Corn-like, recoverable $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ photocatalyst induced by magnetic dipole interactions

Fang Wang$^{1,3}$, Manhong Li$^{1,3}$, Lifang Yu$^{1,3}$, Fan Sun$^2$, Zhuliang Wang$^{4,3}$, Lifang Zhang$^1$, Hao Zeng$^2$ & Xiaohong Xu$^{1,3}$

Corn-like, $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ core/shell heterostructures were synthesized by a modified solvothermal reduction combined with a sol-gel method. SiO$_2$ shells were first deposited on monodisperse Fe$_2$O$_3$ microspheres by a sol-gel method. Fe$_2$O$_3$@SiO$_2$@TiO$_2$ corn-like heterostructures were then obtained by sequential TiO$_2$ coating, during which the magnetic dipolar interactions induced the anisotropic self-assembly process. After annealing at 350 °C, the crystalized TiO$_2$ enhanced photocatalytic activity, while Fe$_2$O$_3$ was converted to $\gamma$-Fe$_2$O$_3$. The corn-like $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ photocatalyst can be recycled and reused by magnet extraction. Despite the photocatalytic activity decreased with each cycle, it can be completely recovered by moderate heating at 200 °C.

Much effort has been devoted to environmental protection by degrading pollutants and developing new clean energy sources in recent years. TiO$_2$ is an attractive material for such applications due to its excellent electronic and optical properties, and high chemical and thermal stability$^{1-5}$. These features make it useful for photocatalytic decomposition of pollutants$^{6-8}$, dye-sensitized solar cells$^{9-11}$, and photochemical water splitting$^{4,5,12}$. Most research focuses on extending the range of its absorption spectrum and thus improving its photocatalytic efficiency$^{3,13,14}$, while their recyclability issue has been scarcely addressed. Typically, aqueous suspensions of TiO$_2$ nanoparticles employed for most of the photocatalytic reactions are difficult to separate and recycle. Because of this, catalyst immobilization has been proposed to recycle the catalysts. For example, researchers have studied TiO$_2$ immobilization over various inactive supports such as glass, quartz and stainless steel substrates$^{15,16}$. However, the photocatalytic activity would be decreased significantly due to the immobilization, which reduces the active surface area for photocatalysis$^{17}$. Therefore, there is a need to develop a multi-functional photocatalytic system with high photoactivity and recyclability.

Recently, magnetic targeting and magnetic recycling technologies were widely used in biomedical$^{18-22}$ and catalysis fields$^{23-25}$. This is realized by employing functional composite materials with a magnetic component, which make them separable in an external magnetic field. Moreover, the dipole interaction can induce particle aggregation to form chain-like structures$^{26-30}$. Butter et al. have directly observed the dipolar chains in iron ferrofluids by cryogenic electron microscopy without applying a magnetic field$^{31}$. Moreover, the dipole-dipole interactions depend on the magnetic particle size and coating molecules$^{27,28}$. Zhang et al. reported that the particle chain length could be effectively adjusted by the intensity of the magnetic field in the range of micrometers and the packing of Fe$_3$O$_4$ microspheres (~150 nm) in the chains became tighter with increasing field strength$^{29}$. Therefore, an effective and repeatable assembly of magnetic chains is a significant step toward realizing their potential applications spreading from nano-scale electronic devices, sensors and high-density data storage media to controlled drug delivery and cancer diagnostics/treatment systems$^{30}$.

Up to now, many types of magnetic photocatalysts have been synthesized, such as $\gamma$-Fe$_2$O$_3@$SnO$_2$$^{31}$, Fe$_3$O$_4@$TiO$_2@$Ag$^{32}$, Fe$_3$O$_4@$TiO$_2$$^{33,34}$, bean-like core/shell Fe$_2$O$_3@$Cu$_2$O$^{35}$, $\alpha$-Fe$_2$O$_3@$TiO$_2$$^{36}$ and $\alpha$-Fe$_2$O$_3$/Ag/SnO$_2$$^{37}$ photocatalysts have also been reported. Here the antiferromagnetic $\alpha$-Fe$_2$O$_3$ primarily acts as a visible-light photocatalyst due to its narrow band gap (2.2 eV). On the other hand, ferrimagnetic Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ with relatively...
high magnetization are chosen as magnetic cores in magnetically separable photocatalysts. It is reported by Li et al. that the direct contact between magnetic Fe₃O₄ and TiO₂ photocatalyst usually results in an increase in electron-hole recombination and photodissolution. In order to overcome the problem of charge recombination, mesoporous TiO₂/SiO₂/Fe₂O₃ hybrid nanoparticles with γ-Fe₂O₃ fine particles dispersed in a TiO₂ matrix, and γ-Fe₂O₃@SiO₂ composite microspheres with SiO₂ barrier layers were synthesized. Compared with Fe₃O₄@TiO₂, the insert of SiO₂ shell between γ-Fe₂O₃ core and TiO₂ shell exhibits two positive effects to enhance the photocatalytic activity. One is to block the electron injection from TiO₂ to γ-Fe₂O₃ at the interface, the other is to provide a porous surface with large surface-to-volume ratio for catalytic reactions. However, the photogenerated electrons can still transfer if the thickness of the SiO₂ is less than 5 nm. Therefore, the thickness of SiO₂ is a key factor responsible for the photocatalytic performance of iron oxide/SiO₂/semiconductor systems. While most works focus on the recoverability of magnetic core-shell photocatalysts, surprisingly little has been reported on the regeneration and reuse of such photocatalysts.

