as described in the literatures. In a typical synthesis process of CaTiO₃ nanoparticles, 0.0075 mol of Ca(NO₃)₂·4H₂O, 0.0075 mol of Ti(OC₄H₉)₄, 0.0225 mol of tartaric acid, 20 g of glucose and 0.135 mol of acrylamide were successively dissolved in 20 mL of dilute nitric acid solution with the aid of magnetic stirring. The mixture solution was adjusted to pH ~2 by adding aqueous ammonia, then made up to 100 mL by adding distilled water. The resultant solution was heated at 70°C, during which the polymerization reaction proceeds. The gel was dried at 120°C for 24 h, followed by calcination at 600°C for 6 h. The product was collected as CaTiO₃ nanoparticles. To prepare NiFe₂O₄ nanoparticles, 0.005 mol Ni(NO₃)₂·6H₂O, 0.01 mol Fe(NO₃)₃·9H₂O, 0.0225 mol acetic acid, 20 g of glucose and 0.135 mol of acrylamide were successively dissolved in 20 mL of dilute nitric acid solution. The obtained mixture solution was then treated following the procedure as described above, and thus NiFe₂O₄ nanoparticles were prepared. CaTiO₃/rGO/NiFe₂O₄ nanocomposite was prepared via a hydrothermal method, as shown in Fig. 1. 15 mg graphene oxide was dispersed into 60 mL ethanol aqueous solution (20 mL ethanol + 40 mL distilled water), followed by sonicating and stirring to obtain a homogeneous suspension. Subsequently, 0.2 g CaTiO₃ nanoparticles and 0.06 g NiFe₂O₄ nanoparticles were added to the above suspension under stirring. Then, the mixture was poured into a 100 mL Teflon-lined stainless steel autoclave and heated at 130°C for 3 h. After completion of the reaction, the autoclave was naturally cooled to room temperature. The formed CaTiO₃/rGO/NiFe₂O₄ nanocomposite was collected by centrifugation, washed with distilled water several times, and then dried in a thermostat oven at 60°C for 4 h. The rGO/NiFe₂O₄ composite was also prepared by hydrothermal method. The fabrication procedure was similar to that for CaTiO₃/rGO/NiFe₂O₄ preparation without the addition of CaTiO₃ nanoparticles.

The photocatalytic activity of the samples was evaluated by the degradation of MB and RhB under simulated sunlight irradiation from a 200 W xenon lamp (PLS-SXE 300, Beijing Perfectlight Technology Co. Ltd., Beijing, China). 0.1 g of the photocatalyst was added into 200 mL of an aqueous solution of the dye (initial concentration: 5 mg L⁻¹). Before photocatalytic measurement, the suspension was stirred for 30 min in dark to ensure the adsorption–desorption equilibrium between the photocatalyst and the dye. After that, the mixture was exposed to simulated sunlight irradiation. At illumination time intervals of 0.5 h, a small amount of the reaction solution was sampled and then centrifuged at 4000 rpm for 10 min to separate the photocatalyst from the solution. The concentration of the dye was determined by detecting the absorbance of the solution at a given wavelength (λₘₐₓ = 665 nm and λᵣₜᵣₜ = 554 nm) using an ultraviolet–visible (UV–vis) spectrophotometer. In order to investigate the photocatalytic reusability of the sample, it was collected by a magnet, washed with water, and dried. The recovered photocatalyst was dispersed in the fresh MB solution for the next cycle of the photocatalytic experiment under the same condition.

The photocurrent responses and electrochemical impedance spectra (EIS) of the samples were measured on an electrochemical workstation (CHI 660E, Shanghai Chenhua Instrument Co. Ltd., Shanghai, China) with a three-electrode cell system. In the three-electrode system, a standard calomel electrode served as the reference electrode and a platinum foil was used as the counter electrode. The working electrode was prepared according to the procedure described in the literature. 15 mg photocatalysts, 0.75 mg carbon black and 0.75 mg polyvinylidene fluoride were introduced into 1-methyl-2-pyrrolidone to obtain slurry. The slurry was coated on a 1.0 × 1.0 cm² fluoride-doped tin oxide glass electrode, followed by drying in an oven at 60°C for 5 h. Simulated sunlight emitted from a 200 W xenon lamp was used as the light source. The electrolyte used in this electrochemical measurement was 0.1 mol·L⁻¹ Na₂SO₄ solution. The photocurrent-time (I-t) curves were tested at a fixed bias potential of 0.2 V. The
EIS measurement was carried out at a sinusoidal voltage signal of 5 mV amplitude and in the frequency range from $10^{-2}$ to $10^3$ Hz.

