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Dendritic $\alpha$-Fe$_2$O$_3$/TiO$_2$ nanocomposites with improved visible light photocatalytic activity

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Abstract

The design and synthesis of unique novel heterostructures for high-performance photocatalytic activity has exerted a tremendous fascination and has recently attracted intensive attention. In this paper, a branch-like \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2 \) heterostructure is synthesized controllably through an electrospinning method combined with a hydrothermal approach. The backbone of the heterostructure is composed of 3D porous \( \text{TiO}_2 \) nanofibers (~70 nm in diameter) network with plenty of \( \alpha\text{-Fe}_2\text{O}_3 \) nanorods (100–200 nm in length) depositing on them. The novel branch-like nanocomposite brings about the abundant porous structure as well as the large surface area (upto 42.8 m\(^2\)/g). In addition, their visible-light photodegradations toward organic dyes, including Congo red (CR), methylene blue (MB), eosin red (ER), methyl orange (MO) were investigated. The excellent photocatalytic performances are attributed to their large surface, improved visible light absorption and high separation efficiency of the photogenerated electron/hole. Furthermore, the degradation process was further studied by varying the amount of \( \alpha\text{-Fe}_2\text{O}_3 \) deposition. \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2\)-3 possesses the best performance to efficiently decolor CR solution even at a high concentration 50 mg/L (160 min 94 mg/g), ascribing to the high adsorption capacity derived from the large surface, strong electrostatic interaction and structure match between \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2\)-3 and CR. These \( \alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2 \) heterostructures exhibit the great potential for decontamination of organic pollutants in waste water under visible light.
1. Introduction

With industrialization and rapid population growth, the environmental pollution has steadily raised awareness of a potential global crisis and is becoming overwhelming concerns all over the world. Thereinto, the growing water contamination is one of the worst environmental problems, and the advancement of pollution-free technologies has become an urgent task. Among available strategies, photocatalysis was regarded as one of the most effective and economical ways to purify the contaminated water.\(^1\text{-}^5\)

Thus, in recent years, many kinds of semiconductor metal oxides, such as Bi\(_2\)O\(_3\), Fe\(_2\)O\(_3\), ZnO, TiO\(_2\) and so forth, have been developed as the catalyst to treat contaminations.\(^6\text{-}^{14}\) Among them, TiO\(_2\) as a widely used wide band-gap (rutile \(\sim\)3.0, anatase \(\sim\)3.2 eV) semiconductor has been extensively studied owing to its abundance, nontoxicity, and stability.\(^15\text{-}^{20}\) However, the rapid combination of an electron–hole pair (\(e^-/h^+\)) goes against the photocatalytic performance. Besides, the wide band-gap of TiO\(_2\) always requires ultraviolet (UV) light to excite the generation of electron–hole pair to make sure the photocatalysis. Nevertheless, UV light takes up only a small fraction (below 10%) of the sun’s energy compared to visible light (about 44%).\(^21\) To improve the utilization of sun light and enhance the photocatalytic performance of TiO\(_2\) catalysts, the decrease of the recombination rate of the photogenerated electrons–holes and improvement of the visible light response of TiO\(_2\) should be paid attention. Currently, the doping by metal or non-metal ions, or through its combination with narrow band gap nanocrystalline semiconductor such as PbS, AgI, InP, CdSe, Ag\(_2\)S and Bi\(_2\)S\(_3\), were carried out, revealing the enhanced...
photocatalysis activity.\textsuperscript{7, 22-33} Furthermore, compared with pure TiO\textsubscript{2} materials, TiO\textsubscript{2}-based binary metal oxides usually exhibit improved thermal and hydrothermal stability that is vital for the repeatable behavior.\textsuperscript{34}

It is known that hematite (\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}), one of the stable forms of iron oxide under ambient condition, has attracted considerable attention due to its high stability, low cost, non-toxicity, environmentally friendliness, narrow band gap (2.0–2.2 eV), natural abundance and very high positive valence band edge potential. And the combination of TiO\textsubscript{2} with Fe\textsubscript{2}O\textsubscript{3} to form the heterostructure was considered as the effective way to decrease the recombination rate of photogenerated electrons-holes and improve the visible light response of the catalyst.\textsuperscript{35} The core–shell Fe\textsubscript{2}O\textsubscript{3}@TiO\textsubscript{2} nanocomposites were synthesized via a heteroepitaxial growth route using the Fe\textsubscript{2}O\textsubscript{3} spindle as a hard template to display improved photocatalytic degradation activity for Rhodamine B dye under visible light irradiation.\textsuperscript{32}

Besides the component, the structure of these composites also plays a significant part in photocatalysis performance. One-dimensional (1D) nanofibers with high length-to-diameter ratio and ultra large special surface area that provides plenty of active sites have been regarded as the potential materials to be used in photocatalysis. Furthermore, these nanofibers always possess the various porous structure derived by the accumulation of many nanoparticles that is beneficial to the vectorial transfer of photo-induced charge carriers through the grain boundaries, leading to the high separation efficiency of electron–hole pairs as well as the superior catalytic properties. In this work, we report a simple two-step route to synthesize branched 1D
α-Fe₂O₃/TiO₂ heterostructures by a combination of the electrospinning and hydrothermal method. Congo red (CR), methylene blue (MB), methyl orange (MO), and eosin red (ER) were adopted as the model dye pollutants, and the photodegradations under the visible light were investigated in detail. Furthermore, the degradation kinetics was further surveyed by varying the amount of α-Fe₂O₃ nanorods to reveal that the ratio of α-Fe₂O₃/TiO₂ coupled with the adsorption capacity to determine the final photocatalytic efficiency.