Here, we report the synthesis and characterization of a corn-like, anisotropic γ-Fe₂O₃@SiO₂@TiO₂ heterostructure. The formation mechanism of the anisotropic heterostructure is proposed, revealing the importance of magnetostatic interaction as a tuning knob for morphological control. The heterostructure demonstrates photocatalytic activity for degradation of Rhodamine B and can be magnetically recycled and reused. Moreover, the lost photocatalytic activity of the used γ-Fe₂O₃@SiO₂@TiO₂ heterostructure can be fully recovered by heating at 200 °C for 30 min. Such magnetically recyclable, easily regenerated γ-Fe₂O₃@SiO₂@TiO₂ composite provides a design paradigm for low cost photocatalysts for renewable energy and environmental applications.

Results and Discussion

Structural and morphology characterizations. Figure 1 shows the XRD patterns of Fe₃O₄, Fe₃O₄@SiO₂@TiO₂ heterostructures before and after annealing. For the Fe₃O₄ microspheres, the characteristic XRD peaks of magnetite with inverse spinel structure were observed, indicating that Fe₃O₄ phase is obtained by the solvothermal method. However, a minor amount of γ-Fe₂O₃ was present in the microspheres. As-synthesized Fe₃O₄@SiO₂@TiO₂ shows only the similar peaks of Fe₃O₄ microspheres without any characteristic peaks of SiO₂ and TiO₂. In contrast, when Fe₃O₄@SiO₂@TiO₂ was annealed at 350 °C for 2 h in air, a clear XRD peak at 25.5° corresponding to the (101) crystal planes of anatase TiO₂ emerged. Meanwhile, a weak TiO₂ (200) was also observed after annealing. Thus, TiO₂ should be an amorphous phase in the as-synthesized Fe₃O₄@SiO₂@TiO₂ composite. As for SiO₂, no XRD peaks is seen after annealing at 350 °C for 2 h, suggesting that it remains amorphous despite the heat treatment. However, all the original peaks of Fe₃O₄ show a shift to higher 2θ values, which correspond to the peaks of γ-Fe₂O₃. Moreover, the change in color of the heterostructures from black to brownish-red also suggests the oxidation of Fe₃O₄ into γ-Fe₂O₃. Thus, γ-Fe₂O₃@SiO₂@TiO₂ heterostructures can be obtained by such heat treatment in air.
In order to further confirm the coating of SiO$_2$ and oxidation of Fe$_3$O$_4$, the elemental and valence state analysis were performed using XPS. Here the chemical states of the constituent elements were calibrated by C 1$s$ peak (284.6 eV). Figure 2(a) shows the survey scan XPS spectrum of $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$, which contains O 1$s$, Ti 2$p$, Si 2$p$ and Si 2$s$ peaks. This indicates the existence of SiO$_2$ and TiO$_2$ in $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ heterostructure. Figures 2(b) and (c) show the core-level XPS spectra of Fe 2$p$ in Fe$_3$O$_4$ microspheres and $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ heterostructures, respectively. For the Fe$_3$O$_4$ in Fig. 2(b), the main-peaks located at 711.0 eV and 724.6 eV are attributed to Fe$^{3+}$ 2$p_{3/2}$ and Fe$^{3+}$ 2$p_{1/2}$, respectively. However, there is a significant asymmetry for both of them. A double peak fitting yields peak positions at 709.3 eV and 722.5 eV, which belong to Fe$^{2+}$ 2$p_{3/2}$ and Fe$^{2+}$ 2$p_{1/2}$, respectively. These results are in agreement with the reported Fe 2$p$ XPS spectrum of Fe$_3$O$_4$. In addition, the area ratio of Fe$^{3+}$/Fe$^{2+}$ is about 3.6, which deviates from the stoichiometry of Fe$_3$O$_4$. Such a deviation indicates that Fe$^{2+}$ ions have been partially oxidized to Fe$^{3+}$ ions, which is in agreement with the XRD results in Fig. 1, which show trace amount of $\gamma$-Fe$_2$O$_3$. Here the FeO$_x$ can reflect the coexistence of Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$. As for the Fe 2$p$ core-level XPS spectrum of $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ [Fig. 2(c)], it presents only the peaks of Fe$^{3+}$ at 710.8 eV and 724.7 eV. But, it is hard to observe the peak of Fe$^{2+}$ at about 709.0 eV and 723 eV. Such results suggest that Fe$_3$O$_4$ in the Fe$_3$O$_4$@SiO$_2$@TiO$_2$ heterostructure has been oxidized to $\gamma$-Fe$_2$O$_3$ after annealing at 350°C for 2 h in air. The difference in color further provides the evidence for oxidation.

