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Electrospun TiO$_2$ Nanofibers Integrating Space-separated Magnetic Nanoparticles and Heterostructures for Recoverable and Efficient Photocatalyst

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TiO$_2$ nanofibers integrating space-separated magnetic nanoparticles and heterostructures have been fabricated to construct multifunctional photocatalysts with excellent photocatalytic activity and magnetic recoverability. Electrospinning technique has been employed to prepare the Fe$_3$O$_4$ embedded TiO$_2$ (Fe$_3$O$_4$@TiO$_2$) magnetic nanofibers. TiO$_2$/CdS heterostructures (Fe$_3$O$_4$@TiO$_2$/CdS) formed by depositing CdS nanoparticles on the Fe$_3$O$_4$@TiO$_2$ nanofibers have been obtained by a hydrothermal process. The heterostructures improve the photocatalytic activity and widen the range in solar light response. Under the visible light irradiation, photocatalytic activity of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers is 5.11 times higher than that of Fe$_3$O$_4$@TiO$_2$ nanofibers, and is 1.22 times of CdS nanoparticles. And, it exhibits a slight increase under the simulated solar light with the photocatalytic degradation ratio of 1.1 times higher than that under visible light. The loading amounts of CdS only have effects on the photocatalytic activity under visible light and simulated solar light. Besides, the Fe$_3$O$_4$@TiO$_2$/CdS nanofiber exhibits the saturation magnetization strength of 1.572 emu g$^{-1}$, and can be effortlessly separated and recovered by applying a contactless magnetic field. The cycling stability is durable after the magnetic separation and recycling.

1 Introduction

TiO$_2$ nanofibers are fascinating fibrous morphology nanomaterials with many applications in environmental and energy issues, such as photocatalysts, Dye-sensitized solar cells (DSSC), Li-ion battery, and membrane filtration. For applications in photocatalysis, the nanofiber morphology exhibits advantages in providing large external surface area and the inner space in the fiber to integrate functional components to construct efficient photocatalysts with high activity and recoverable separation for large scale water treatment. Electrospinning technique is a low-cost and convenient approach to fabricate the one-dimensional (1D) nanostructure and assemblies with hierarchical and core-shell structures.

Magnetic TiO$_2$ nanofibers as heterogeneous photocatalysts are easily separated from the reaction solution system after utilization by applying a contactless magnet. The traditional strategy to endow TiO$_2$ nanofibers with magnetism is to decorate the surface of the nanofibers with iron-based magnetic compounds. CoFe$_2$O$_4$ and Fe$_3$O$_4$ are loaded on the surface of the nanofibers by combining electrospinning with co-precipitation or hydrothermal treatment. However, the external surface of the TiO$_2$ nanofiber as a photocatalyst is extremely important to the photocatalytic activity and the construction of hierarchical heterostructures. Thus, we need to embed the magnetic functional components into the nanofiber to form a core-shell structure. The one-step electrospinning of a solution containing poly(vinyl pyrrolidone) (PVP) and alkoxide precursors of titanium and iron oxides is a direct method to achieve the embedded morphology. But, a direct contact between the embedded Fe$_3$O$_4$ and TiO$_2$ nanofiber would lead to the Fe$^{3+}$-doped TiO$_2$ after the calcination, which has negative effects on the photocatalytic activity. An approach to resolve this problem is to coat the magnetic iron oxide nanoparticles with an isolating shell. Silica (SiO$_2$) is usually chosen as a versatile shell in the configuration of the core-shell structure. The extended Stöber method has been applied to fabricate a uniform and porous SiO$_2$ shell on magnetic Fe$_3$O$_4$ core.

Heterostructures design on the surface of TiO$_2$ nanofibers is an effective means to improve the photocatalytic activity by forming heterojunctions. Semiconductors, plasmonic nanoparticles and photosensitive metal complexes are deposited or assembled on the TiO$_2$ nanofibers to form heterojunctions, such as SrTiO$_3$, SnO$_2$, SnS$_2$, WO$_3$, Ba$_4$Ti$_3$O$_7$, CeO$_2$, In$_2$O$_3$, V$_2$O$_5$, Ag and Au nanoparticles, and copper (II) phthalocyanine. CdS is a typical narrow band gap semiconductor with a band gap of 2.4 eV and a more negative conduction band (C.B.) electrochemical potential than that of TiO$_2$. When the CdS/TiO$_2$ composite is exposed to the low energy photons of visible light, in principle, the electrons which are photo-excited to...
the C.B. of CdS are transferred to that of TiO$_2$. Accordingly, the electrons and holes produced in CdS/TiO$_2$ heterostructure are separated and its spectrum response is extended to visible light, which could contribute to improve the catalytic activity.