2. Experimental

2.1 Materials

Polyvinylpyrrolidone (PVP, Mw=1,300,000), Iron chloride hexahydrate (FeCl₃·6H₂O) was purchased from Aladdin (China). N, N-dimethylformamide (DMF) was bought from Tianjin Fengchuan Chemical Co. (China). Glacial cetic acid was purchased from Tianjin Fuyu Chemical Co. (China). Tetrabutyl titanate (TBOT, Ti(OCH₃)₄), Sodium sulfate (Na₂SO₄) was purchased from Sinopharm Chemical Reagent Co.,Ltd (China). Congo red (CR), methylene blue (MB), eosin red (ER) and methyl orange (MO), were obtained from Tianjin Guangfu Chemical Co. (China). All the reagents were of analytical grade and used without further purification.

2.2 Preparation of TiO₂ nanofibers

In the typical procedure, 0.85 mL of tetrabutyl titanate (TBOT, Ti(OCH₃)₄) was added to a mixed solution containing 1.5 mL of glacial cetic acid and 3.58 mL of N,N-Dimethylformamide (DMF) and stirred continuously 2h. Then, 0.6 g of poly(vinyl pyrrolidone) (PVP) powder (Mw= 1,300,000) was added to the above
solution. Then stirring at room temperature for 6 h, and the precursor solution of PVP/Ti(OC$_4$H$_9$)$_4$ composites was obtained. Subsequently, the viscous precursor solution was then loaded into a 5 ml syringe connected to 7-gauge stainless steel needle. A variable high voltage power supply (Gamma FL 32174) was used to provide a high voltage (15 kV) for the electrospinning. The positive electrode of the high voltage power supply was connected to the needle tip and the grounded electrode was connected to an aluminum foil. Finally, the prepared precursor fibers were calcined at 500 °C for 3 h under air at a rate of 1 °C /min to obtain the pure TiO$_2$ nanofibers.

2.3 Fabrication of branched α-Fe$_2$O$_3$/TiO$_2$ heterostructures

In a typical procedure, FeCl$_3$·6H$_2$O (0.04 M) and Na$_2$SO$_4$ (0.04 M) were dissolved in the 20 mL of H$_2$O under ultrasonication 30 min to become uniform solution. The resulting solution and the obtained TiO$_2$ nanofibers (16 mg) were transferred into a Teflon-lined stainless autoclave, sealed and maintained at 120 °C for 12 h. After it was cooled to room temperature, the precipitate was collected, rinsed using deionized water and finally dried at 60 °C for 12 h. The last products were annealed to 400 °C for 2h. With different amount of FeCl$_3$·6H$_2$O and Na$_2$SO$_4$ in growth solution, the resultant composites named as α-Fe$_2$O$_3$/TiO$_2$-1 (0.01 M), α-Fe$_2$O$_3$/TiO$_2$-2 (0.03 M), α-Fe$_2$O$_3$/TiO$_2$-3 (0.04 M), and α-Fe$_2$O$_3$/TiO$_2$-4 (0.05 M), respectively.

2.4. Photocatalytic test

The photocatalytic activity was measured by the degradation of eosin red (ER), Congo red (CR), methylene blue (MB) and methyl orange (MO), respectively. In a typical process, 0.05 g of α-Fe$_2$O$_3$/TiO$_2$ sample was suspended in 200 ml Congo red
aqueous solution (10 mg/L). The suspensions were magnetically stirred 1h in the dark to ensure adsorption/desorption equilibrium, and the solution was then exposed to the Xenon lamp (HSX-F/UV300), which was placed at about 10 cm from the reactor. A 400 nm cut-off filter was placed above the reactor to cut off UV light. At given irradiation time intervals, the samples were collected regularly to measure the Congo red degradation by UV-vis spectroscopy. The α-Fe$_2$O$_3$/TiO$_2$-3 structures were then separated from the solution by centrifuging, washed with ethanol to fully remove the residual organic species, then reused for the next run. Finally, the experiments of the photocatalytic degradation of eosin red aqueous solution, methylene blue and methyl orange aqueous solution were also conducted under the same conditions. After the photocatalytic test of degrading 10mg/L CR, the α-Fe$_2$O$_3$/TiO$_2$-3 heterostructure was then separated from the solution by centrifuging, washing clean exhaustive with ethanol to fully remove the residual organic species and dried in oven at 60℃ the whole night, then reused for the next run to test the recycle ability.

2.5. Hydroxyl radical test

In the analysis of hydroxyl radical, 50 mg sample and 20 mL 5 mg/L coumarin aqueous solution were fixed in a quartz reactor. The irradiation condition is the same to that of the above photodegradation testing. Finally, a certain amount of the solution was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxyl coumarin under the light excitation of 324 nm.

