This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Controlled Synthesis and Photocatalysis of Sea Urchin-Like Fe$_3$O$_4$@TiO$_2$@Ag Nanocomposite

Yilin Zhao, Chengran Tao, Gang Xiao, Guipeng Wei, Linghui Li, Changxia Liu, Haijia Su*

Based on the synergistic photocatalytic activities of nano-sized TiO$_2$ and Ag, as well as the magnetic property of Fe$_3$O$_4$, a sea urchin-like Fe$_3$O$_4$@TiO$_2$@Ag nanocomposite (Fe$_3$O$_4$@TiO$_2$@AgNCs) is controllably synthesized with tunable cavity size, adjustable shell layer of TiO$_2$ nanofiber, higher structural stability and larger specific surface area. Here, Fe$_3$O$_4$@TiO$_2$@AgNCs are obtained with Fe$_3$O$_4$ as core and nanofiber TiO$_2$/Fe$_3$O$_4$/Ag nanoheterojunctions as shell; and Ag nanoparticles with diameter of approximately 4 nm are loaded both on TiO$_2$ nanofibers and inside the cavities of sea urchin-like Fe$_3$O$_4$@TiO$_2$ nanocomposites uniformly. Ag nanoparticles leads to the production of more photogenerated charges in

Beijing Key Laboratory of Bioprocess, Beijing University of Chemical Technology (BUCT)

15 BeiSanhuan East Road, ChaoYang District, Beijing, 100029, P. R. China

E-mail: suhj@mail.buct.edu.cn, Tel.: +86-10-64452756, Fax.: +86-10-64414268
TiO$_2$/Fe$_3$O$_4$/Ag heterojunction via LSPR absorption, and enhances band-gap absorption of TiO$_2$, while Fe$_3$O$_4$ cocatalyst provides as active sites for oxygen reduction by the effective transfer of photogenerated electrons to oxygen. So the photocatalytic performance is improved due to the synergistic effect of synergistic effect of TiO$_2$/Fe$_3$O$_4$/Ag nanoheterojunctions. As photocatalysts under UV and visible irradiation, the as-synthesized nanocomposites display enhanced photocatalytic and recycling properties for the degradation of Ampicillin. Moreover, they present better broad-spectrum antibiosis under visible irradiation. The enhanced photocatalytic activity and excellent chemical stability, in combination with the magnetic recyclability, make this multifunctional nanostructure promising a candidate for antibiosis and remediation in aquatic environmental contamination in the future.

**Keywords:** Sea urchin-like Fe$_3$O$_4$@TiO$_2$@Ag nanocomposites, magnetic materials, controllable preparation, photocatalytic activities under visible irradiation, recycling properties.

**1. Introduction**

Since the discovery of the phenomenon of photocatalytic splitting of water under ultraviolet light by Fujishima and Honda in 1972,$^1$ titanium dioxide (TiO$_2$), as an interesting semiconductor material, has been widely investigated for environmental applications because of its chemical inertness, strong oxidizing power, cost effectiveness, and long term stability against photo- and chemical corrosion.$^{2,3}$ Its wide band gap energy($E_g$)3.0–3.2 eV, allows the absorption of UV light and the generation of electrons (e$^-$) and holes (h$^+$), which subsequently provides a favorable condition for red-ox reactions.$^4$ It has been determined that a highly crystalline structure for TiO$_2$ material is essential to enhance the generation and migration of photo generated electrons/holes.$^{5,6}$ On the other
hand, the photocatalytic activity of TiO$_2$ is related with its size, shape, surface area, morphology, and dimensionality. Nanometer-scaled TiO$_2$ based catalysts, such as nanoparticles, nanorods, nanosheets, and nanotubes, exhibit promising photocatalytic performance, but they tend to aggregate during the photocatalysis process, and therefore reduce their active surface area.