Herein, we reported the fabrication of TiO$_2$ nanofibers integrating embedded magnetic Fe$_3$O$_4$ nanoparticles and TiO$_2$/CdS heterostructures as efficient photocatalysts with magnetic recoverability. The Fe$_3$O$_4$ embedded TiO$_2$ (Fe$_3$O$_4@$TiO$_2$) magnetic nanofibers were prepared through electrospinning process combined with heat treatment at 753 K. The CdS nanoparticles were then deposited on the surface of Fe$_3$O$_4@$TiO$_2$ nanofibers (Fe$_3$O$_4@$TiO$_2$/CdS nanofiber) through a hydrothermal process. The XRD pattern shows that TiO$_2$ nanofibers are converted to anatase phase after heat treatment. The characteristic SEM and TEM morphologies directly illustrate that the Fe$_3$O$_4$ nanoparticles are completely encapsulated in TiO$_2$ nanofibers with the CdS nanoparticles well dispersed on the surface. The UV-Vis diffuse reflectance spectra (UV-Vis DRS) show that the light absorption of Fe$_3$O$_4@$TiO$_2$/CdS nanofiber is enhanced, and adsorption edge is extended to the visible spectrum range. The photocatalytic degradation ratio of Fe$_3$O$_4@$TiO$_2$/CdS-3 nanofibers for Rhodamine B (RhB) is 97.65% under UV irradiation, which is similar to the control sample of TiO$_2$ nanofibers with photocatalytic degradation ratio of 92.06% and Fe$_3$O$_4@$TiO$_2$ nanofibers with the one of 97.86%. Under the visible light irradiation, photocatalytic activity of Fe$_3$O$_4@$TiO$_2$/CdS nanofibers is 5.11 times higher than that of Fe$_3$O$_4@$TiO$_2$ nanofibers, and 1.22 times of CdS nanoparticles. And, it exhibits a slight increase under the simulated solar light with the photocatalytic degradation ratio of 1.1 times higher than that under visible light. The loading amounts of CdS only have effects on the photocatalytic activity under visible light and simulated solar light. Besides, Fe$_3$O$_4@$TiO$_2$/CdS nanofibers exhibit strong magnetism and can be easily separated and recovered by adding a contactless magnetic field. The cycling stability is durable after the magnetic separation and recycling.

2 Materials and Methods

2.1 Preparation of Fe$_3$O$_4@$SiO$_2$ core-shell structure

Fe$_3$O$_4$ nanoparticles were prepared by solution precipitation according to the literature. FeCl$_3$.6H$_2$O (1.817g, analytic purity, Sinochemical Sinopharm Chemical Reagent Co., Ltd) was mixed with FeCl$_2$.4H$_2$O (1.113g, analytic purity, Sinochemical Sinopharm Chemical Reagent Co., Ltd) under N$_2$ atmosphere to react for 5 hours at 50 °C. After 0.5 hour, concentrated ammonia (15ml, analytic purity, Sinochemical Sinopharm Chemical Reagent Co., Ltd) was added to precipitate the Fe$_3$O$_4$. For the preparation of Fe$_3$O$_4@$SiO$_2$, 0.4 g Fe$_3$O$_4$ was added in the mixed solution containing 80 mL absolute ethanol (analytic purity, Sinochemical Sinopharm Chemical Reagent Co., Ltd) and 20 mL deionized water. After ultrasonic dispersion, 1mL of concentrated ammonia (28 wt%) was added into the solution. The mixed solution was stirred and, at the same time, 0.6 mL tetraethyl orthosilicate (analytic purity, Sinochemical Sinopharm Chemical Reagent Co., Ltd) and 5 mL absolute ethanol were added into the mixed solution which was stirred constantly in the water bath at 30 °C for 8 h. The product was recovered with a magnet and washed with deionized water and absolute ethanol three times, followed by drying at 80 for 2 h in vacuum oven.