2.6. Characterization

The phase and composition of the as-obtained products were characterized by X-ray
diffraction (XRD, Rigaku Dmax-rB, Cu Kα radiation, 40 KV, 100 mA). X-ray photoelectron spectroscopy (XPS) was characterized using a PHI 5000 ESCA X-ray photoelectron spectrometer with a monochromated Al Kα X-ray source (1486.6 eV) to investigate the chemical structure of the materials. The morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM, Hitachi-4800) and transmission electron microscopy (TEM, JEOL 2010EX). A specific surface area analyzer (NOVA2000E) was used to measure the N₂ adsorption/desorption. The Brunauer–Emmett–Teller (BET) formula was further used to calculate the specific surface area. The efficiency of the photocatalytic degradation was analyzed by monitoring dye decolorization at the maximum absorption wavelength, using a UV-Vis spectrometer (Shimadzu UV-2550). UV–Vis absorption spectra of these samples were recorded at a Cary 4000 spectrophotometer in the wavelength range of 200–800 nm. Zeta potential was carried out on Zeta PALS zeta potential analyzer.

3. Results and discussion

The general synthesis of α-Fe₂O₃/TiO₂ involves two individual steps: the preparation of TiO₂ nanofibers via electrospinning technology and the deposition of α-Fe₂O₃ by hydrothermal reaction (Scheme 1). And the corresponding structure and morphology of the composite were characterized by SEM and TEM as shown in Fig. 1. It can be clearly observed that the TiO₂ substrates reveal the uniform nanofiber morphology with length up to several micrometers and a relatively uniform diameter of ~70 nm (Fig. 1a). And the staggered nanofibers make up a 3D interconnected framework
which can not only facilitate the continuous transfer of electrons but also provide a
large surface area, making it an ideal supporting material for the deposition of α-
Fe$_2$O$_3$. From the TEM image as displayed in Fig. 1b, all TiO$_2$ fibers are composed of a
large amount of nanoparticles about 10–20 nm in size and the accumulation of these
nanoparticles also brings plenty of porous structure. After the facile hydrothermal
treatment, α-Fe$_2$O$_3$ nanorods deposit on almost the external surface of TiO$_2$ nanofibers,
and the novel heterostructures looks like the branches as visible in inset of Fig. 1c.
The diameter of the individual hierarchical α-Fe$_2$O$_3$ /TiO$_2$ increases to about 300 nm,
much longer than those of the pristine TiO$_2$ nanofibers (Fig. 1c, d). TEM observations
were performed to further confirm the unique heterostructures of α-Fe$_2$O$_3$/TiO$_2$ hybrid.
It can be clearly observed that the nanostructures are composed of a TiO$_2$ nanofiber
(70 nm in diameter) and α- Fe$_2$O$_3$ nanorods (100–200 nm in length and ~30 nm in
diameter) and the TiO$_2$ nanofibers are uniformly covered by the nanorods, forming a
typical branched heterostructure (Fig. 1e and f), which is highly in agreement with the
observations from SEM images (Fig. 1c and d). The high-magnification TEM image
(Fig. 1g) demonstrates that the interplanar spacing of 0.24 and 0.25 nm agrees well
with the spacing of the (103) lattice plane of anatase TiO$_2$ (A) and (101) lattice plane
of rutile TiO$_2$ (R), respectively. The measured lattice spacing of 0.37 nm corresponds
to the (012) plane of hematite Fe$_2$O$_3$. Fig. 1h further demonstrates the single crystal
structure of Fe$_2$O$_3$ nanorods with the lattice spacing of d$_{110}$ = 0.25 nm. In addition,
there are some pores present in each Fe$_2$O$_3$ nanorod. The obtained hybrid
nanocomposites consist of porous nanofiber structures with a homogeneous
distribution of $\alpha$-Fe$_2$O$_3$ nanorods, which can not only shorten ion-transport distance, but also accelerate the redox reactions for photocatalytic degradation organic dyes.

Subsequently, by adjusting the amount of Fe sources, $\alpha$-Fe$_2$O$_3$/TiO$_2$-1, $\alpha$-Fe$_2$O$_3$/TiO$_2$-2 and $\alpha$-Fe$_2$O$_3$/TiO$_2$-4 were prepared as exhibited in Fig. 2. From Fig. 2, all samples also reveal the TiO$_2$ fibers networks combined with $\alpha$-Fe$_2$O$_3$ nanorods. Furthermore, with the increase of the amount of Fe sources, the surface of the composites becomes rougher and rougher derived from more $\alpha$-Fe$_2$O$_3$ nanorods with bigger size growing on. As shown in Fig. 2f, further increasing Fe sources, these $\alpha$-Fe$_2$O$_3$ nanorods tend to pyramidal structure about 200 nm in length of $\alpha$-Fe$_2$O$_3$/TiO$_2$-4.