Many studies found that three-dimensional (3D) hierarchical nanoarchitecture assemblies of one dimensional (1D) nanostructures, including nanorods, nanowires, and nanotubes, are highly desired due to their high surface-to-volume ratio, high organic pollutant adsorption, and excellent incident light scattering within the structures. Similarly, flower-like multineedle TiO$_2$ nanostructures were successfully fabricated by mild aqueous chemistry. An alternative approach for producing high-surface-area anatase materials is the creation of mesoscale porosity in such materials. The synthesis of mesoporous structures has been most extensively reported.

Finely dispersed TiO$_2$ particles have a large reactive surface area, but it is difficult to separate and recover them from liquid phase. The recovery and reusability of TiO$_2$ particles are, however, crucial for their further applications. Conventional separation methods, including centrifugation and filtration, may lead to catalyst loss and energy consumption. Even though photocatalysts fixed on thin films, allowing easy recovery, have been successfully prepared, the activity of such photocatalysts is considerably reduced, as the effective surface area is significantly decreased during the preparation. On the basis of practicality, immobilizing TiO$_2$ catalysts on to the surface of magnetic nano- or microparticles has been a trend because they can be easily separated and recovered from the solution with the help of an external magnet. By this method, to some degree, the loss of catalysts can be avoided, less energy is required, and some required specifications of applied materials can be obtained. A number of materials with different elemental compositions
have been used as the magnetic core, such as Fe$_3$O$_4$, γFe$_2$O$_3$, NiFe$_2$O$_4$, CoFe$_2$O$_4$, FeCo, and Co$_3$O$_4$. Among these materials, Fe$_3$O$_4$ has drawn a great attention due to its remarkable magnetic properties, low toxicity, and biocompatibility. The mesoporous TiO$_2$ shell in the composites is usually prepared by sol–gel method to prevent Fe$_3$O$_4$ nanoparticles from being oxidized. However, after introducing Fe$_3$O$_4$ as the cores of Fe$_3$O$_4$@TiO$_2$ hybrid nanostructures, photodissolution may occur in the hybrid nanoparticles, which may decrease the photocatalytic efficiency of TiO$_2$ materials.

Chemically inert surface of magnetic nanoparticles was provided by silica membranes, helping to inhibit the oxidation of the Fe$_3$O$_4$ core by the holes photogenerated in outer TiO$_2$ layer. However, the coating process of silicon membrane on the corn of Fe$_3$O$_4$ is complicated, the synthesis of structure is unstable, and the superparamagnetic characteristic of the hybrid nanoparticles significantly decreases. Up to now, considerable efforts have been devoted to explore novel, versatile and magnetically-separable photocatalysts with core-shell nanostructures.

How to improve the photocatalytic activity of TiO$_2$ in visible region is another focus of recent research on TiO$_2$ photocatalysis. Over the past decades, TiO$_2$ photocatalysts doped with metal or metallic oxide, e.g., Pb, Au, Ag, Ag$_2$O, AgPO$_3$, BiVO$_4$, have been widely studied for improving photocatalytic performance on the degradation of various organic pollutants under the irradiation of visible light. Here, metal nanoparticles act as a mediator in storing and shuttling photogenerated electrons from TiO$_2$ surface to an acceptor. A peculiar case of Ag was reported, where its nanocomposite with TiO$_2$ can efficiently retard the e$^{-}$-h$^{+}$ recombination because of the Schottky barrier formed at the metal TiO$_2$ interface. The decrease of charge carriers recombination enhances its photoactivity. Furthermore, silver itself has been recognized as a natural antimicrobial agent.
since ancient times, and silver can also act as an antimicrobial auxiliary agent as deposit on a TiO₂
surface.⁹,³⁴,³⁵