The phase purity of the samples was examined by X-ray diffraction (XRD) on a D8 Advance X-ray diffractometer (Bruker AXS, Karlsruhe, Germany). The morphology of the products was observed by the field-emission scanning electron microscope (SEM) on a JSM-6701F scanning electron microscope (JEOL Ltd., Tokyo, Japan) and field emission transmission electron microscope (TEM) on a JEM-1200EX transmission electron microscope (JEOL Ltd., Tokyo, Japan). The Fourier transform infrared (FTIR) spectra of the samples were measured on an IFS 66v/S infrared spectrometer (Bruker, Karlsruhe, Germany). The UV–vis diffuse reflectance spectra of the samples were measured using a TU-1901 double beam UV–Vis spectrophotometer with an integrating sphere attachment (Beijing Purkinje General Instrument Co. Ltd., Beijing, China). The room temperature magnetic hysteresis loop of the samples was tested via a vibrating sample magnetometer (Lake Shore 7410, USA). The chemical composition and chemical state of elements were measured by X-ray photoelectron spectroscopy (XPS) on a PHI-5702 multi-functional electron spectroscopy (X-ray photoelectron spectrometer (Physical Electronics, hahnassen, MN, USA). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the samples were tested by N2 adsorption–desorption technique using an ASAP 2020 analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA). The photoluminescence (PL) spectra of the samples were recorded on a fluorescence spectrophotometer (Shimadzu RF-6000, Kyoto, Japan) with the excitation wavelength of $\sim 254$ nm.

3. Results and discussion

Figure 2 shows the FTIR spectra of graphene oxide, CaTiO$_3$, NiFe$_2$O$_4$ and CaTiO$_3$/rGO/NiFe$_2$O$_4$ nanocomposite. In the spectrum of graphene oxide, the absorption peak at $\sim 1726$ cm$^{-1}$ is ascribed to the C=O stretching of the COOH group. The peak at $\sim 1620$ cm$^{-1}$ is assigned to the C=C skeletal vibration of graphene sheets. The absorption peak at $\sim 1396$ cm$^{-1}$ comes from the O–H deformation vibration in C–OH. The absorption bands at $\sim 1224$ and $\sim 1050$ cm$^{-1}$ are caused by the C–O stretching vibration. For CaTiO$_3$, the two absorption bands at $\sim 448$ and $\sim 627$ cm$^{-1}$ are attributed to TiO$_6$ octahedron bending and stretching vibrations, respectively. For NiFe$_2$O$_4$, the broad absorption bands at $\sim 403$ and $\sim 592$ cm$^{-1}$ are due to the vibrations of octahedral and tetrahedral in the spinel structure, respectively.

In the spectrum of the nanocomposite, the absorption peaks at $\sim 450$ and $\sim 625$ cm$^{-1}$ are the overlay of the characteristic peaks of CaTiO$_3$ and NiFe$_2$O$_4$. Moreover, the intensity for the absorption peaks of oxygen-containing functional groups in the graphene oxide obviously decreases. The FTIR results suggest that graphene oxide is reduced and simultaneously CaTiO$_3$ and NiFe$_2$O$_4$ nanoparticles are assembled onto the reduced graphene oxide during the hydrothermal reaction.

Figure 3 shows the XRD patterns of CaTiO$_3$, NiFe$_2$O$_4$ and CaTiO$_3$/rGO/NiFe$_2$O$_4$ nanocomposite. It can be seen that all the diffraction peaks of CaTiO$_3$ particles and NiFe$_2$O$_4$ particles are consistent with the standard diffraction data of the orthorhombic CaTiO$_3$ structure (PDF card No. 42-0423) and cubic NiFe$_2$O$_4$ structure (PDF card No. 86-2267), respectively. For the nanocomposite, the XRD pattern consists of two sets of diffraction peaks separately corresponding to CaTiO$_3$ and NiFe$_2$O$_4$, and no additional peak of impurity phase is detected. This result indicates that the hydrothermal condition has no perceptible influence on the structure and purity of CaTiO$_3$ and NiFe$_2$O$_4$. In addition, no obvious diffraction peaks of rGO are observed in the XRD pattern, which is mainly attributed to the low content and relatively weak diffraction intensity of rGO.