XRD measurements were carried out to characterize the phase and crystal structures and the typical XRD patterns of the as-prepared materials are shown in Fig. 3. All the diffraction peaks can be indexed to anatase TiO$_2$ (JCPDS No. 73-1764), rutile TiO$_2$ (JCPDS No. 73-1765) and hematite $\alpha$-Fe$_2$O$_3$ (JCPDS No. 89-0597). No other impurity diffraction peaks are discovered, which confirms the purity of the product. Moreover, with the increase of Fe sources, the diffractions of hematite increase as well due to the more $\alpha$-Fe$_2$O$_3$ nanorods with bigger size growth. Thus, it is confirmed that the successful synthesis of $\alpha$-Fe$_2$O$_3$/TiO$_2$ heterostructure.

The chemical composition of $\alpha$-Fe$_2$O$_3$/TiO$_2$-3 was further investigated by the XPS technique. Fig 4a shows the survey-scan XPS spectra of $\alpha$-Fe$_2$O$_3$/TiO$_2$, and the chemical binding energies of C 1s, O 1s, Fe 2p, and Ti 2p suggest the present O, Fe, and Ti elements, while the carbon peak originated from the adventitious carbon
(below 0.9 wt % from TG). The high-resolution XPS spectrum of Ti 2p shows that the
binding energies of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ (Fig. 4b) were located at 458.66 and 463.8 eV,
which matched well with the typical binding energy values of TiO$_2$. The binding
energy situated around 710.77 and 723.86 eV correspond to Fe 2p$_{3/2}$ and Fe2p$_{1/2}$ of
Fe$_2$O$_3$, with the satellite peak at 718.57 eV which corresponds to Fe$^{3+}$ in α-Fe$_2$O$_3$ (Fig.
4c). The O 1s spectrum can be deconvoluted into peaks located at 529.74 eV and
531.27 eV (Fig. 4d), which are mainly attributed to crystal oxygen in the lattice, i.e.,
oxygen atoms that are bound to iron (Fe-O) and titanium (Ti-O). XPS analysis further
demonstrates the successful preparation of α-Fe$_2$O$_3$/TiO$_2$ nanocomposite.

In addition, N$_2$ adsorption/desorption analysis was applied to determine the
porous structure of these α-Fe$_2$O$_3$/TiO$_2$ composites and TiO$_2$ nanofibers. The
adsorption/desorption isotherm and the corresponding BJH pore diameter distribution
curves of above five samples are presented in Fig. 5. From Fig. 5a, with the increase
of the pressure, the adsorption amount increases obviously. All the isotherms can be
ascribed to the typical H3 hysteresis loops, implying the accumulative porous
structure of the samples. From Fig. 5b, all samples reveal wide pore size distribution
that is because it is difficult for accumulation pore to possess the uniform pore size.
The increase of Fe source, the macropore about 10-30 nm in size is present derived
from α-Fe$_2$O$_3$ nanorods deposition. With various porous structures, all samples show
the large average surface area about 20.4, 36.2, 42.8, 41.2, and 14.7 m$^2$/g for
α-Fe$_2$O$_3$/TiO$_2$-1, α-Fe$_2$O$_3$/TiO$_2$-2, α-Fe$_2$O$_3$/TiO$_2$-3, α-Fe$_2$O$_3$/TiO$_2$-4 and pure TiO$_2$
nanofibers, respectively (Table 1). α-Fe$_2$O$_3$/TiO$_2$s reveal the increased surface area
compared with pure TiO$_2$ nanofibers owing to the new surface derived from α-Fe$_2$O$_3$ nanorod deposition.

Fig. 6 shows the comparison of diffuse reflectance spectroscopy of single TiO$_2$, commercial Fe$_2$O$_3$ and α-Fe$_2$O$_3$/TiO$_2$ composites. The pure TiO$_2$ nanofibers present the typical absorption with an intense transition in the UV region, which could be assigned to the intrinsic band-gap absorption of TiO$_2$ (3.0, 3.2 eV). However, α-Fe$_2$O$_3$/TiO$_2$ should show enhanced absorption in the visible light region due to the visible sensitive component α-Fe$_2$O$_3$ (2.0–2.2 eV). The band gap energies estimated from the intercept of the tangents to the plots are 3.2 and 2.0 eV for the pure TiO$_2$ nanofibers and α-Fe$_2$O$_3$, agreeing well with the theoretical value. The band gap energy of the α-Fe$_2$O$_3$/TiO$_2$ nanocomposites can be confirmed by roughly comparing to the plot in Fig. 6b, which is obtained via the transformation based on the Kubelka–Munk function ($F(R) = (1 - R)^2/(2R)$, where $R =$ reflectance with the reflectance at 1000 nm set at 100%). And α-Fe$_2$O$_3$/TiO$_2$ complex reveal the decreased band gap energy (2.0-2.06 eV). With the more α-Fe$_2$O$_3$ deposition, the lower band gap energy can be found. The enhanced absorption in the visible light region of these α-Fe$_2$O$_3$/TiO$_2$ heterostructure is expected to induce the improved photocatalysis under visible light irradiation.