Figure 3 shows the SEM images of Fe$_3$O$_4$ microspheres synthesized by different surfactants and $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ corn-like heterostructures. As seen from Fig. 3(a)–(c), the surfactants play an important role in controlling the surface morphology of Fe$_3$O$_4$ microspheres. For the ED surfactant, it can be seen that the spherical morphology is not completely formed, and Fe$_3$O$_4$ shows some irregular shape [Fig. 3(a)]. When PEG is chosen as the surfactant, Fe$_3$O$_4$ microspheres with a smooth surface can be obtained [Fig. 3(b)]. On the other hand, as NaPAA is chosen as the surfactant, the Fe$_3$O$_4$ microspheres demonstrate rough surface. The surface consists of uniformly sized nanoparticles, and the mean diameter of the microspheres is about 450 nm [Fig. 3(c)]. These well-dispersed, rough Fe$_3$O$_4$ microspheres with large surface-to-volume ratio were chosen as templates for coating the SiO$_2$ coupling layer and subsequently the TiO$_2$ functional shell. It can be seen from Fig. 3(d)–(f) that $\gamma$-Fe$_2$O$_3$@SiO$_2$@TiO$_2$ shows anisotropic corn-like structure after TiO$_2$ coating. The discrete Fe$_3$O$_4$ microspheres are now linked by the SiO$_2$/TiO$_2$ coating to self-assemble into corn-like heterostructures with length exceeding 10 μm. The newly formed TiO$_2$ shell is uniformly coated onto the magnetic Fe$_3$O$_4$ core, leading to a smoother surface than that of the starting Fe$_3$O$_4$ microspheres. Interestingly, this corn-like heterostructure is only found after coating with TiO$_2$ shell, while not observed in the Fe$_3$O$_4$@SiO$_2$ composite. Therefore, the TiO$_2$ shell should play a crucial role in forming the corn-like heterostructure.
In order to reveal the structural characteristics of corn-like Fe₃O₄@SiO₂@TiO₂ heterostructure, HRTEM images were done on Fe₃O₄ and Fe₃O₄@SiO₂@TiO₂ before and after annealing. As seen from Fig. 4(a), the diameter of Fe₃O₄ is about 450 nm, and Fe₃O₄ porous microspheres possess a hierarchical structure consisting of densely packed nanoparticles with sizes of about 20 nm. Such morphology is beneficial for the subsequent surface coating. In Fig. 4(b), the uniform SiO₂ and TiO₂ shells are coated on Fe₃O₄ spheres to form one-dimensional chain-like...
Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@TiO\textsubscript{2} structures, which act as basic units to assemble into corn-like heterostructures. As shown in Fig. 4(c), one can clearly distinguish SiO\textsubscript{2} and TiO\textsubscript{2} shells from Fe\textsubscript{3}O\textsubscript{4} cores in the as-prepared Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@TiO\textsubscript{2} microspheres. The thickness of SiO\textsubscript{2} and TiO\textsubscript{2} shells are close to 60 nm and 15 nm, respectively. The 60 nm SiO\textsubscript{2} shell can not only act as a coupling layer for TiO\textsubscript{2} coating, but also preserve the photocatalytic activity of TiO\textsubscript{2} by inhibiting the electron transfer between the magnetic core and TiO\textsubscript{2} shell. After annealing, the chain-like structural unit and a thinner TiO\textsubscript{2} shell can be clearly observed in Fig. 4(d) and (e). Furthermore, the (103) and (200) lattice fringes of anatase TiO\textsubscript{2} shown in Fig. 4(f) indicates that the TiO\textsubscript{2} shell has been well-crystallized. This is in agreement with the XRD results of \textgamma-Fe\textsubscript{2}O\textsubscript{3}@SiO\textsubscript{2}@TiO\textsubscript{2} (Fig. 1). The average grain size of TiO\textsubscript{2} is about 5 nm.

**Magnetic properties.** The room temperature magnetic properties of Fe\textsubscript{3}O\textsubscript{4} microspheres, corn-like Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@TiO\textsubscript{2} and \textgamma-Fe\textsubscript{2}O\textsubscript{3}@SiO\textsubscript{2}@TiO\textsubscript{2} heterostructures are shown in Fig. 5. Fe\textsubscript{3}O\textsubscript{4} microspheres have a saturation magnetization (\textit{M}_s) of about 58 emu/g. After coating of SiO\textsubscript{2} and TiO\textsubscript{2} shells, \textit{M}_s of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@TiO\textsubscript{2} heterostructure decreases to 45 emu/g due to the increased volume fraction of nonmagnetic materials. After annealing at 350 °C for 2 h in air, \textit{M}_s of the \textgamma-Fe\textsubscript{2}O\textsubscript{3}@SiO\textsubscript{2}@TiO\textsubscript{2} heterostructure is further reduced to 37 emu/g, which is about 18% lower than that of Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@TiO\textsubscript{2}. Such reduction in \textit{M}_s is mainly due to the lower \textit{M}_s of \textgamma-Fe\textsubscript{2}O\textsubscript{3} than that of Fe\textsubscript{3}O\textsubscript{4}. Nevertheless, the anisotropic corn-like heterostructures respond strongly to an external magnetic field, and can be efficiently extracted, as shown in the upper left inset. Such efficient separation is necessary for recyclable photocatalysts. For example, the collection time of 0.1 g \textgamma-Fe\textsubscript{2}O\textsubscript{3}@SiO\textsubscript{2}@TiO\textsubscript{2} in 20 ml ethanol is less than 10 seconds.

As seen from the lower right inset of Fig. 5, the isolated Fe\textsubscript{3}O\textsubscript{4} microspheres show typical ferrimagnetic behavior but with insignificant remanent magnetization (\textit{M}_r). The low \textit{M}_r is attributed to the multi-domain structure of the 450 nm-sized microspheres with small anisotropy. However, a higher \textit{M}_r of about 5 emu/g is found for Fe\textsubscript{3}O\textsubscript{4}@ SiO\textsubscript{2}@TiO\textsubscript{2} which changes very little after annealing. The enhanced remanent magnetization of the heterostructure, on the other hand, is due to the formation of the anisotropic shape. As will be further discussed below, it is the magnetic dipole interactions between the microspheres lead to their self-assembly into chain-like structures and further corn-like heterostructure; while the chain formation in turn changes the magnetic behavior of the heterostructure. In the chain-like unit of the heterostructure, when the magnetization lies along the chain, there is a reduction of the stray field. This effective shape anisotropy results in the magnetic easy axis to lie along the chain. While this anisotropy is generally not large, it does increase both the remanent magnetization and coercivity of the assembly. Upon annealing, Fe\textsubscript{3}O\textsubscript{4} is oxidized into \textgamma-Fe\textsubscript{2}O\textsubscript{3} with higher magnetocrystalline anisotropy, which further increases the coercivity of the \textgamma-Fe\textsubscript{2}O\textsubscript{3}@SiO\textsubscript{2}@TiO\textsubscript{2} corn-like assembly. The enhanced remanence is responsible for the enhanced magnetic recyclability under weak magnetic fields.