Figure 4(a) shows the UV–vis diffuse reflectance spectra of CaTiO$_3$, NiFe$_2$O$_4$ and CaTiO$_3$/rGO/NiFe$_2$O$_4$ nanocomposite. Compared with CaTiO$_3$ nanoparticles, the nanocomposite shows much higher light absorbance in the whole wavelength range. This is mainly due to the strong light absorption of rGO and NiFe$_2$O$_4$ in the UV–vis light region.

Figure 4(b) shows the first derivative curves corresponding to the UV–vis diffuse reflectance spectra, from which the absorption edge of the samples can be obtained. As seen from the spectra, CaTiO$_3$ exhibits a sharp absorption edge at $\sim 342$ nm, which is attributed to the electron transition from valence band (VB) to CB.

![Fig. 2. FTIR spectra of graphene oxide, CaTiO$_3$, NiFe$_2$O$_4$ and CaTiO$_3$/rGO/NiFe$_2$O$_4$ sample.](image1)

![Fig. 3. XRD patterns of CaTiO$_3$, NiFe$_2$O$_4$ and CaTiO$_3$/rGO/NiFe$_2$O$_4$ nanocomposite.](image2)
According to the absorption edge, the bandgap energy of CaTiO₃ nanoparticles is calculated to be ~3.62 eV. For NiFe₂O₄, the absorption edge is observed at ~669 nm, from which its bandgap energy is obtained to be ~1.85 eV. In the case of CaTiO₃/rGO/NiFe₂O₄ nanocomposite, the absorption edges of CaTiO₃ and NiFe₂O₄ undergo almost no change, indicating that the rGO has no obvious impact on their bandgap structures. The energy-band potentials of CaTiO₃ and NiFe₂O₄ can be determined based on the method described in the literature. The VB potentials of CaTiO₃ and NiFe₂O₄ nanoparticles are estimated to be 2.71 and 2.29 V vs. NHE, and the CB potentials of CaTiO₃ and NiFe₂O₄ nanoparticles are calculated to be ~0.91 and 0.44 V vs. NHE, respectively.

Figure 5(a) shows the SEM image of CaTiO₃ nanoparticles. It is seen that the particles are regularly spherical in shape and uniform in size with an average diameter of ~36 nm. Figure 5(b) shows the SEM image of NiFe₂O₄ nanoparticles, revealing that they exhibit a sphere- or ellipsoid-like shape. The NiFe₂O₄ particles have a relatively wide size distribution and the average particle size is centered ~75 nm. Figure 5(c) shows the SEM image of graphene oxide, which indicates that it has a sheet structure feature with ripples. The SEM image of CaTiO₃/rGO/NiFe₂O₄ nanocomposite is shown in Fig. 5(d), revealing the assembly of CaTiO₃ and NiFe₂O₄ nanoparticles on the surface of the rGO sheet.

Figure 6(a) shows the TEM image of CaTiO₃/rGO/NiFe₂O₄ nanocomposite. It is seen that the nanoparticles with different sizes are attached on the rGO sheet. Furthermore, the elemental mapping was employed to confirm the existence of CaTiO₃ and NiFe₂O₄ nanoparticles on the surface of rGO. Figure 6(b) presents the dark field scanning TEM (DF-STEM) image of CaTiO₃/rGO/NiFe₂O₄ nanocomposite. The corresponding elemental maps of the selected region in Fig. 6(b) are shown in Figs. 6(c)–6(h). It is clear that the C element distributes over the entire sheet.
structure, which is confirmed to be rGO. The O, Ca, Ti, Ni and Fe elements distribute homogeneously on the surface of rGO, further suggesting that CaTiO3 and NiFe2O4 nanoparticles are successfully assembled onto the surface of the rGO sheet. Moreover, the elemental maps indicate the content of NiFe2O4 is obviously lower than that of CaTiO3, which confirms to the stoichiometric ratio of NiFe2O4 to CaTiO3 (0.6/2).

The chemical composition and chemical state of CaTiO3/rGO/NiFe2O4 nanocomposite were studied by XPS. Figures 7(a)–7(f) show the high-resolution XPS spectra of Ca 2p, Ti 2p, Ni 2p, Fe 2p, C 1s and O 1s, respectively. As seen from Fig. 7(a), the two obvious signals at binding energies of 346.8 and 350.4 eV are assigned to Ca 2p3/2 and Ca 2p1/2, respectively, which is consistent with the chemical state of Ca2+. As seen from Fig. 7(b), the Ti 2p XPS spectrum manifests two peaks at 458.8 and 464.5 eV, which correspond to the Ti 2p3/2 and Ti 2p1/2 binding energies of Ti4+. The Ni 2p XPS spectrum [Fig. 7(c)] displays two strong peaks at 873.2 and 854.7 eV, which correspond to the binding energies of Fe 2p1/2 and Fe 2p3/2, respectively.