In the present paper, uniform sea urchin-like Fe₃O₄@TiO₂ nanocomposites, Fe₃O₄@TiO₂ NCs,
were successfully synthesized at 100% morphological yield by a modified hydrothermal method,
and sea urchin-like Fe₃O₄@TiO₂@Ag nanocomposites, Fe₃O₄@TiO₂@Ag NCs, were fabricated in
AgNO₃ solution under visible light by a photochemical reduction technique. Fe₃O₄@TiO₂@Ag NCs
were prepared in order to possess the potential advantages: (i) easy recovery and multi-reuse ability;
(ii) excellent photocatalytic activities under visible irradiation; (iii) degradation and complete
mineralization for organics. The morphology, elemental composition, crystallinity and phase, pore
properties, and magnetic properties were studied by Transmission Electron Microscope (TEM),
field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), (X-ray
photoelectron spectroscopy )XPS, UV–vis spectroscopy (UV-vis-DR), pore-size
distributions , and vibrating sample magnetometer (VSM). The catalytic activities of
Fe₃O₄@TiO₂@Ag NCs were estimated by the catalytic reduction of Ampicillin under UV and
visible light. Furthermore, the intermediate products of the photocatalytic degradation of AMP at
different periods was investigated by high performance liquid chromatography-tandem mass
spectrometry (HPLC-MS) analysis, and the mineralization of AMP molecules was studied by TOC
analysis. And the multi-reuse property of Fe₃O₄@TiO₂@Ag NCs was examined for the better
understanding of its potential capability for practical applications. Then, the photoinactivation
toward *E. coli*, *S. aureus* and *Asper. Niger* was carried out under visible-light irradiation.

2. Experimental Section
2.1. Materials

FeCl₃·6H₂O, sodium acetate, ethylene glycol, hydrochloric acid(36.5wt%), anhydrous ethanol, ammonium hydroxide (NH₃·H₂O, 28wt %), sodium hydroxide, macrogol 4000-991, tetrabutyl titanate (TBOT), silver nitrate (AgNO₃) were of analytical grade and purchased from Beijing Chemical Reagent Company. Sodium ampicillin (AMP) was purchased from Sigma Aldrich (CAS: 69-52-3). Acetonitrile and methanol were of Chromatographic grade and bought from the TEDIA Company, United States. Beef peptone, beef extract powder, yeast extract powder, glucose and agar were of biochemical grade and purchased from Beijing AoBoXing Bio-Tech Co., Ltd. (China). Ultrapure water (18 MΩ cm⁻¹) was used in all experiments.

2.2. Synthesis of Fe₃O₄@TiO₂ microspheres (Fe₃O₄@TiO₂ MSs)

As shown in Fig. 1 (a) step 1, Fe₃O₄ microspheres (Fe₃O₄ MSs) with an average size of 350 nm were fabricated using the method introduced by C. Liu.³⁶ Fe₃O₄@TiO₂ microspheres (Fe₃O₄@TiO₂ MSs) were prepared through a sol-gel process. The Fe₃O₄ MSs were redisposed into a mixture of ethanol (40 mL) and ammonium hydroxide (0.3 mL, 28 wt. %) under ultrasound for 20 min. Then the dispersion was transferred into a flask and heated at 45 °C under stirring. A mixture of TBOT (0.8 mL)/ethanol (20 mL) was added into the suspension drop wise at a rate of 4 mL min⁻¹, and the sol gel process was allowed to proceed at 45 °C for 24 h. The resultant Fe₃O₄@TiO₂ core-shell microspheres were magnetically collected, washed with ultrapurewater and ethyl alcohol, and dried at 40 °C for 12 h.

2.3. Synthesis of sea urchin-like Fe₃O₄@TiO₂ nanocomposites (Fe₃O₄@TiO₂ NCs).
As shown in Fig. 1 (a) step 2, Fe$_3$O$_4$@TiO$_2$ NCs were fabricated through a modified hydrothermal method. The Fe$_3$O$_4$@TiO$_2$ core-shell microspheres were transferred into a Teflon-lined stainless-steel autoclave (100 mL) containing 10 mL of 1.0 M NaOH solution, and the system was hydrothermally treated. The powders were collected, washed with ultrapure water and ethyl alcohol, and dried at 40 °C for 12 h. Sea urchin-like corn-shell hollow Fe$_3$O$_4$@titanate nanocomposites (Fe$_3$O$_4$/titanate NCs) were obtained. In order to prepare anatase TiO$_2$ crystal, sea urchin-like Fe$_3$O$_4$@titanate hollow microspheres (0.1 g) were immersed in 10 mL 0.1 M HCl for 20 min, washed with ultrapure water until neutral and then subsequently annealed under N$_2$ at a rate of 0.5 mL min$^{-1}$ at 450 °C for 4 h to obtain Fe$_3$O$_4$@TiO$_2$ NCs.