**Formation mechanism.** It is interesting to note that the corn-like heterostructure is formed only in the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@TiO\textsubscript{2}, while in neither the Fe\textsubscript{3}O\textsubscript{4} microspheres nor the Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} core-shell structures. The chain-like structure is the basic component of these corn-like heterostructures. The formation is primarily a consequence of the competition between the magnetic dipole interactions, which favor chain-formation, and Brownian motion, which tends to randomize the assembly. We propose the following formation mechanism, as shown schematically in Fig. 6. During the first stage of synthesis [Fig. 6(a)], each isolated Fe\textsubscript{3}O\textsubscript{4} microspheres can be regarded as a magnetic dipole. The dipole-dipole interactions between the microspheres tend to arrange the particles head-to-tail, forming a linear chain. However, the dipole moment in each microsphere is relatively...
small, due to the multidomain configuration. The random Brownian motion thus disrupts the chain formation. Moreover, the NaPAA ligand exerts steric forces, increasing the spacing between Fe₃O₄ microspheres, further reducing the dipole interactions. Therefore, Fe₃O₄ microspheres are dispersed as isolated entities at this stage. After SiO₂ coating, the core/shell Fe₃O₄@SiO₂ still maintains good dispersibility due to the long-chain capping groups of TEOS precursor on the microspheres [Fig. 6(b)]⁴⁴. However, during the TiO₂ coating, the TiO₂ colloidal sol caused by the hydrolysis of TTIP fill in the voids between Fe₃O₄@SiO₂ microspheres, acting as a binder to fuse the neighboring microspheres. Once a Fe₃O₄@SiO₂ dimer is formed, the symmetry is broken, and the axis along the dimer defines the magnetic easy axis, as shown in Fig. 6(c). The magnetization now tends to align along the dimer axis, increasing the effective dipole moment of the dimer. It is now energetically more favorable to connect more particles head-to-tail along the long axis to form a linear chain [Fig. 6(d)]. Thus, the chain-formation is a self-assembly process induced by magnetic dipole interactions, and assisted by the fusing effect of the TiO₂ shell. Klokkenburg et al. first directly observed this dipolar chain formation in zero fields in a ferrofluid containing the largest synthetic single-domain magnetite particles⁴⁵. The dipole-dipole interactions induced the anisotropic features, favoring a head-to-tail orientation. Moreover, Zhang et al. found that the Fe₃O₄ nanoparticles can self-assemble into one-dimensional chains in a colloidal dispersion through magnetic dipolar interaction without the help of an applied magnetic field⁴⁶. As more chains are nucleated in the solution, when they touch by random motion, they tend to align side-by-side. This is akin to two bar magnets sticking together by aligning their north- and south- poles in opposite directions for flux closure to minimize magnetostatic interactions [Fig. 6(e)]. The flux closure is in Co particles simulated by Chantrell et al.⁴⁷ We postulate that with increase in the numbers of chains, they order into tight bundles, forming corn-like heterostructures as depicted in the SEM image of Fig. 6. Moreover, the formation of corn-like heterostructures may be aided by Van der Waals interactions between the chains, as was reported in Fe₃C microfiber assemblies⁴⁸.

**Photocatalytic and magnetic recovery properties.** The photocatalytic activity of Fe₃O₄, corn-like Fe₃O₄@SiO₂@TiO₂ and γ-Fe₂O₃@SiO₂@TiO₂ heterostructures were tested by measuring the photocatalytic degradation of RhB in water (10 mg/L) under the illumination of a Xe lamp (300 W). In order to ensure the reliability of the experiments, two control experiments, namely Blank I with catalysts only without light illumination (dark adsorption) and Blank II with light illumination only without catalysts (pure photolysis), were also performed. Figure 7(a) shows the normalized concentration of RhB (Cₜ/C₀) as a function of irradiation time for different photocatalyst and blank samples, in which Cₜ and C₀ denotes the concentration of RhB aqueous solution at the irradiation time of t and t = 0 h, respectively. It can be seen that there is no measurable RhB degradation up to 5 h under light irradiation with Fe₃O₄ alone. However, RhB can be degraded rapidly in the presence of Fe₃O₄@SiO₂@TiO₂ and γ-Fe₂O₃@SiO₂@TiO₂ catalysts under light illumination. The normalized concentration Cₜ/C₀ reaches to nearly zero with the illumination time of 5 h for γ-Fe₂O₃@SiO₂@TiO₂, while it is only 0.55 for Fe₃O₄@SiO₂@TiO₂. It has been reported that the decrease in the bulk defects of TiO₂ can enhance the separation of photogenerated electrons and holes, which results in improved photocatalytic activity. Kong et al. have also found that TiO₂ synthesized at 120 °C exhibits the lower photocatalytic efficiency than the one prepared at 180 °C and calcined at 480 °C for 3 h, which is attributed to the recombination of most photogenerated charge carriers in the bulk defects for the former⁴⁹. Moreover, Guo et al. have shown that the photocatalytic activity can be enhanced in ZnO tetrapods with less nonradiative defects⁵⁰. Here the lower photocatalytic efficiency of Fe₃O₄@SiO₂@TiO₂ is attributed to the amorphous TiO₂ shell. Amorphous TiO₂ has high concentration of bulk defects, which may act as charge trapping centers, preventing the photo-generated carriers to be used for reactions. After annealing, TiO₂ in the assembly is converted into highly crystalline anatase structure with low concentration of bulk defects, which

---

**Figure 6.** A schematic of the formation mechanism of Fe₃O₄@SiO₂@TiO₂ heterostructure.
possesses high photocatalytic activity. Thus the corn-like \(\gamma\)-Fe\(_2\)O\(_3\)@SiO\(_2\)@TiO\(_2\) heterostructure demonstrates the highest degradation rate for RhB dye.