2.2 Preparation of magnetic Fe$_3$O$_4@$TiO$_2$ nanofibers

1.5 g PVP (MW 1300000, Aladdin Chemistry Co. Ltd) was dissolved in 15 mL anhydrous ethanol (> 99 wt%) and stirred until the solution turned transparent. 0.1 g Fe$_3$O$_4@$SiO$_2$ nanoparticles were added into the above solution. After ultrasound treatment, the dispersion was intensively stirred for 24 h. The obtained dispersion was signed as A. 2 mL tetrabutyl orthotitanate was added dropwise into the mixed solution of 4 mL anhydrous ethanol and 4 mL acetic acid (99.5%). The mixed solution was stirred for 30 min, and the formed yellow solution named B. Solution B was slowly added into A and strongly stirred for 4 h. The above gel was injected into a syringe of the self-made electropinning apparatus with a copper electrode that inserted into the syringe. Then aluminum foil as cathode was placed in front of the nozzle with a distance of 20 cm and operated at 9 kV. After 10 h, a large fiber mat was produced.

After hydrolyzing completely in the air, the products were dried under vacuum at 80 °C for 4 h. The products were then heated in a muffle furnace with heating rate of 1 °C/min from room temperature to 480 °C and kept at 480 °C for 10 h to obtain Fe$_3$O$_4@$TiO$_2$ nanofibers.

2.3 Integrating TiO$_2$/CdS heterostructures on Fe$_3$O$_4@$TiO$_2$ nanofibers (Fe$_3$O$_4@$TiO$_2$/CdS)

The Fe$_3$O$_4@$TiO$_2$/CdS nanofibers were synthesized by a hydrothermal method. Three portions (each 0.050 g) of magnetic Fe$_3$O$_4@$TiO$_2$ nanofibers were added into the three reaction solutions composed of 20 mL of deionized water (DI water), cadmium acetate and thiourea with the molar ratio of cadmium acetate and thiourea of 1:3, while the cadmium acetate are 0.1 mmol, 0.5 mmol and 0.8 mmol, respectively. The three solutions were transferred to Teflon-lined stainless autoclaves. The hydrothermal treatment was conducted at 130 °C for 12 h and then cooled at room temperature. The magnetic products were collected by a magnet, and were washed with DI water and ethanol three times followed by drying at 80 °C for 12 h. The obtained products were denoted as Fe$_3$O$_4@$TiO$_2$/CdS-1, Fe$_3$O$_4@$TiO$_2$/CdS-2, and Fe$_3$O$_4@$TiO$_2$/CdS-3 nanofibers.

2.4 Characterization

X-ray diffraction (XRD) patterns were recorded on a D8 Tool diffractometer using Cu Kα (λ=0.15418 nm). SEM images were performed on a JEOL JSM-6700F field emission scanning electron microscope. The TEM images were observed on H-7650 transmission electron microscope operated at 120 kV. UV-Vis diffuse reflectance spectra (DRS) were recorded on a DWS 003 spectrophotometer. The magnetization curve was obtained on LaKe Shole7304 ibrating Sample Magnetometer (VSM). The concentration of cadmium ion (Cd$^{2+}$) in the solution was tested on a prodigy XP ICP-AES.

2.5 Adsorption and photocatalytic process

The photocatalytic activity was tested by examining the degradation of RhB in aqueous solution. The ultraviolet (UV) light was illuminated by a 50 W high-pressure mercury lamp. Visible light and simulated solar light were illuminated by a Xe
lamp with UV cut-off filter and simulated solar light filter. Samples (0.010 g and 0.020 g) was added into 100 mL of the new prepared Rhodamine B (RhB) solution (1.0 x 10^{-5} mol L^{-1}) and stirred for 10 min at room temperature to obtain a good dispersion. Then, the system was kept in the dark to reach saturation adsorption for 1 hour. The irradiation started and the reaction system temperature was kept at 23±3 °C by water cooling. After centrifugation to remove the photocatalyst, the concentration of RhB in the solution was measured by UV-Vis spectroscopy.