2.4. Synthesis of sea urchin-like Fe$_3$O$_4$@TiO$_2$@Ag nanocomposites (Fe$_3$O$_4$@TiO$_2$@Ag NCs).

As shown in Fig. 1 (a) step 3, the Fe$_3$O$_4$@TiO$_2$@Ag NCs were synthesized via a photoreduction process under visible light. Initially, Fe$_3$O$_4$@TiO$_2$ NCs was added into 20 mL AgNO$_3$ aqueous solution (Ag$^+$ mass concentration 20 mg L$^{-1}$); then, the mixtures were shaken for 30 min in a reciprocal shaker with agitation rate of 100 rpm under visible irradiation, obtained by three multifilament lamps of 8 W with irradiation, at 25 °C. Agitation was provided by horizontal shaker. After illumination, Fe$_3$O$_4$@TiO$_2$@Ag NSs were collected, washed with ultrapure water and ethanol, and finally dried in vacuum at 40 °C for 12 h.

2.5. Characterization.

The morphology of the sample examined with a field emission scanning electron microscope (FESEM JSM-7100F), high-resolution transmission electron microscope (TEM FEIF20) equipped
with an energy dispersive X-ray (EDX). The crystallinity and phase of Fe$_3$O$_4$@TiO$_2$@Ag NSs was determined by X-ray diffraction (XRD, D8 Advanced, Bruker). UV-Vis diffuse reflectance spectra were conducted on a UV-Vis spectrophotometer (UV-3150, Shimadzu, Japan) attached with integrating sphere. Barium sulfate (BaSO$_4$) pellets were used as reference to measure the visible light absorption of Fe$_3$O$_4$@TiO$_2$@Ag NSs. Nitrogen sorption isotherms were carried out at 77 K using an Autosorb-1-C analyzer (USA Quantachrome Instruments), and the pore-size distributions were derived from the adsorption branch of the isotherms using the BJH method. The magnetic properties were measured with a vibrating sample magnetometer (VSM), Physical Property Measurement System-9, at 25°C as a function of the applied magnetic field between −12 and 12 kOe.

2.6. Photocatalytic Experiments.

The photocatalytic activities of the as-prepared Fe$_3$O$_4$ MSs, Fe$_3$O$_4$@TiO$_2$ NSs and Fe$_3$O$_4$@TiO$_2$@Ag NSs were evaluated by the degradation of AMP under ultraviolet and visible irradiation. AMP is a common antibiotic used in human and animal medicine, and is an amphoteric, beta-lactam of the penicillin class. 37 0.02g of the sample was dispersed within a 20 mL AMP solution with a concentration of 20ppm, which was stirred in the dark or light at 25°C in the process of reaction. Ultraviolet lamps (365 nm, 8 W) and visible lamps were used as the light source, which was placed 10 cm away from the reaction vessel. The photocatalytic reaction was started by turning on the lamp. All experiments were carried out at the natural pH of the solution (~7) and the process was maintained at a constant temperature controlled by a thermoregulator. The degradation of AMP was monitored by high performance liquid chromatography (HPLC) analysis.
Shimadzu, Japan) with a C$_{18}$ (5 µm, 4.6 mm×150 mm) column. Acetic acid (1 M), KH$_2$PO$_4$ buffer solution (1 M), acetonitrile and ultrapure water (v/v/v/v=1:10:80:909) was used as mobile phase, at a flow rate of 1 mL·min$^{-1}$. The detector wavelength was set as 220 nm and injection volume was 20 µL. The degradation rate of AMP could be calculated using Eq. (1) shown below.

\[
\text{Degradation rate (\%)} = \frac{C_0 - C_t}{C_0} \times 100\% \\
\text{Eq. (1)}
\]

Where $C_0$ and $C_t$ are the initial and final concentration (mgL$^{-1}$), respectively. The intermediate products of the photocatalytic degradation of AMP by Fe$_3$O$_4$@TiO$_2$@Ag NSs at different periods of exposure to light were investigated by high performance liquid chromatography-tandem mass spectrometry (LC-MS) analysis using acetonitrile/water as the eluent.