Figure 7(b) shows the corresponding evolution of UV-vis spectra for RhB as a function of time for \(\gamma\)-Fe\(_2\)O\(_3\)@SiO\(_2\)@TiO\(_2\). The relative concentration of RhB (C\(_t\)/C\(_0\)) is extracted from the integrated UV-vis peak intensity. The decrease and shift in the maximum of the absorption peak suggest the reduction of the chromophoric group and thus the degradation of RhB molecules. As shown in Fig. 7(b), the maximum absorbance of RhB shifts gradually from 553 nm to 510 nm, and it remarkably fade away at the illumination time of 5 h. The final product has an absorption peak at 510 nm, which can be identified as an incompletely N-deethylated outcome of RhB, N-ethyl rhodamine (MER). Such a process indicates that RhB has been degraded in the presence of \(\gamma\)-Fe\(_2\)O\(_3\)@SiO\(_2\)@TiO\(_2\) sample. The similar photodegradation process of RhB by TiO\(_2\) has been studied in detail earlier\(^{51, 52}\).

To assess the magnetic recyclability and photoactivity after recycling of the \(\gamma\)-Fe\(_2\)O\(_3\)@SiO\(_2\)@TiO\(_2\) catalysts, the above experiment was performed, after which the catalysts were recycled by a magnet and re-used for the same experiment. This procedure was repeated for ten times. The percentage of degradation of RhB (at 5 h) after each experiment was calculated using (1 - C\(_t\)/C\(_0\)) \(\times\) 100%. As shown in Fig. 8, a degradation percentage of 65% is retained after eight cycles, with an average loss of \(~5\)% activity after each cycle. There is a large drop of the activity at the 9th and 10th cycles. We attribute the reduced activity to the adsorbed by-product from RhB photodegradation, which blocks the active sites of TiO\(_2\). We thus postulate that the photoactivity can be recovered by heating to remove the adsorbates. To ensure dispersibility of the catalysts, and prevent aggregation (reduces active surface area) and oxidation of \(\gamma\)-Fe\(_2\)O\(_3\) to antiferromagnetic \(\alpha\)-Fe\(_2\)O\(_3\), the temperature should be as low as possible. We found that moderate heat treatment at 200 °C for 30 min in air is the optimal condition for regeneration of the photocatalysts. As can be seen in Fig. 8, after the recycled \(\gamma\)-Fe\(_2\)O\(_3\)@SiO\(_2\)@TiO\(_2\) sample was subjected to the treatment, 100% RhB degradation was achieved at 5 h again, suggesting that the photocatalytic activity was fully recovered. The photocatalytic activity does not decrease after repeated regeneration (11th and 12th cycles in Fig. 8), demonstrating the reusability and durability of the catalysts.
Conclusions

In summary, we have successfully synthesized anisotropic corn-like \( \gamma-\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2 \) core/shell heterostructures by modified solvothermal and sol-gel methods. The formation mechanism of the hierarchical heterostructures is attributed to a self-assembly process induced by magnetic dipole interactions assisted by fusing effect of \( \text{TiO}_2 \). The magnetic remanence is enhanced in the chain-like structure, facilitating magnetic recovery. The assembly demonstrates good photocatalytic activity and magnetic recyclability. While the catalytic activity decreases after each cycle due to adsorption of contaminants, it can be completely recovered by moderate heating. Therefore, our material is a robust and durable photocatalyst with excellent magnetic recyclability, and does not suffer from reduced surface area in supported catalysts.

Methods

Synthesis of \( \text{Fe}_3\text{O}_4 \) microspheres. All the reagents were analytical grade without further purification. Deionized water was used for all synthesis and post-treatment processes. \( \text{Fe}_3\text{O}_4 \) microspheres were synthesized by a modified solvothermal method\(^{35} \). Ferric chloride (FeCl\(_3\), 0.4 g) was dissolved in ethylene glycol (EG, 20 mL) to form a clear solution, and then sodium acetate (NaAc, 1.8 g) and sodium polyacrylate (NaPAA, 0.07 g) were added into it to obtain a mixture. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (20 mL capacity). The autoclave was maintained at 200 °C for 12 h, and allowed to cool to room temperature naturally. \( \text{Fe}_3\text{O}_4 \) microspheres were obtained. They were rinsed with ethanol, and then suspended in ethanol. This suspension was added into it to obtain a mixture. The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (20 mL capacity). The autoclave was maintained at 200 °C for 12 h, and allowed to cool to room temperature naturally. \( \text{Fe}_3\text{O}_4 \) microspheres were obtained. They were rinsed with ethanol, and then suspended in ethanol for later use. In addition, polyethylene glycol (PEG) and ethylene diamine (ED) were also tried as surfactants to control the morphology of \( \text{Fe}_3\text{O}_4 \).