To demonstrate the photocatalytic activity of the as-synthesized samples toward organic dye pollutants, these α-Fe$_2$O$_3$/TiO$_2$ composites were adopted as the catalysts and the photocatalytic degradation tests toward CR were carried out. Fig. S1a-f present the absorption spectra of CR aqueous solution (initial concentration is 10
mg/L) in the presence of the samples under exposure to visible light for different durations. With the increase of the irradiation time, the absorption peak corresponding to CR at 498 nm diminishes gradually, testifying the degradation of CR. And the degradation rate curves are summarized in Fig. 7a. It takes 160, 160, 30, and 80 min for α-Fe₂O₃/TiO₂-1, α-Fe₂O₃/TiO₂-2, α-Fe₂O₃/TiO₂-3, and α-Fe₂O₃/TiO₂-4 to decolor about 77.2, 92.6, 95.1 and 94.1 % CR, respectively. In addition, the photocatalysis of TiO₂ nanofibers and commercial Fe₂O₃ towards CR also was investigated as contrast. As shown in Fig. S1e, under visible light irradiation for 160 min, merely 29.5 % of CR is decomposed by using the TiO₂ nanofibers as the photocatalyst. And pure Fe₂O₃ also reveals the degradation rate of 31.0 % toward CR at 160 min. From Fig. 7, α-Fe₂O₃/TiO₂ heterostructures reveal the improved visible light degradation capacity than the pure TiO₂ and Fe₂O₃. α-Fe₂O₃/TiO₂-3 exhibits the highest photocatalytic ability.

To further demonstrate the degradation process, the photocatalytic degradation kinetic was also investigated. The linear simulation of degradation of dye concentration can be accounted for by a pseudo first-order model, just so called the Langmuir-Hinshelwood (L-H) model. The L-H model is well established for heterogeneous photocatalysts (at low dye concentration). The relevant equation is as below:

\[ \frac{dC}{dt} = -k'C/1 + KC \]

(1)
Where \( r \) is the rate of dye mineralization, \( k' \) is the rate constant, \( C \) is the dye concentration, and \( K \) is the adsorption coefficient. By integration, eqn (1) can be arranged into the following:

\[
\ln\left(\frac{C}{C_0}\right) = -kt
\]

Where \( C_0 \) is the initial concentration of the dye solution and \( k \) is a rate constant. According to eqn (2), rate constant \( k \) can be given by the slope of fitting curves, when plotting \( \ln(C/C_0) \) against. We are able to find out \( k \) from the gradient of the graph of \( \ln(C/C_0) \) versus time (t) which is shown in Fig. 7b. All samples exhibit the good linear relationship between \( \ln(C/C_0) \) and irradiation time t. From Fig. 7b, TiO\(_2\) nanofibers displays lower rate constant \( k = 0.00160 \text{ min}^{-1} \) that is because pure TiO\(_2\) needs UV light to generate photogenerated electron-hole pairs to make sure the photodegradation. After the combination with \( \alpha\)-Fe\(_2\)O\(_3\), \( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\) heterostructures possess the enhanced degradative rate constant as well as the photocatalysis ability owing to the improved the utilization of visible light. \( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-1 displays rate constant \( k=0.00637 \text{ min}^{-1} \) more than TiO\(_2\) nanofibers. As displayed in Fig. 6, with the increase of \( \alpha\)-Fe\(_2\)O\(_3\) the absorption of visible light is enhanced, so that \( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-2 and \( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-3 possesses the improved rate constant \( k = 0.01076 \) and 0.04336 min\(^{-1}\). Further increasing of \( \alpha\)-Fe\(_2\)O\(_3\), the rate constant of \( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-4 decreases to \( k=0.0158 \text{ min}^{-1} \) that is caused by its decreased surface area/pore volume. The photocatalytic reactivity order is \( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-3>\( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-4>\( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-2>\( \alpha\)-Fe\(_2\)O\(_3\)/TiO\(_2\)-1> TiO\(_2\) nanofibers >commercial Fe\(_2\)O\(_3\). Based on the above investigation, the enhanced
visible light catalysis efficiency of $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$ is ascribed to: 1) the improved visible light utilization owing to the doping of visible sensitive $\alpha$-$\text{Fe}_2\text{O}_3$. 2) The spatial transfers of the visible-excited energetic electrons from $\alpha$-$\text{Fe}_2\text{O}_3$ to TiO$_2$ in favorable to promote the separation and to prolong the lifetime of photogenerated charge carriers. 3) The decreased charge transportation resistance of the heterojunction interface. 4) The high surface area and pore volume derived from the novel branch-like heterostructure that is benefit of the dyes toward the surface of the catalyst to enhance the degradation. The fastest degradation ability of $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$-3 is derived from the largest surface area (42.8 cm$^2$/g) and appropriate content of the two components.

Considering the excellent performance of $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$-3 on dye decomposition, photocatalytic degradation activities of $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$-3 heterostructure to ER, MB, and MO dyes were also investigated. Fig. S2a-c displays the UV/Vis absorption spectra of dyes in the presence of $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$-3 heterostructure under visible light at different time intervals. From Fig. S2a-c, it is clearly seen that the absorption peaks corresponding to dyes diminish gradually with the illumination time prolonged, implying the degradation of dyes. And the photocatalytic activities of $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$-3 toward the four dyes are summarized in Fig.8. As exhibited in Fig. 8, $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$-3 reveals the fastest degradation toward CR, about 95.1 % decolored efficiency in 30 min. At the same time, just about 76.7 % ER and 15.3 % MB is degraded. And after 90 and 160 min irradiation, degradation percentage reaches 98.4 % and 67.6 % for ER and MB, respectively. However, it displayed the poor degradation evolution of MO
(1.1%, 160 min). It is known that, the high adsorption capacity benefits for the dye molecules close to the catalyst and always induces the enhanced the degradation rate.