The Fe 2p XPS spectrum [Fig. 7(d)] displays two strong peaks at 873.2 eV (Ni 2p1/2) and 854.7 eV (Ni 2p3/2), and the peaks at 885.9 and 861.6 eV are characterized as the corresponding satellites of Ni 2p1/2 and Ni 2p3/2. This implies the presence of the +2 oxidation state of Ni ion. On the Fe 2p spectrum [Fig. 7(d)], the peaks located at 724.1 and 710.8 eV are attributed to the binding energies of Fe 2p1/2 and Fe 2p3/2, respectively. By further deconvoluting the Fe 2p3/2 signal, two peaks at 711.5 and 710.5 eV are observed, which correspond to Fe3+ and Fe2+, respectively. In addition, the Fe2+ and Fe3+ peaks are associated with the satellite peaks at 714.8 and 717.8 eV, respectively, which is consistent with the results reported previously. This suggests the coexistence of Fe2+ and Fe3+ in the composite. Another weak peak at 727.7 eV belongs to the satellite peak of Fe 2p1/2. The existence of Fe2+ is mainly caused by the formation of oxygen vacancies, which is further confirmed by the analysis of O 1s XPS spectrum [Fig. 7(f)]. The C 1s XPS spectrum [Fig. 7(e)] can be divided into four peaks at 282.1 eV for Ti–C, 284.7 eV for C–C, 286.1 eV for C–O and 289.0 eV for C=O, indicating the presence of rGO and the chemical bonding between CaTiO3 and rGO. On the O 1s spectrum [Fig. 7(f)], four peaks are observed at 530.1, 530.9, 531.5 and 532.9 eV. The signal at binding energy of 530.1 eV belongs to the lattice oxygen. The peak at 530.9 eV is mainly assigned to the O–NiFe2O4 interfacial bonding structure. The binding energy located at 531.5 eV comes from chemisorbed oxygen caused by oxygen vacancies. This reveals the existence of oxygen vacancies and chemical bonding between NiFe2O4 and residue oxygen of rGO. The peak at 532.9 eV is mainly ascribed to the residual oxygen-containing groups in rGO, such as –OH and –COOH.

Figure 8 presents the N2 adsorption/desorption isotherm plot of CaTiO3/rGO/NiFe2O4 nanocomposite. Based on the IUPAC classification, the nanocomposite exhibits type IV isotherm with a hysteresis loop at higher relative pressure, which suggests the existence of the mesopores. This is further confirmed by the pore size distribution plot in the inset of Fig. 8, from which one can see that the nanocomposite possesses a wide pore size distribution. The BET surface area of the nanocomposite is estimated to be ~26.6 m²·g⁻¹.

The photocatalytic activities of CaTiO3, NiFe2O4 and CaTiO3/rGO/NiFe2O4 nanocomposite were evaluated by the degradation of MB and RhB under simulated sunlight irradiation. Figures 9(a) and 9(b) show the time-dependent photocatalytic degradation of MB and RhB,
respectively, along with the blank experiment result. The dye degradation percentage is determined by the following equation:

\[
\left( \frac{C_0}{C_t} \right) \times 100\% = \text{degradation percentage}
\]

where \(C_0\) = initial dye concentration and \(C_t\) = residual dye concentration after reaction for \(t\) min. The blank experiment shows that the self-degradation of MB (\(\sim 6\%\)) and RhB (\(\sim 4\%\)) is negligible after 3 h exposure, implying that MB and RhB exhibit good stability under short-time irradiation of simulated sunlight. The photocatalytic results reveal that pure NiFe\(_2\)O\(_4\) and CaTiO\(_3\) nanoparticles exhibit weak photocatalytic activity for the degradation of the dyes under simulated sunlight irradiation. After 3 h irradiation, the degradation percentage of MB is \(\sim 11\%\) and \(\sim 38\%\) for bare NiFe\(_2\)O\(_4\) and CaTiO\(_3\), respectively, whereas \(\sim 10\%\) and \(\sim 31\%\) of RhB is decomposed using pure NiFe\(_2\)O\(_4\) and CaTiO\(_3\) under the same conditions, respectively. In con-

Fig. 7. High-resolution XPS spectra of CaTiO\(_3\)/rGO/NiFe\(_2\)O\(_4\) nanocomposite: (a) Ca 2p XPS spectrum; (b) Ti 2p XPS spectrum; (c) Ni 2p XPS spectrum; (d) Fe 2p XPS spectrum; (e) C 1s XPS spectrum; (f) O 1s XPS spectrum.