Synthesis of anisotropic, corn-like \( \gamma-\text{Fe}_2\text{O}_3@\text{SiO}_2@\text{TiO}_2 \) heterostructure. To obtain the anisotropic \( \gamma-\text{Fe}_2\text{O}_3@\text{SiO}_2@\text{TiO}_2 \) heterostructure, a \( \text{SiO}_2 \) coupling layer was first coated on \( \text{Fe}_3\text{O}_4 \) by a sol-gel process\(^{36} \). \( \text{Fe}_3\text{O}_4 \) solution was maintained in a water bath at 40 °C, and then ammonia (25%, 89.5 mL), water (75 mL), and tetraethyl orthosilicate (TEOS, 1.5 mL) were added sequentially into the above \( \text{Fe}_3\text{O}_4 \) solution. The mixture was stirred vigorously for 2 h and followed by sonication for 1 h. Thus, \( \text{Fe}_3\text{O}_4 \) microspheres with a \( \text{SiO}_2 \) shell can be obtained. The microspheres were rinsed with ethanol, and then resuspended in ethanol. This suspension was heated up to 60 °C for 12 h to strengthen the Si-O-Fe cross-linking on the surface of the \( \text{Fe}_3\text{O}_4 \) microspheres. The \( \text{Fe}_2\text{O}_3@\text{SiO}_2 \) magnetic microspheres were then flocculated by applying a magnetic field to allow convenient removal of the free silica.

For \( \text{TiO}_2 \) shell coating, 0.15 mL water and 5 mL ethanol were added into the suspension of \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \) microspheres, and then subjected to vortex-mixing for 15 min. Subsequently, a solution of titanium (IV) isopropoxide (TTIP, 0.5 mL) in 10 mL ethanol was added into the mixture, and then stirred vigorously in a 70 °C water bath for 4 h. The mixture was then sealed in an autoclave, heated at 120 °C for 5 h, and cooled to room temperature. The product was then rinsed and dried. To improve the crystallinity of \( \text{TiO}_2 \) for better photocatalytic properties, the \( \text{Fe}_2\text{O}_3@\text{SiO}_2@\text{TiO}_2 \) heterostructures were annealed at 350 °C for 2 h in air. Upon annealing, \( \text{TiO}_2 \) crystallized and \( \text{Fe}_2\text{O}_3 \) was oxidized into \( \gamma-\text{Fe}_2\text{O}_3 \), and as a result, the color turned from black for \( \text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2 \) to brown-red for \( \gamma-\text{Fe}_2\text{O}_3@\text{SiO}_2@\text{TiO}_2 \) heterostructures.

Photocatalytic activity measurement. The photocatalytic activity of the samples was evaluated by the degradation of Rhodamine B (RhB) under the irradiation of a Xe lamp (300 W). 100 mL RhB aqueous solution with a concentration of 10 mg/L was mixed with 0.1 g catalysts in an optically matched Pyrex vessel. The reactor is magnetically collected, and then rinsed with water for the next cycle use.

Characterizations. X-ray diffraction (XRD) patterns were recorded with a powder X-ray diffraction instrument with Cu Kα radiation (λ = 1.54 Å). The elements and valence states were characterized using X-ray photoelectron spectroscopy (XPS). The morphologies were observed on a field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). Magnetic properties were carried out in a vibrating sample magnetometer (VSM) at room temperature.

References

1. Liu, S., Yu, J. G. & Jaroniec, M. Tunable photocatalytic selectivity of hollow \( \text{TiO}_2 \) microspheres composed of anatase polyhedra with exposed {001} facets. J. Am. Chem. Soc. 132, 11914–11916 (2010).
2. Chen, X. B. & Burda, C. The electronic origin of the visible-light absorption properties of C-, N- and S-Doped \( \text{TiO}_2 \) nanomaterials. J. Am. Chem. Soc. 130, 5018–5019 (2008).
3. Chen, X. B., Liu, L., Yu, P. Y. & Mao, S. S. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystallins. Science 331, 746–750 (2011).
4. Khan, S. U. M., Al-Shahry, M. & Ingler, W. B. Jr. Efficient photochemical water splitting by a chemically modified n-\( \text{TiO}_2 \). J. Am. Chem. Soc. 130, 11914–11916 (2010).
5. Chen, X. B. & Burda, C. The electronic origin of the visible-light absorption properties of C-, N- and S-Doped \( \text{TiO}_2 \) nanomaterials. J. Am. Chem. Soc. 130, 5018–5019 (2008).
6. Liu, S., Yu, J. G. & Jaroniec, M. Tunable photocatalytic selectivity of hollow \( \text{TiO}_2 \) microspheres composed of anatase polyhedra with exposed {001} facets. J. Am. Chem. Soc. 132, 11914–11916 (2010).
7. Chen, X. B. & Burda, C. The electronic origin of the visible-light absorption properties of C-, N- and S-Doped \( \text{TiO}_2 \) nanomaterials. J. Am. Chem. Soc. 130, 5018–5019 (2008).
8. Chen, X. B., Liu, L., Yu, P. Y. & Mao, S. S. Increasing solar absorption for photocatalysis with black hydrogenated titanium dioxide nanocrystallins. Science 331, 746–750 (2011).
9. Khan, S. U. M., Al-Shahry, M. & Ingler, W. B. Jr. Efficient photochemical water splitting by a chemically modified n-\( \text{TiO}_2 \). Science 297, 2243–2245 (2002).
10. Pu, Y. C. et al. An nanostructure-decorated \( \text{TiO}_2 \) Nanowires exhibiting photocactivity across entire UV-visible region for photoelectrochemical water splitting. Nano Lett. 13, 3817–3823 (2013).
11. Lee, H. U. et al. Innovative three-dimensional (3D) eco-\( \text{TiO}_2 \) photocatalysts for practical environmental and bio-medical applications. Sci. Rep. 4, 6740 (2014).
12. Tian, B. Z. et al. Sandwich-structured AgCl@Ag\@\text{TiO}_2 with excellent visible-light photocatalytic activity for organic pollutant degradation and \( \text{E. coli} \) K12 inactivation. Appl. Catal. B: Enviro. 158–159, 76–84 (2014).
13. Uddin, M. T. et al. New insights into the photocatalytic properties of \( \text{RuO}_2/\text{TiO}_2 \) mesoporous heterostructures for hydrogen production and organic pollutant photodecomposition. J. Phys. Chem. C 119, 7006–7015 (2015).
9. Du, J., Qi, J., Wang, D. & Tang, Z. Y. Facile synthesis of Au@TiO2 core–shell hollow spheres for dye-sensitized solar cells with remarkably improved efficiency. *Energy Environ. Sci.* 5, 6914–6918 (2012).