2.7. Mineralization studies by TOC analysis. The mineralization of Fe$_3$O$_4$@TiO$_2$@Ag NSs for AMP was studied by measuring the total organic carbon (TOC) contents of AMP solution after the degradation with different time spans using a TOC analyzer (TOC-L CPH, Shimadzu, Kyoto, Japan). The corresponded concentrations were also monitored for comparison by HPLC analysis at the wavelength of 220 nm.

2.8. Antibacterial Tests. In general, suspensions (40 mL) of the as-prepared photocatalyst nanoparticles (0.04 g) were uniformly dripped by ultrasonic dispersion onto filter papers (Φ5 mm) separately. After being dried in air, the filter papers were then placed onto the bottom of a Petri dish for antibacterial experiments. The characteristics of different Antibacterial Films are showed in Table S3. Control samples were prepared using filter paper without loading any nanoparticles. Antibacterial activities were evaluated using Gram-negative Escherichia coli (E. coli, ATCC 8099), Gram-positive staphylococcus aureus (S. aureus, ATCC 6538), and a common mycosis-Candida
albicans (*Asper. Niger*, ATCC 16404). Before the microbiological experiments, all glasswares were sterilized by autoclaving at 120 °C for 30 min. *E. coli* and *S. aureus* suspensions (0.2 mL, $10^4$-$10^5$ CFU mL$^{-1}$) were spread on the surface of LB plates, and *Asper. Niger* suspensions ($10^4$-$10^5$ CFU mL$^{-1}$) on the surface of YPD plates, then, antibacterial and blank films were placed on the plates. The plates were incubated at 37 °C under visible light for 24 h. All tests were performed in triplicate, and the results were averaged.

3. Results and discussion

3.1. Controllable synthesis of Fe$_3$O$_4$@TiO$_2$@Ag NCs

3.1.1. Synthesis of Fe$_3$O$_4$@TiO$_2$@Ag NCs

![Diagram](attachment:Figure_1.png)

**Fig. 1** Formation of Fe$_3$O$_4$@TiO$_2$@Ag NCs. Proposed mechanism can be considered as three steps: (1) formation of Fe$_3$O$_4$@TiO$_2$ core-shell microspheres; (2) formation of TiO$_2$ nanofiber and yolk-shell hollow shell; (3) coating
of Ag nanoparticals. a-d) TEM images of Fe$_3$O$_4$ MSs (a) Fe$_3$O$_4$@TiO$_2$ MSs (b), Fe$_3$O$_4$@TiO$_2$ NCs (c), Fe$_3$O$_4$@TiO$_2$@Ag NCs (d); e-h) FESEM images of Fe$_3$O$_4$ MSs (e) Fe$_3$O$_4$@TiO$_2$ MSs (f) Fe$_3$O$_4$@TiO$_2$ NCs (g), Fe$_3$O$_4$@TiO$_2$@Ag NCs(h)