Fig. 8. \(\text{N}_2\) adsorption–desorption isotherm and pore size distribution plot of CaTiO\(_3\)/rGO/NiFe\(_2\)O\(_4\) nanocomposite.
trast, the CaTiO3/rGO/NiFe2O4 nanocomposite exhibits much higher photocatalytic activity than bare NiFe2O4 and CaTiO3. The degradation percentage of MB and RhB is observed as ≈83 and ≈74% after reaction for 3 h, respectively. The corresponding degradation process of MB and RhB over the nanocomposite is detected by time-dependent UV−vis absorption spectra of the dyes, as shown in Figs. 9(c) and 9(d). The characteristic adsorption peak of MB (≈665 nm) and RhB (≈554 nm) obviously decreases with the increase of exposure time, and no additional absorption peak appears during the photocatalytic process, which demonstrates that the dyes are indeed decomposed. In addition, the photocatalytic reaction kinetics analysis was also performed. As shown in Fig. 9(e) and 9(f), the degradation of the dyes can be modeled by the following first-order kinetic equation:

\[
\ln\left(\frac{C_0}{C_t}\right) = k_{\text{app}}t,
\]

where \(k_{\text{app}}\) is the apparent first-order reaction rate constant.\(^{60}\) For MB degradation, the composite exhibits the highest \(k_{\text{app}}\) value of 0.56799 h\(^{-1}\), which is ≈3.4 times higher than that of pure CaTiO3 (0.16572 h\(^{-1}\)) [Fig. 9(e)]. A similar result is observed in the RhB degradation, where the \(k_{\text{app}}\) of the composite is 0.45828 h\(^{-1}\), which is ≈3.8 times as large as that of bare CaTiO3 (0.11893 h\(^{-1}\)) [Fig. 9(f)]. During above photocatalytic process, CaTiO3 is considered to be predominant in the photocatalytic activity of the composite. This can be attributed to the following reasons: (i) The recombination rate of the photogenerated charges in bare CaTiO3 is low because the bandgap of CaTiO3 (3.62 eV) is larger than that of NiFe2O4 (1.85 eV); (ii) According to the calculation results of energy-band potentials, the photogenerated charges in CaTiO3 exhibit stronger redox ability than those in NiFe2O4.

In this work, the ratio between NiFe2O4 and CaTiO3 reaches the optimal value. Further increase of NiFe2O4...
content results in a decrease of photocatalytic activity. When excess NiFe$_2$O$_4$ nanoparticles are loaded, the opportunity of direct contact between NiFe$_2$O$_4$ and CaTiO$_3$ increases. The photogenerated electrons in the CB of CaTiO$_3$ tend to migrate to that of NiFe$_2$O$_4$; and the photogenerated holes simultaneously transfer from the VB of CaTiO$_3$ to that of NiFe$_2$O$_4$. Considering the relatively smaller bandgap of NiFe$_2$O$_4$, this charge transfer process is expected to promote the recombination of the photogenerated charges, leading to a reduction of the photocatalytic activity.

The visible-light-driven photocatalytic activities of CaTiO$_3$, NiFe$_2$O$_4$ and CaTiO$_3$/rGO/NiFe$_2$O$_4$ nanocomposite for the degradation of MB were also investigated under the irradiation of 200 W xenon lamp with a 420-nm cut-off filter, and the result is presented in Fig. 10. It can be seen that the degradation percentage of MB over CaTiO$_3$ is small, and this photocatalytic performance is mainly attributed to the dye sensitization effect. When bare NiFe$_2$O$_4$ is used as photocatalyst, about 18% of dye is degraded after 6h irradiation. Compared with CaTiO$_3$ and NiFe$_2$O$_4$, CaTiO$_3$/rGO/NiFe$_2$O$_4$ nanocomposite exhibits obviously enhanced visible-light-driven photocatalytic activity.