3. Results and discussion

The crystalline phase of the as-prepared samples was analyzed by powder X-ray diffraction (XRD). Fig.1 presents the XRD pattern of Fe_{3}O_{4} nanoparticles, Fe_{3}O_{4}@TiO_{2} nanofibers, and the CdS deposited Fe_{3}O_{4}@TiO_{2} nanofibers (Fe_{3}O_{4}@TiO_{2}/CdS-2 nanofibers). All of the diffraction peaks in Fig. 1a can be indexed to the Fe_{3}O_{4} structure (JCPDS 17-0300) which illustrate a high purity and crystallinity of the prepared Fe_{3}O_{4} nanoparticles. As shown in Fig. 1b, the intensity of the Fe_{3}O_{4} diffraction peaks weakens apparently and the identified peak at 25.4° is in good agreement with that of anatase TiO_{2}. The result in Fig. 1c shows the characteristic peaks of CdS at 26.80°, 28.08°, 43.90° and 52.20° (2θ), which is corresponded to (002), (101), (110) and (201) crystal faces and agreed with the standard peaks of hexagonal crystal of CdS (JCPDS 10-077-2306). According to the Scherrer equation, the average CdS particle size along (002) is 16.08 nm. Therefore, it is concluded that integration of magnetic nanoparticles and heterostructures on the Fe_{3}O_{4}@TiO_{2}/CdS nanofibers were successfully fabricated by the combination of an electrospinning technique with a hydrothermal synthesis.

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![Fig.1 XRD pattern of the electrospun TiO_{2} nanofibers integrating space-separated magnetic Fe_{3}O_{4} nanoparticles and TiO_{2}/CdS heterostructures. (a) Fe_{3}O_{4} nanoparticles. (b) Fe_{3}O_{4}@TiO_{2} nanofibers. (c) Fe_{3}O_{4}@TiO_{2}/CdS-2 nanofibers.](image)

Magnetic nanoparticles and heterostructures space-separated morphology of the Fe_{3}O_{4}@TiO_{2}/CdS nanofibers with different CdS loading amounts was examined. Fig. 2 shows typical scanning electron microscopy (SEM) images. It can be clearly seen in Fig. 2a that the diameter of uniform nanofibers is in the range of 150-200 nm. The surface of Fe_{3}O_{4}@TiO_{2} nanofibers is relatively smooth with fiber lengths above 10 µm. The scanning electron microscope (SEM) images from Fig. 2b to Fig. 2d reveal that Fe_{3}O_{4}@TiO_{2}/CdS nanofibers are composed of numerous highly dispersed CdS nanoparticles with size of 15 nm attached onto the surface of the Fe_{3}O_{4}@TiO_{2} nanofibers, thus resulting in the hierarchical heterostructures with a rough surface. To investigate the effects of CdS loading amounts on the photocatalytic activity, we have prepared Fe_{3}O_{4}@TiO_{2}/CdS nanofibers with different CdS loading amounts. As the concentrations of cadmium acetate and thiourea increase under the hydrothermal process, the loading amount of CdS on the Fe_{3}O_{4}@TiO_{2} nanofibers increases. The results in Fig. 2c exhibit that when the amount of CdS reaches 59.1 wt%, the fibrous morphology is well retained with a little increase in the diameter due to CdS nanoparticles loading and with a rough surface. When the amount of CdS reaches 70.0 wt%, the loading density of CdS nanoparticles on nanofibers increases, and simultaneously the aggregation of CdS nanoparticles occurs, as shown in Fig. 2d.

![Fig. 2 SEM images of the electrospun TiO_{2} nanofibers integrating space-separated magnetic Fe_{3}O_{4} nanoparticles and TiO_{2}/CdS heterostructure. (a) Fe_{3}O_{4}@TiO_{2} nanofibers. (b) Fe_{3}O_{4}@TiO_{2}/CdS-1 nanofibers with CdS 22.4 wt%. (c) Fe_{3}O_{4}@TiO_{2}/CdS-2 nanofibers with CdS 59.1 wt%. (d) Fe_{3}O_{4}@TiO_{2}/CdS-3 nanofibers with CdS 70.0 wt%](image)