Fig. 1 illustrates the diagrammatic sketch of the synthesis of Fe$_3$O$_4$@TiO$_2$@Ag NCs. (a), and shows the corresponding TEM images (b-e) and FESEM images (f-i), different nanostructures. In step (1), the diameter of Fe$_3$O$_4$ microspheres, Fe$_3$O$_4$ MSs, was approximately 350 nm as shown in Fig. 1b, and the magnetic core ensures the easy separation of nanocomposites from reactant mixture. A uniform interlayer of TiO$_2$ with a thickness of about 80 nm was coated onto Fe$_3$O$_4$ MSs through a controlled sol-gel process to formation Fe$_3$O$_4$@TiO$_2$ core-shell microspheres, Fe$_3$O$_4$@TiO$_2$ MSs as in Fig. 1c. Fe$_3$O$_4$ MSs and Fe$_3$O$_4$@TiO$_2$ MSs were monodispersed uniformly in size as in Fig. 1f,g. In step (2), Fe$_3$O$_4$@TiO$_2$NCs with diameter of approximately 700nm was synthesized by a modified hydrothermal method, and its shell consists of radically assembling nanofibers with average diameter of 10 nm and average length of 100 nm as in Fig. 1d. The formation of radial nanofiber structure can be explained as that, when the Fe$_3$O$_4$@TiO$_2$ MSs were immersed in alkaline solution, the alkaline solution permeated into the inner cavity, which is benefited by the porous of the TiO$_2$ shell. Simultaneously, titanate appeared on the interface of the TiO$_2$ layer from the interaction between the OH$^-$ ions and amorphous TiO$_2$. As the reaction prolonged, the TiO$_2$ layer was etched from its interior and exterior surfaces, and sodium titanate gradually generated on the surface of the layer. Then the TiO$_2$ layer was exhausted and the outer cavity in situ appeared. As the sodium titanate grew from short nanowires to long nanofibers, the sea urchin-like yolk-shell structure of double shells was fabricated. The process, that the tiny sodium titanate seeds were dissolved and recrystallized into large and long sodium titanate nanofibers, can be attributed to Ostwald ripening.
There was no damage on three dimensional structure during the formation of the structure of both radial and uniform TiO$_2$ nanofibers and novel shells as in Fig. 1h. In step (3), the structure of Fe$_3$O$_4$@TiO$_2$@Ag NCs with a Fe$_3$O$_4$ magnetic core and a shell of TiO$_2$/Fe$_3$O$_4$/Ag nanoheterojunctions nanofiber were formatted. The diameter of Fe$_3$O$_4$@TiO$_2$@Ag NCs remained approximately 700 nm, and the nanofibers on the surface became a little shorter and thicker after coating with Ag nanoparticle as in Fig. 1e. The surface appearance of Fe$_3$O$_4$@TiO$_2$@Ag NCs remained about the same with Fe$_3$O$_4$@TiO$_2$ NCs Fig. 1i.

3.1.2. Influence of hydrothermal time on Fe$_3$O$_4$@TiO$_2$@Ag NCs

![Fig. 2 Effect of hydrothermal time on Fe$_3$O$_4$@TiO$_2$@Ag NCs for 1h (a), 2h (b), 3h (c).](image)

Hydrothermal time normally has a great effect on the morphology of nanomaterial. TEM images of nanofibers and hollow shells with different structures were created by hydrothermally treating the as-synthesized Fe$_3$O$_4$@TiO$_2$ MCs in a hydroxide solvent sodium at various hydrothermal times as displayed in Fig. 2. The porosity of the nanocomposite was enhanced and the hybrid shell on the microsphere was getting longer and thicker nanofibers, as the hydrothermal time changed from 1h, to 2h, to 3h under otherwise identical conditions. After 1 h reaction, short and thin
hybrid nanofibers were formed with about 50 nm in length and 2 nm in diameter as shown in Fig. 1. More hybrid nanofibers grew to the size of approximately 100 nm in length and 10 nm in diameter, and yolk–shell morphologies were observed after 2 h reaction as in Fig. 2b. Compared with reported methods, for instance, a SiO$_2$ sandwich layer method,$^{27,28}$ the presence of a hollow provided a novel approach to inhibit the oxidation of the Fe$_3$O$_4$ core by the holes photogenerated in the outer layer TiO$_2$. After 3 h reaction, the nanofibers in the outer shell still grew to possess an average diameter of 20 nm and length of 150 nm, however, leaving the yolk–shell hollow morphologies almost disappear as in Fig. 2c. The result was further confirmed in the FESEM images as in Fig. S1, Supporting Information. It can be seen that the fiber-like nanocrystals on the shells were formed after 1 h; as the reaction continued, the crystallization extended into the internal layer to yield a considerable amount of nanocrystals, and this was accompanied by the continuous growth of the superficial nanofiber crystals.