To investigate the transfer behavior of photogenerated charges in the samples, the transient photocurrent responses and EIS spectra of samples were measured and the results are shown in Figs. 11(a) and 11(b). It can be seen from Fig. 11(a) that CaTiO$_3$/rGO/NiFe$_2$O$_4$ nanocomposite exhibits remarkable enhanced photocurrent density compared with NiFe$_2$O$_4$ and CaTiO$_3$, indicating the efficient charge migration and separation of the nanocomposite. The EIS Nyquist plots of CaTiO$_3$/rGO/NiFe$_2$O$_4$, CaTiO$_3$ and NiFe$_2$O$_4$ are presented in Fig. 11(b). It is found that the samples possess a typical semicircle shape. In general, the radius of the semicircle is highly associated with the charge-transfer resistance, and the smaller radius corresponds to the lower charge-transfer resistance. The semicircle radius of CaTiO$_3$/rGO/NiFe$_2$O$_4$ is much smaller than that for NiFe$_2$O$_4$ and CaTiO$_3$ [Fig. 11(b)], which suggests the enhanced interfacial charge migration in the nanocomposite. For more detailed analysis, the Nyquist plots are fitted into an equivalent circuit model based on the ZSimDemo software, which is shown in the inset of Fig. 11(b). In this equivalent circuit, $R_1$ is the solution resistance, $R_2$ and $C_1$ are the interfacial resistance and capacitance between the working electrode and electrolyte, $R_3$ and $C_2$ are the interfacial resistance and capacitance...
between the prepared sample and substrate, \( W \) is the Warburg impedance. The fitting value of \( R^2 \) follows the sequence: \( \text{CaTiO}_3/\text{rGO}/\text{NiFe}_2\text{O}_4 (104.5 \ \Omega \cdot \text{cm}^2) < \text{CaTiO}_3 (131.9 \ \Omega \cdot \text{cm}^2) < \text{NiFe}_2\text{O}_4 (246 \ \Omega \cdot \text{cm}^2) \). It can be seen that the \( \text{CaTiO}_3/\text{rGO}/\text{NiFe}_2\text{O}_4 \) nanocomposite possesses the lowest \( R^2 \) value, which further demonstrates that the construction of ternary \( \text{CaTiO}_3/\text{rGO}/\text{NiFe}_2\text{O}_4 \) leads to more effective transfer of photogenerated charges.

Figure 11(c) shows the Bode phase angle plots of samples derived from the corresponding Nyquist plots. Among these samples, the \( \text{CaTiO}_3/\text{rGO}/\text{NiFe}_2\text{O}_4 \) nanocomposite exhibits the smallest peak frequency value (117 Hz) at the frequencies ranging from 10 to 1000 Hz, which indicates a low recombination of photogenerated electrons and holes in nanocomposite. This phenomenon is similar to that reported in the literature.\(^{61}\) In addition, the photogenerated charges migration between \( \text{NiFe}_2\text{O}_4 \) and rGO was also evaluated based on PL spectrum of rGO/\( \text{NiFe}_2\text{O}_4 \) composite, as shown in Fig. 11(d). It is seen that the obvious emission peaks at \( \sim 575 \) nm are found. Notably, the PL intensity of the rGO/\( \text{NiFe}_2\text{O}_4 \) composite is much smaller than that of \( \text{NiFe}_2\text{O}_4 \), which suggests that the migration and separation of photogenerated electrons and holes in bare \( \text{NiFe}_2\text{O}_4 \) can be promoted after the introduction of rGO.

Figure 12(a) shows the magnetic hysteresis loop of \( \text{CaTiO}_3/\text{rGO}/\text{NiFe}_2\text{O}_4 \) nanocomposite measured at room temperature, indicating that the composite exhibits obvious ferromagnetism. Such favorable ferromagnetic behavior of the nanocomposite allows it to be recycled by an external magnetic field, as shown in Fig. 12(b). When a magnet is placed in close to the suspension, the composite photocatalyst suspended in the aqueous solution can be readily separated. However, the solution containing
CaTiO₃ nanoparticles do not undergo obvious change by the application of external magnet. The stability of the CaTiO₃/rGO/NiFe₂O₄ nanocomposite was investigated by the magnetic separation of the photocatalyst and recyclable photocatalytic experiment. As shown in Fig. 12(c), the nanocomposite maintains relatively high photocatalytic activity after three successive runs. The XRD pattern and TEM image of the recycled composite are shown in Figs. 12(d) and 12(e), respectively. It can be seen that no obvious crystal structure change is detected, and the nanoparticles are still well attached on the surface of rGO. The results indicate that the CaTiO₃/rGO/NiFe₂O₄ nanocomposite exhibits good photocatalytic reusability.