Transmission electron microscopy (TEM) has been used to investigate the functional components space-separated morphology of the typical Fe_{3}O_{4}@TiO_{2}/CdS-2 nanofibers. As shown in Fig. 3a, it can be observed that the surface of the

![Fig.3 TEM images of the electrospun TiO_{2} nanofibers integrating space-separated magnetic Fe_{3}O_{4} nanoparticles and TiO_{2}/CdS heterostructures. (a) Fe_{3}O_{4}@TiO_{2} nanofibers. (b) Fe_{3}O_{4}@TiO_{2}/CdS-2 nanofibers](image)
nanofiber appears smooth, and Fe$_3$O$_4$@SiO$_2$ nanoparticles were uniformly embedded in the nanofibers. The TEM images in Fig. 3b clearly show the rough surface of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers with small branches. They are the uniformly dispersed CdS nanoparticles, which is in accordance with the SEM image of Fig. 2c.

Fig. 4 shows the UV-Vis diffuse reflectance spectra (UV-Vis DRS) of the electrospun TiO$_2$ nanofibers with embedd magnetic Fe$_3$O$_4$ nanoparticles and surface CdS heterostructures. The light absorption of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers is extended to 510 nm, and the absorption edge shows an apparent red-shift. Moreover, its absorption intensity is enhanced by comparasion with magnetic Fe$_3$O$_4$@TiO$_2$ nanofibers. This result indicates that the photo-response range after CdS surface deposition is extended and photoabsorption ability is enhanced.

![Graph showing UV-Vis diffuse reflectance spectra](image)

**Fig. 4** UV-Vis diffuse reflectance spectra (UV-Vis DRS) of the electrospun TiO$_2$ nanofibers integrating space-separated magnetic Fe$_3$O$_4$ nanoparticles and TiO$_2$/CdS heterostructures. (a) TiO$_2$ nanofibers (TiO$_2$ NF). (b) Fe$_3$O$_4$@TiO$_2$ nanofibers (Fe$_3$O$_4$@TiO$_2$ NF). (c) Fe$_3$O$_4$@TiO$_2$/CdS-2 nanofibers (Fe$_3$O$_4$@TiO$_2$/CdS-2 NF).

Photocatalytic activities of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers with different CdS loading amounts were investigated through examining the degradation of RhB in aqueous solution (See Fig. S1, ESI†). The adsorption and photocatalytic activity of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers under UV light, visible light and simulated solar light were also examined by employing TiO$_2$ nanofibers, Fe$_3$O$_4$@TiO$_2$ nanofibers and CdS nanoparticles as control to justify the contribution of heterostructures to the Fe$_3$O$_4$@TiO$_2$/CdS nanofibers. The results in Fig. 5a and Table 1 (See ESI†) show that the CdS on the surface of Fe$_3$O$_4$@TiO$_2$ nanofibers has little effects on the increase of photocatalytic activity under UV irradiation. The photocatalytic degradation ratio of Fe$_3$O$_4$@TiO$_2$/CdS-3 nanofibers for RhB is 97.65%, which is similar to the control sample of TiO$_2$ nanofibers with photocatalytic degradation ratio of 92.06% and Fe$_3$O$_4$@TiO$_2$ nanofibers with the one of 97.86%. And, the variable CdS loading amounts for Fe$_3$O$_4$@TiO$_2$/CdS-1 and Fe$_3$O$_4$@TiO$_2$/CdS-2 nanofibers also exhibit little contribution to the photocatalytic activity under UV irradiation.

![Graph showing adsorption and photocatalytic activity](image)

**Fig. 5** Adsorption and photocatalytic activity of the electrospun TiO$_2$ nanofibers integrating space-separated magnetic Fe$_3$O$_4$ nanoparticles and TiO$_2$/CdS heterostructure (Fe$_3$O$_4$@TiO$_2$/CdS) for degradation of RhB.