10. Ahn, S. H., Kim, D. J., Chi, W. S. & Kim, J. H. Hierarchical double-shell nanostructures of TiO2 nanosheets on SnO2 hollow spheres for high-efficiency, solid-state, dye-sensitized solar cells. *Adv. Funct. Mater.* 24, 5037–5044 (2014).

11. Wu, W. Q. et al. Hydrothermal fabrication of hierarchically anatase TiO2 nanowire arrays on FTO glass for dye-sensitized solar cells. *Sci. Rep.* 3, 1352 (2013).

12. Fujishima, A. & Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238, 37–38 (1972).

13. Asahi, R., Morikawa, T., Ohsaki, T., Aoki, K. & Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* 293, 269–271 (2001).

14. Ansari, S. A. & Cho, M. H. Highly visible light responsive, narrow band gap TiO2 nanoparticles modified by elemental red phosphorus for photocatalysis and photoelectrochemical applications. *Sci. Rep.* 5, 25465 (2015).

15. Fernandez, A. et al. Preparation and characterization of TiO2 photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification. *Appl. Catal. B: Environ.* 7, 49–63 (1995).

16. Eskandarloo, H., Badiei, A. & Behnajady, M. A. Study of the effect of additives on the photocatalytic degradation of a triphenylmethane dye in the presence of immobilized TiO2/NiO nanoparticles: artificial neural network modeling. *Ind. Eng. Chem. Res.* 53, 6881–6895 (2014).

17. Yu, X. X., Yu, J. G., Cheng, B. & Jaroniec, M. Synthesis of hierarchical flower-like ALOOH and TiO2/AlOOH superstructures and their enhanced photocatalytic properties. *J. Phys. Chem. C* 113, 17527–17533 (2009).

18. Cho, N. H. et al. A multifunctional core-shell nanoparticle for dendritic cell-based cancer immunotherapy. *Nat. Nanotechnol.* 6, 675–682 (2011).

19. Liu, F., Hou, Y. L. & Gao, S. Exchange-coupled nanocomposites: chemical synthesis, characterization and applications. *Chem. Soc. Rev.* 43, 8098–8113 (2014).

20. Wu, W., Jiang, C. Z. & Roy, V. A. L. Recent progress in magnetic iron oxide–semiconductor composite nanomaterials as promising photocatalysts. *Nanoscale* 7, 38–58 (2015).

21. Butter, K., Romans, P. H. H., Frederik, P. M., Vroege, G. J. & Filippe, A. P. Direct observation of dipolar chains in iron ferrofluids by cryogenic electron microscopy. *Nat. Mater.* 2, 88–91 (2003).

22. Lalatonne, Y., Richardi, J. & Pileni, M. P. Van der Waals versus dipolar forces controlling mesoscopic organizations of magnetic nanoparticles. *Nanoscale* 8, 19421–19474 (2016).

23. Hao, R. et al. Synthesis, functionalization, and biomedical applications of multifunctional magnetic nanoparticles. *Adv. Mater.* 22, 2729–2742 (2010).

24. Hao, Z. H., Yang, S. L. & Wu, W. Shape control of inorganic nanoparticles from solution. *Nanoscale* 8, 1237–1239 (2016).

25. Wu, L. H., Mendoza-Garcia, A., Li, Q. & Sun, S. H. Organic phase syntheses of magnetic nanoparticles and their applications. *Chem. Rev.* 116, 10473–10512 (2016).

26. Butter, K., Romans, P. H. H., Frederik, P. M., Vroege, G. J. & Filippe, A. P. Direct observation of dipolar chains in iron ferrofluids by cryogenic electron microscopy. *Nat. Mater.* 2, 88–91 (2003).

27. Lalatonne, Y., Richardi, J. & Pileni, M. P. Van der Waals versus dipolar forces controlling mesoscopic organizations of magnetic nanoparticles. *Nat. Mater.* 3, 121–125 (2004).

28. Trusty, T. & Safran, S. A. Defect-induced phase separation in dipolar fluids. *Science* 290, 1328–1331 (2000).

29. Zhang, Y. et al. The shape anisotropy in the magnetic field-assisted self-assembly chain-like structure of magnetite. *J. Phys. Chem. C* 113, 8152–8157 (2009).

30. Singamaneni, S., Bliznyuk, V. N., Binek, C. & Tymbal, E. Y. Magnetic nanoparticles: recent advances in synthesis, self-assembly and applications. *J. Mater. Chem.* 21, 16819–16845 (2011).

31. Zhang, S. F. et al. Controllable synthesis of recyclable core–shell γ-Fe2O3@SnO2 hollow nanoparticles with enhanced photocatalytic and gas sensing properties. *Phys. Chem. Chem. Phys.* 15, 8228–8236 (2013).