The photocatalytic mechanism of the CaTiO₃/rGO/NiFe₂O₄ nanocomposite is shown in Fig. 13. When CaTiO₃ or NiFe₂O₄ nanoparticles are irradiated by simulated sunlight, electrons are excited to the CB from the VB, thus creating photogenerated electrons-holes pairs. It is generally accepted that the photogenerated charges in the CB, thus creating photogenerated electrons-holes pairs. It is generally accepted that the photogenerated charges in the CB, thus creating photogenerated electrons-holes pairs. These can suppress the recombination of photogenerated charges because it can act as the hole transport layer.⁶² These can suppress the recombination of photogenerated charges, which results in an increased availability of photogenerated electrons and holes for photocatalytic reaction, thus enhancing the photocatalytic efficiency.

The photocatalytic results indicate that the CaTiO₃/rGO/NiFe₂O₄ nanocomposite exhibits much higher photocatalytic activity in MB and RhB degradation under simulated sunlight irradiation than that of pure CaTiO₃ and NiFe₂O₄. This enhancement of photocatalytic activity is attributed to the fact that photogenerated electrons of the photocatalysts can be captured by rGO, which results in an increased separation and availability of electrons and holes for photocatalytic reaction. More importantly, the CaTiO₃/rGO/NiFe₂O₄ nanocomposite can be readily recovered by external magnetic field, and exhibits good photocatalytic reusability.

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22) J. Zeng, T. Song, M. Lv, T. Wang, J. Qin and H. Zeng, *RSC Adv.*, 6, 54964–54975 (2016).

23) D. Lv, D. Zhang, X. Liu, Z. Liu, L. Hu, X. Pu, H. Ma, D. Li and J. Dou, *Sep. Purif. Technol.*, 158, 302–307 (2016).

24) M. Gen and Z. Hu, *Ceram. Int.*, 42, 6510–6514 (2016).

25) H. Y. Zhu, R. Jiang, Y. Q. Fu, R. R. Li, J. Yao and S. T. Jiang, *Appl. Surf. Sci.*, 369, 1–10 (2016).

26) K. P. Loh, Q. Bao, P. K. Ang and J. Yang, *J. Mater. Chem.*, 20, 2277–2289 (2010).

27) A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, *Rev. Mod. Phys.*, 81, 109–162 (2009).

28) C. P. Liang, G. Niu, X. F. Chen, Z. G. Zhou, Z. Yi, X. Ye, T. Duan, Y. Yi and S. Y. Xiao, *Opt. Commun.*, 436, 57–62 (2019).

29) J. L. Jiang, X. X. He, J. F. Du, X. J. Pang, H. Yang and Z. Q. Wei, *Mater. Lett.*, 220, 178–181 (2018).

30) R. Simoes and V. Neto, *J. Mater. Res.*, 31, 1633–1647 (2016).

31) Y. A. Yang, L. Xia, T. Zhang, B. Shi, L. N. Huang, B. Zhong, X. Y. Zhang, H. T. Wang, J. Zhang and G. W. Wen, *Chem. Eng. J.*, 352, 510–518 (2018).

32) X. X. Wang, X. X. Wu, Y. Z. Chen, X. L. Bai, Z. Y. Pang, H. Yang, Y. P. Qi and X. L. Wen, *AIP Adv.*, 8, 105029 (2018).

33) T. Soltani and B. K. Lee, *Chem.-Eur. J.*, 306, 204–213 (2016).

34) H. Y. He and J. Lu, *Separ. Purif. Methods*, 172, 374–381 (2016).

35) H. J. Sun, Y. Liu, Y. Zhang, L. Lv, J. Zhou and W. Chen, *J. Mater. Sci.-Mater. El.*, 25, 4212–4218 (2014).

36) P. Y. Dong, Y. H. Wang, L. N. Guo, B. Liu, S. Y. Xin, J. Zhang, Y. R. Shi, W. Zeng and S. Yin, *Nanoscale*, 4, 4641–4649 (2012).

37) X. X. Zhao, H. Yang, Z. M. Cui and Z. Yi, *Micro-machines*, 10, 66 (2019).

38) Y. C. Ye, H. Yang, H. M. Zhang and J. L. Jiang, *Environ. Technol.*, (https://doi.org/10.1080/09593330.2018.1538261).