We consider that the reason would be ascribed to unexcuted CdS under UV irradiation, and the photocatalytic activity is derived from TiO$_2$ nanofibers. To further investigate this hypothesis, we carried out adsorption and photocatalytic experiments for Fe$_3$O$_4$@TiO$_2$/CdS nanofibers under visible light and simulated solar light by using CdS nanoparticles, Fe$_3$O$_4$@TiO$_2$ nanofibers and TiO$_2$ nanofibers as control. The results in Fig. 5b show that the photocatalytic activity of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers is 5.11 times higher than that of Fe$_3$O$_4$@TiO$_2$ nanofibers, and is 1.22 times of CdS nanoparticles. The increased photocatalytic activity of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers under visible light irradiation is ascribed to the heterojunctions between the TiO$_2$ nanofibers and CdS nanoparticles, which benefits the separation of excited holes and electrons. Besides, the photocatalytic degradation ratio of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers for RhB ascends from 71.27% to 90.25% as the loading amounts of CdS nanoparticles increases from 22.4wt% for Fe$_3$O$_4$@TiO$_2$/CdS-1 to 70.0 wt% for Fe$_3$O$_4$@TiO$_2$/CdS-3.

To further demonstrate the roles of heterostructures in improving the photocatalytic activity and widening the range of solar light response, we have also compared the activity of Fe$_3$O$_4$@TiO$_2$/CdS for degrading RhB solution under the irradiation of simulated solar light with that under visible light. The Fig. 5c shows that the Fe$_3$O$_4$@TiO$_2$/CdS nanofibers as photocatalysts exhibit higher photocatalytic degradation ratio for RhB under simulated solar light irradiation. The photocatalytic activity of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers is 1.68 times higher than that of Fe$_3$O$_4$@TiO$_2$ nanofibers, and is 1.36 times of CdS nanoparticles. Moreover, the photocatalytic degradation ratio of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers for RhB ascends from 71.61% to 92.55% as the loading percent of CdS nanoparticles increases from 22.4wt% for Fe$_3$O$_4$@TiO$_2$/CdS-1 to 70.0 wt% for Fe$_3$O$_4$@TiO$_2$/CdS-3. The photocatalytic degradation ratio of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers for RhB is 3.6 times of that under visible light irradiation. In contrast with the CdS control, Fe$_3$O$_4$@TiO$_2$/CdS nanofibers exhibit a slight increase in photocatalytic activity under the simulated solar light with photocatalytic degradation ratio of 1.1 times higher than that under visible light irradiation.
Fe$_3$O$_4$@TiO$_2$/CdS-1 with CdS 22.4 wt% and Fe$_3$O$_4$@TiO$_2$/CdS-2 with CdS 59.1 wt% and Fe$_3$O$_4$@TiO$_2$/CdS-3 with CdS 70.0 wt% (a) UV irradiation (high pressure Hg lamp) with TiO$_2$ nanofibers (TiO$_2$/NF), Fe$_3$O$_4$@TiO$_2$ nanofibers (Fe$_3$O$_4$@TiO$_2$/NF) as control. (b) Visible light irradiation (Xe lamp with visible light cut-off filter (>400 nm)) with CdS nanoparticles, TiO$_2$ nanofibers (TiO$_2$/NF), Fe$_3$O$_4$@TiO$_2$ nanofibers (Fe$_3$O$_4$@TiO$_2$/NF) as control. (c) Solar light irradiation (Xe lamp with simulated solar light filter) with CdS nanoparticles, TiO$_2$ nanofibers (TiO$_2$/NF), Fe$_3$O$_4$@TiO$_2$ nanofibers (Fe$_3$O$_4$@TiO$_2$/NF) as control. (d) Cycling stability of Fe$_3$O$_4$@TiO$_2$/CdS-3 NF under solar light irradiation (Xe lamp with simulated solar light filter). (A): adsorption and (I): irradiation under solar light. The minus value in the time axis denotes the adsorption in the dark.

The cycling stability of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers as a magnetically recoverable photocatalyst was also investigated. As shown in Fig. 5d, adsorption in the dark and photocatalytic activity under simulated solar light irradiation are retainable during the 3 cycles. But, photocatalytic degradation ratio of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers for RhB decreases from 85.6% at 3$^{\text{th}}$ cycle to 61.8% at 5$^{\text{th}}$ cycle (See Fig. S2, ESI†).