32. Zhao, Y. L. et al. Controlled synthesis and photocatalysis of sea urchin-like Fe3O4@TiO2@Ag nanocomposites. *Nanoscale* 8, 5313–5326 (2016).

33. Chalasani, R. & Vasudevan, S. Cyclodextrin-functionalized Fe3O4@TiO2: reusable, magnetic nanoparticles for photocatalytic degradation of endocrine-disrupting chemicals in water supplies. *ACS Nano* 7, 4093–4104 (2013).

34. Beydoun, D., Amal, R., Low, G. K. C. & McEvoy, S. Novel photocatalyst: titanate-coated magnetite. activity and photodissolution. *J. Phys. Chem. B* 104, 4387–4396 (2000).

35. Li, S. K. et al. Magnetic Fe3O4@CaCO3 composites with bean-like core/shell nanostructures: Synthesis, properties and application in recyclable photocatalytic degradation of dye pollutants. *J. Mater. Chem.* 21, 7459–7466 (2011).

36. Liu, J. et al. 3D flowerlike α-Fe2O3@TiO2 core–shell nanostructures: general synthesis and enhanced photocatalytic performance. *ACS Sustainable Chem. Eng.* 3, 2975–2984 (2015).

37. Sun, L. L. et al. Template and silica interlayer tailorable synthesis of spindles-like multilayer α-Fe2O3/Ag/Al2O3 ternary hybrid architectures and their enhanced photocatalytic activity. *Appl. Catal. B: Environ.* 113, 1113–1124 (2014).

38. Li, X. C., John, V. T. & Zhan, J. J. The synthesis of mesoporous TiO2/SiO2/Fe3O4 hybrid particles containing micelle-induced macropores through an aerosol based process. *Langmuir* 27, 6252–6259 (2011).

39. Wang, C. X., Yin, L. W. & Zhang, L. Y. Magnetic γ-Fe2O3@SiO2)n@TiO2 functional hybrid nanoparticles with activated photocatalytic ability. *J. Phys. Chem. C* 113, 4008–4101 (2009).

40. Yu, X. X., Liu, S. W. & Yu, J. G. Superparamagnetic γ-Fe2O3@SiO2@TiO2 composite microspheres with superior photocatalytic properties. *Appl. Catal. B: Environ.* 104, 12–20 (2011).

41. Wu, W. et al. One-pot reaction and subsequent annealing to synthesis hollow spherical magnetite and maghemite nanocages. *Nanoscale Res. Lett.* 4, 926–931 (2009).

42. Zhou, J. et al. SiO2–Ag–SiO2–TiO2 multi-shell structures: plasmon enhanced photocatalysts with wide-spectral-response. *J. Mater. Chem. A* 1, 13128–13138 (2013).

43. Ran, F. et al. Angle-resolved photoemission study of Fe3O4(001) films across Verwey transition. *J. Phys. D: Appl. Phys.* 45, 275002 (2012).

44. Stöber, W., Fink, A. & Bohn, E. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.* 26, 62–69 (1968).

45. Klokkenburg, M. et al. Direct imaging of zero-field dipolar structures in colloidal dispersions of synthetic magnetite. *J. Am. Chem. Soc.* 126, 16706–16707 (2004).

46. Zhang, F. & Wang, C. C. Fabrication of one-dimensional iron oxide/silica nanostructures with high magnetic sensitivity by dipole-directed self-assembly. *J. Phys. Chem. C* 112, 15151–15156 (2008).

47. Chantrill, R. W., Bradbury, A., Popplewell, J. & Charles, S. W. Particle cluster configuration in magnetic fluids. *J. Phys. D: Appl. Phys.* 13, L119–L122 (1980).

48. Liang, Y. et al. A microfibre assembly of an iron-carbon composite with giant magnetization. *Sci. Rep.* 3, 3051 (2013).

49. Gong, M. et al. Tuning the relative concentration ratio of bulk defects to surface defects in TiO2 nanocrystals leads to high photocatalytic efficiency. *J. Am. Chem. Soc.* 133, 16414–16417 (2011).

50. Guo, M. Y. et al. Effect of native defects on photocatalytic properties of ZnO. *J. Phys. Chem. C* 115, 11095–11101 (2011).
51. Zhuang, J. D. et al. Photocatalytic degradation of RhB over TiO₂ bilayer films: effect of defects and their location. *Langmuir* **26**, 9686–9694 (2010).
52. Wu, T. X. et al. Photoassisted degradation of dye pollutants. V. self-photosensitized oxidative transformation of Rhodamine B under visible light irradiation in aqueous TiO₂ dispersions. *J. Phys. Chem. B* **102**, 5845–5851 (1998).
53. Deng, H. et al. Monodisperse magnetic single-crystal ferrite microspheres. *Angew. Chem. Int. Ed.* **117**, 2842–2845 (2005).

**Acknowledgements**
The work was supported by the National Natural Science Foundation of China (Grant Nos 51571135, 61434002), US NSF (Grant Nos DMR-1104994, CBET-1510121), Shanxi scholars program (Grant No. [2012]12), "One Hundred Talented People" of Shanxi Province and Shanxi Province Foundations (Grant No. [2013]9).

**Author Contributions**
F.W. and H.Z. conceived and designed the research. F.W. performed the data analysis. M.L., L.Y., Z.W., L.Z. and F.S. carried out the sample preparation and characterization. F.W., H.Z. and X.X. wrote the manuscript. All authors discussed and approved the final version.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

**Publisher's note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit [http://creativecommons.org/licenses/by/4.0/](http://creativecommons.org/licenses/by/4.0/).

© The Author(s) 2017