41 From Fig.8, after the dark treatment, α-Fe₂O₃/TiO₂-3 reveals about 80.3, 35.0, 0.5 and 0.9 % adsorption amount for CR, ER MB and MO. Thus it is believed that the fastest degradation to CR can be ascribed to the highest adsorption capacity. Based on the previous reports, the adsorption capacity would be ascribed to the interaction and structure/size matching between the adsorbent and the adsorbate. It is known to all that, CR is a typical anionic dye that would possess the strong electrostatic interaction with α-Fe₂O₃/TiO₂-3 (Zeta potential: 2.50 ± 1.57 mV). Furthermore, the 1D fiber structures always reveal the high adsorption capacity to 1D long-chain dye, such as CR, so α-Fe₂O₃/TiO₂-3 exhibits the highest adsorption ability to CR. 42 However, the decreased adsorption capacity to the other anionic dye ER due to the low structure matching between the 2D planar molecular structure of ER and the 1D α-Fe₂O₃/TiO₂-3 nanofibers (with the slit pore). As shown in Fig.8, α-Fe₂O₃/TiO₂-3 displays the faster degradation rate of ER than that of MB and MO, the fast degradation rate of ER makes 98.4% degradation within 90 min irradiation.

To further investigate photo-degradation of α-Fe₂O₃/TiO₂-3 toward CR, various CR solutions (10-50 mg/L) were further used to demonstrate the adsorption and degradation activity of α-Fe₂O₃/TiO₂-3. As shown in Fig. S3a-d, it costs 30, 160, 160, 160 and 160 min for α-Fe₂O₃/TiO₂-3 to decompose about 95.1 % (10 mg/L), 81.5 % (20 mg/L), 63.7 % (30 mg/L), 54.9 % (40 mg/L) and 47.0 % (50 mg/L) CR, respectively. And the equilibrium adsorption isotherm (dark treatment) of
α-Fe₂O₃/TiO₂-3 to CR solution was calculated as exhibited in Fig. 9a. With the increase of the dye concentration, the adsorption amount increases dramatically until the adsorption reaches saturation (47.9 mg/g) that is a rather high adsorption amount. Furthermore, as revealed in Fig. 9a, the adsorption isotherm belongs to a type I curve, characteristic of a Langmuir isotherm. And the experimental equilibrium adsorption of dye on the sample was also analyzed by fitting the equilibrium adsorption data using the Langmuir equation:

\[
\frac{c_e}{q_e} = \frac{1}{q_m k} + \frac{c_e}{q_m}
\]

Where \(q_m\) is the theoretical maximum monolayer adsorption capacity (mg/g), \(k\) is the Langmuir constant, \(c_e\) is equilibrium concentration, and \(q_e\) is the equilibrium adsorption amount (mg/g). The corresponding linear Langmuir transform of the isotherm is exhibited in the Fig. 9a inset. From Fig. 9a inset, the adsorption behavior displays a good linear Langmuir relationship with the theoretical maximum adsorption values (\(q_m = 48.47\) mg/g) close to the experimental capacity (47.9 mg/g). The good Langmuir adsorption relationship between CR and α-Fe₂O₃/TiO₂-3 associated with the high adsorption amount are expected to bring up the enhanced degradation capability. To visualize the degradation capability of α-Fe₂O₃/TiO₂-3 to CR, the variation of the degradation capability (dye/catalyst, mg/g) to degradation time was recorded as displayed in Fig. 9b. α-Fe₂O₃/TiO₂-3 displays 38.04 mg/g degradation capability for 10 mg/L CR under irradiation for 30 min. As increasing the CR concentration to 50 mg/L, the degradation capability increases to 94.0 mg/g after
160 min exposed in visible light. The high adsorption capacity benefits the dye molecules to be adsorbed on to the surface of the catalyst to enhance the photocatalysis performance. With the great decoloration capability, $\alpha$-Fe$_2$O$_3$/TiO$_2$-3 is expected to possess the potential application on dye adsorption.

The 400 cut-off filter was used to make sure the irradiation wavelength is above 400 nm which can excite the electrons from the valence band (VB) of Fe$_2$O$_3$ to the different energy-level conduction band (CB), including the high-energy region (-0.16 eV to -1.0 eV/potential) and low energy region (0.1 eV to-0.16 eV/potential). In the high-energy region, some of the photogenerated electrons with the higher energy level than the CB position of TiO$_2$ (-0.16 eV/potential) could thermodynamically transfer to the CB of TiO$_2$ (Fig. 10), while photogenerated holes accumulated in the valence band of Fe$_2$O$_3$. The negative electrons in the valence band of TiO$_2$ will further react with molecular oxygen O$_2$ dissolved in the CR solution to form the superoxide anion O$_2^-$ and hydrogen peroxide H$_2$O$_2$. While the accumulated holes in the valence band of Fe$_2$O$_3$ will react with OH$^-$ species existing on the surface of the catalyst, producing reactive hydroxyl radicals (·OH). The reactions can be described as follows:

$$\begin{align*}
\text{Fe}^{3+} + h\nu & \rightarrow \text{Fe}^{2+} + \text{Fe}^{4+} + (h_{vb}^+ + e_{cb}^-) \\
\text{Ti}^{4+} + e_{cb}^- & \rightarrow \text{Ti}^{3+} \\
e_{vb}^-(\text{Ti}^{3+}) + \text{O}_2 & \rightarrow \text{O}_2^- \\
h_{vb}^+(\text{Fe}^{4+}) + \text{OH}^- & \rightarrow \cdot\text{OH} \\
\text{OH}^- + \text{dyes} & \rightarrow \text{degraded products}
\end{align*}$$

It is known that many dye molecules also can absorb a certain visible light, so that the contribution of the dye excitation to the photodegradation also should be considered. First, these dye molecules were excited from the ground state (Dye) to the
triplet excited state (Dye*) under the visible irradiation. This excited state dye species is further converted into a semi-oxidized radial cation (Dye⁺) by an electron injection into the conduction band of TiO₂. Due to reaction between these trapped electrons and dissolved oxygen in the system superoxide radical anions (O₂⁻) are formed which in turn result into hydroxyl radicals (·OH) formation. These ·OH radicals are mainly responsible for the oxidation of the organic compounds represented by the equations.

\[
\text{dye} + h\gamma \rightarrow \text{dye}^* \\
\text{dye}^* + \text{TiO}_2 \rightarrow \text{dye}^{\cdot} + \text{TiO}_2^{-}
\]

According to the previous investigation, the contribution of dye-sensitization to dye degradation is much lower than the visible light initiated mechanism.⁴⁸⁻⁵¹

And the radicals (·OH) measurement was carried out to study on charge separation efficiency. Herein, the coumarin (C₉H₆O₂) fluorescent method is utilized to detect the amount of ·OH, in which the introduced coumarin could easily react with ·OH to produce luminescent 7-hydroxy-coumarin. Fig.11 α-Fe₂O₃/TiO₂-3 shows the strongest fluorescent response at 449 nm, implying the most ·OH generation. In addition, these results are consistent with the photodegradation performance as displayed in Fig. 7. Thus, in this paper it is believed that the high visible adsorption and prolonged separation of the photogenerated electron/hole induce the excellent performance on visible light degradation.⁴²

The recyclable photocatalytic degradation results of CR in the presence of α-Fe₂O₃/TiO₂-3 heterostructure for the 1st, 2nd, 3rd, 4th and 5th cycle are illustrated in Fig.12. It is noted that even after 5 cycles, α-Fe₂O₃/TiO₂-3 heterostructure also
reveals 90% purification for CR solution (10 mg/L), indicating that α-Fe₂O₃/TiO₂-3 heterostructure can be used as a recyclable catalyst for the degradation of CR under visible light irradiation.

4. Conclusions

In summary, we report the synthesis of α-Fe₂O₃/TiO₂ with hierarchical branched structure by a two-step process (electrospinning and hydrothermal approach). MB, MO, CR, and ER were adopted as the model dyes and the photocatalytic tests were carried out in detail. All α-Fe₂O₃/TiO₂ heterostructures reveal the enhanced visible light degradation ability owing to the improved visible light adsorption and separation of photogenerated electrons-holes. Especially, α-Fe₂O₃/TiO₂-3 possesses the most efficient decoloration capacity (94.0 mg/g) to CR even at the high concentration (50 mg/L), attributing to the high surface area (42.8 m²/g), appropriate proportion of the two components, and the interaction/structural matching of catalyst and dye molecule. The above factors should be paid great attentions on the design and synthesis of other highly efficient visible-light photocatalysts. What more, the developed strategy would provide us with a simple and feasible route to greatly improve the photocatalytic performance of visible-response nano-semiconductors.

Acknowledgments

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References


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Scheme 1

Electrospinning → Precursor solution → Calcination → Primary fibers → TiO$_2$ Nanofibers → Hydrothermal Growth → α-Fe$_2$O$_3$ /TiO$_2$ Nanostructure
Fig. 1
Fig. 2
Fig. 3

![Graph showing X-ray diffraction patterns for different samples.](image)

- **A**: Anatase
- **R**: Rutile
- **H**: Hematite

Graph legend:
- **H(102)**: Hematite peak
- **A(101)**: Anatase peak
- **R(110)**: Rutile peak

Graph data:
- Sample (a): \(\alpha-\text{Fe}_2\text{O}_3/\text{TiO}_2\) - 1
- Sample (b): \(\alpha-\text{Fe}_2\text{O}_3/\text{TiO}_2\) - 2
- Sample (c): \(\alpha-\text{Fe}_2\text{O}_3/\text{TiO}_2\) - 3
- Sample (d): \(\alpha-\text{Fe}_2\text{O}_3/\text{TiO}_2\) - 4

*2 Theta (degree)*

*Intensity (a.u.)*
Fig. 4
Fig. 5

(a) Volume absorbed (cm$^3$ g$^{-1}$) vs. Relative pressure ($P/P_0$)