As a concern that cadmium ion (Cd$^{2+}$) would remain in the solution after the adsorption and photocatalytic process, we have checked the Cd$^{2+}$ in the solution by ICP-AES after separating the powder photocatalysts with a high speed centrifugation. Under the same adsorption and irradiation conditions for the Fe$_3$O$_4$@TiO$_2$/CdS-3 nanofibers with 70 wt% CdS and the CdS control, the Cd$^{2+}$ concentration (C$_{\text{Cd}^{2+}}$) in the solution after adsorption and simulated solar light irradiation is 56.86 mg L$^{-1}$ for CdS control and 53.2 mg L$^{-1}$ for Fe$_3$O$_4$@TiO$_2$/CdS-3 nanofibers. Fortunately, the C$_{\text{Cd}^{2+}}$ in the solution declines during the following cycles, and it decreases to 9.7 mg L$^{-1}$ after the 4$^{\text{th}}$ cycle (See Fig. 5, S3, ESI†).

Figure 6 Magnetization and magnetic field induced separation and recoverability of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers. (a) Magnetization curve of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers. (b) Photo images of separation and recoverability of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers by a contactless magnet.

Magnetization curve of Fe$_3$O$_4$@TiO$_2$/CdS nanofibers exhibits near-zero coercivity and remanence, suggesting a super paramagnetic nature as shown in Fig. 6a. The saturation magnetization strength is 1.572 emu g$^{-1}$. It can be separated and recovered by applying a contactless magnetic field. As shown in Fig. 6b, the Fe$_3$O$_4$@TiO$_2$/CdS nanofibers were separated and collected from the solution with a magnet placed outside the bottle. Comparatively, the technology of contactless magnetic separation is easier to operate than the methods of traditional filter and centrifugal separation, and shows a promising potential in large scale industrial application.

Conclusions

In this work, anatase TiO$_2$ nanofibers integrating space-separated magnetic Fe$_3$O$_4$ nanoparticles and TiO$_2$/CdS heterostructures with magnetic recoverability and enhanced photocatalytic activity have been fabricated. Magnetic Fe$_3$O$_4$ nanoparticles with SiO$_2$ shells have been successfully embedded in the TiO$_2$ nanofiber (Fe$_3$O$_4$@TiO$_2$) through an electrospinning process. TiO$_2$/CdS heterostructures constructed by depositing CdS nanoparticles on the surface of Fe$_3$O$_4$@TiO$_2$ nanofiber has been formed through a hydrothermal process. The heterostructures increases the photocatalytic activity of the Fe$_3$O$_4$@TiO$_2$/CdS nanofibers, and the loading amounts of CdS nanoparticles only show positive effects on the photocatalytic activity under visible light and simulated solar light irradiation. The embedded magnetic Fe$_3$O$_4$ nanoparticles allow the integrated Fe$_3$O$_4$@TiO$_2$/CdS nanofibers to be effortlessly separated and recovered by applying a magnet. The strategy of integrating space-separated functional components on nanofibers provides a promising approach to design multifunctional components integration on fibrous morphology towards advanced photocatalysts with higher activity, effortless recoverability and durable recyclability.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Fig.S1 UV-Vis absorption of RhB during photocatalytic process. Fig.S2 Cycling performances of adsorption and photocatalytic activity of Fe$_3$O$_4$@TiO$_2$/CdS-3 nanofibers. Fig.S3 Cadmium ion (Cd$^{2+}$)
concentration ($C_{\text{CdS}}$) in the solution. Table 1 Comparison of adsorption and photocatalytic activity of FeO@TiO$_2$-CdS nanofiber (NF) and control samples.] See DOI: 10.1039/b000000x/c

TiO$_2$ nanofibers integrating space-separated magnetic Fe$_3$O$_4$ nanoparticles and TiO$_2$/CdS heterostructure (Fe$_3$O$_4$@TiO$_2$/CdS nanofiber) have been fabricated to construct multifunctional photocatalyst with excellent photocatalytic activity and magnetic recoverability. The heterostructures improve the photocatalytic activity and widen the range in solar light response. The loading amounts of CdS only have effects on the photocatalytic activity under visible light and simulated solar light. Besides, the Fe$_3$O$_4$@TiO$_2$/CdS nanofibers exhibit strong magnetism and can be effortlessly separated and recovered by applying a simple contactless magnetic field. The cycling stability is durable after the magnetic separation and recycling.