39) C. X. Zheng, H. Yang, Z. M. Cui, H. M. Zhang and X. X. Wang, *Nanoscale Res. Lett.*, 12, 608 (2017).

40) J. T. Last, *Phys. Rev.*, 105, 1740–1750 (1957).

41) M. Srivastava, A. K. Ojha, S. Chaubey and A. Materny, *J. Alloy. Compd.*, 481, 515–519 (2009).

42) L. Ren, X. Qi, Y. D. Liu, Z. Y. Huang, X. L. Wei, J. Li, L. Yang and J. Zhong, *J. Mater. Chem.*, 22, 11765 (2012).

43) Q. Li, B. Guo, J. Yu, J. Ran, B. Zhang, H. Yan and J. Gong, *J. Am. Chem. Soc.*, 133, 10878–10884 (2011).

44) J. T. Adeleke, T. Theivisanthi, M. Thiruppathi, M. Swaminathan, T. Akomolafe and A. B. Alab, *Appl. Surf. Sci.*, 455, 195–200 (2018).

45) L. J. Di, H. Yang, T. Xian and X. J. Chen, *Micro-machines*, 9, 613 (2018).

46) T. Y. Peng, X. H. Zhang, H. J. Lv and L. Zan, *Catal. Commun.*, 28, 116–119 (2012).

47) S. R. Morrison, *New York: Plenum* (1980).

48) S. W. Lee, L. M. Lozano-Sánchez and V. Rodriguez-González, *J. Hazard. Mater.*, 263P, 20–27 (2013).

49) H. Y. Zhao, Y. W. Duan and X. Sun, *New J. Chem.*, 37, 986–991 (2013).

50) X. W. Li, L. Wang, L. Zhang and S. P. Zhuo, *Appl. Surf. Sci.*, 419, 586–594 (2017).

51) H. Y. Ji, X. C. Jing, Y. Q. Xu, J. Yan, H. P. Li, Y. P. Li, L. Y. Huang, Q. Zhang, H. Xu and H. M. Li, *RSC Adv.*, 5, 57960 (2015).

52) J. Zeng, T. Song, M. X. Lv, T. T. Wang, J. Y. Qin and H. P. Zeng, *RSC Adv.*, 6, 54964–54975 (2016).

53) Y. C. Ye, H. Yang, X. X. Wang and W. J. Feng, *Mat. Sci. Semicon. Proc.*, 82, 14–24 (2018).

54) S. Q. Huang, Y. G. Xu, T. Zhou, M. Xie, Y. Ma, Q. Q. Liu, L. Q. Jing, H. Xu and H. M. Li, *Appl. Catal. B-Environ.*, 225, 40–50 (2018).

55) M. A. Fitri, M. Ota, Y. Hirota, Y. Uchida, K. Harada, D. Ino and N. Nishiyama, *Mater. Chem. Phys.*, 198, 42–48 (2017).

56) Y. Wang, Y. Q. Fu, X. M. Wu, W. Z. Zhang, Q. G. Wang and J. H. Li, *Ceram. Int.*, 43, 11367–11375 (2017).

57) Y. L. Li, Z. Q. Zhang, L. Y. Pei, X. G. Li, T. Fan, J. Ji, J. F. Shen and M. X. Ye, *Appl. Catal. B-Environ.*, 190, 1–11 (2016).

58) L. J. Di, H. Yang, T. Xian and X. J. Chen, *Nanoscale Res. Lett.*, 13, 257 (2018).

59) Z. Yi, X. B. Xu, X. L. Kang, Y. L. Zhao, S. L. Zhang, W. T. Yao, Y. G. Yi, J. S. Luo, C. W. Wang, Y. Yi and Y. T. Wang, *Surf. Coat. Tech.*, 324, 257–263 (2017).

60) C. X. Zheng and H. Yang, *J. Mater. Sci.-Mater. El.*, 29, 9291–9300 (2018).

61) K. Y. Si, J. Y. Ma, Y. H. Guo, Y. X. Zhou, C. H. Lu, X. X. Xu and X. L. Xu, *Ceram. Int.*, 44, 21153–21158 (2018).

62) N. T. Ho, V. Senthilkumar, H. S. Cho, S. H. No, S. Cho, M. C. Jung, Y. B. Qi and Y. S. Kim, *Phys. Status Solidi A*, 211, 1873–1876 (2014).