(b) dV/dD vs. Pore size diameter (nm)

Legend:
- $\alpha$-Fe$_2$O$_3$/TiO$_2$-1
- $\alpha$-Fe$_2$O$_3$/TiO$_2$-2
- $\alpha$-Fe$_2$O$_3$/TiO$_2$-3
- $\alpha$-Fe$_2$O$_3$/TiO$_2$-4
- TiO$_2$ nanofibers
Fig. 6

(a) Absorbance (a.u.) vs. Wavelength (nm)

(b) F(R) vs. hν (eV)

- $\alpha$-Fe$_2$O$_3$/TiO$_2$:1
- $\alpha$-Fe$_2$O$_3$/TiO$_2$:2
- $\alpha$-Fe$_2$O$_3$/TiO$_2$:3
- $\alpha$-Fe$_2$O$_3$/TiO$_2$:4
- TiO$_2$ nanofibers
- Commercial Fe$_2$O$_3$
Fig. 7
Fig. 8
Fig. 9
Visible light (>400nm)

Fe$_2$O$_3$ TiO$_2$ nanofiber

OH ·OH

Fe$_2$O$_3$ TiO$_2$

Potential /eV

O$_2^-$

CB VB

Highest Level

O$_2$
Fig. 11
Fig. 12
Table 1 The porous parameters of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α- Fe₂O₃ /TiO₂-1</td>
<td>20.4±8.8</td>
<td>0.006±0.0007</td>
<td>3.44, 20.39</td>
</tr>
<tr>
<td>α- Fe₂O₃ /TiO₂-2</td>
<td>36.2±15.9</td>
<td>0.011±0.0012</td>
<td>3.44, 21.08</td>
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<tr>
<td>α- Fe₂O₃ /TiO₂-3</td>
<td>42.8±18.8</td>
<td>0.012±0.0017</td>
<td>2.12, 20.33</td>
</tr>
<tr>
<td>α- Fe₂O₃ /TiO₂-4</td>
<td>41.2±17.7</td>
<td>0.013±0.0021</td>
<td>3.48, 21.34</td>
</tr>
<tr>
<td>TiO₂ nanofibers</td>
<td>14.7±7.5</td>
<td>0.003±0.0007</td>
<td>1.71, 9.57</td>
</tr>
</tbody>
</table>

a,b: these data are calculated from three parallel assays.
Captions:

Scheme 1 The possible formation mechanism of α-Fe₂O₃/TiO₂ heterostructures.

Fig. 1 SEM images of the TiO₂ nanofibers (a) and α-Fe₂O₃/TiO₂-3 heterostructure (c, d). TEM images of TiO₂ nanofibers (b), TEM images (e, f) and the high-resolution TEM images (g, h) of α-Fe₂O₃/TiO₂-3.

Fig. 2 SEM images of α-Fe₂O₃/TiO₂-1 (a, d), α-Fe₂O₃/TiO₂-2 (b, e), and α-Fe₂O₃/TiO₂-4 (c, f).

Fig. 3 XRD patterns of the as-fabricated products: (a) α-Fe₂O₃/TiO₂-1, (b) α-Fe₂O₃/TiO₂-2, (c) α-Fe₂O₃/TiO₂-3 and (d) α-Fe₂O₃/TiO₂-4.

Fig. 4 Survey-scan XPS spectra α-Fe₂O₃/TiO₂-3 (a); XPS Ti 2p spectra (b); XPS Fe 2p spectra (c); XPS O 1s spectra (d).

Fig. 5 N₂ adsorption-desorption isotherm (a) and BJH pore size distribution (b) of the five samples.

Fig. 6 (a) The UV–Vis absorption spectra of α-Fe₂O₃/TiO₂-1, α-Fe₂O₃/TiO₂-2, α-Fe₂O₃/TiO₂-3, α-Fe₂O₃/TiO₂-4, TiO₂ nanofibers and commercial Fe₂O₃, (b) The corresponding F(R) versus hγ curves.

Fig. 7 (a) Photocatalysis degradation rate of all samples, (b) Kinetic linear simulation curves of Congo red photocatalytic degradation under the visible light.

Fig. 8 Photocatalysis degradation rate of all the dyes of the α-Fe₂O₃/TiO₂-3 heterostructure irradiated by a visible light for different time periods.

Fig. 9 (a) Effect of the initial dye concentration, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L, on the degradation capacity of the α-Fe₂O₃/TiO₂-3 heterostructure, and
the inset is the corresponding linear Langmuir transform of the isotherm; (b) variation of the degradation capability of the α- Fe$_2$O$_3$/TiO$_2$-3 (dye/catalyst, mg/g) to degradation time.

**Fig. 10** The schematic of interfacial charge carries generation, transfer, and separation between TiO$_2$ and Fe$_2$O$_3$ in the α- Fe$_2$O$_3$/TiO$_2$ heterostructure under the visible light.

**Fig. 11** The fluorescence spectra for the formed hydroxyl radicals under visible irradiation.

**Fig. 12** Cycling tests of photocatalytic activity of the α- Fe$_2$O$_3$/TiO$_2$-3 heterostructure for CR solution (10 mg/L) degradation.