It has been proved that the hydrothermal time not only promoted the crystal growth of the surface, but also facilitated the formation of the homogenously structured porous shell. The mesoporous hollow shell was created by hydrothermally treating the as-synthesized Fe$_3$O$_4$@TiO$_2$ MSs with NaOH as porosity modifier. The shells appeared to have different controllable pore feature. Specific surface area and average pore size were measured by N$_2$ adsorption–desorption experiments with the samples, and the results are shown in Table S1 (Supporting Information). When the hydrothermal treating time was 1 h, the abundant disordered micro-mesoporous were observed on the shells of nanocomposites; more mesoscale porous-looking shells became significant as the reaction time increased, which is good for the adsorption of organic contaminant and heavy metal ion.$^{30}$ As the pore size of the Fe$_3$O$_4$@TiO$_2$@Ag NSs increases along with the
growth of crystallite, there is a constant decrease in surface area. Considering the specific structure after 2h hydrothermal treatment, it was selected for further studies.

3.1.3. Influence of hydrothermal temperature on Fe₃O₄@TiO₂@Ag NCs

Fig. 3 - Effect of hydrothermal temperature reaction 2 h for 120°C (a), 140°C (b), and 160°C (c).

In addition to hydrothermal time, hydrothermal temperature also had a great effect on the structures of the Fe₃O₄@TiO₂@Ag NCs, and TEM images were also displayed in Fig. 3. Different volumes of hollow shells were fabricated by hydrothermally treating the as-synthesized Fe₃O₄@TiO₂ MCs in a hydroxide solvent sodium at various hydrothermal temperatures. As the reaction continued, the volume of nanospheres went up gradually due to the dramatic increase of the hollow volume in TiO₂/Ag shells. The diameters of Fe₃O₄@TiO₂@Ag NCs were respectively 700 nm, 905 nm, 1012 nm after hydrothermally treating at 120 °C, 140 °C and 160 °C. As can be seen from FESEM images, there are no significant differences on the surface morphology of Fe₃O₄@TiO₂@Ag NCs at various hydrothermally temperatures (Fig. S2). The nanostructures after 2h hydrothermal treating at 120°C was selected as photocatalysts in this study.
3.2 Characterization

3.2.1 HRTEM and elemental mapping

To confirm the distribution of Fe$_3$O$_4$@TiO$_2$@Ag NCs, samples were analyzed by EDX elemental mapping as in Fig. 4. The different color areas, shown in Fig. 4b–e, indicate O–, Fe–, Ti–, and Ag-enriched areas of the sample respectively. It showed that the well-dispersed of TiO$_2$ nanofiber of the hollow cavities and Ag nanoparticles are loaded both on the nanofibers and inside the hollow cavities, and the structure of Fe$_3$O$_4$@TiO$_2$@Ag NCs with a Fe$_3$O$_4$ magnetic core and a TiO$_2$/Fe$_3$O$_4$/Ag nanoheterojunctions shell with hollow cavity were further conformed. In conclusion, high-density TiO$_2$ and Ag NPs have been immobilized on the surface of Fe$_3$O$_4$ MSs and Fe$_3$O$_4$@TiO$_2$ NCs, respectively. The content of Ag NPs in the Fe$_3$O$_4$@TiO$_2$@Ag NCs is 2.1wt. %. The mesoporous characteristic and large surface area improved the effective contact area with Ag nanoparticals, and the excellent photocatalytic properties of TiO$_2$ nanofiber and shell provided a favorable environment for coating Ag both on the nanofibers and inside the hollow cavities as in Fig. 4e. While Fe$_3$O$_4$ on shell may come from the Fe$_3$O$_4$ magnetic core during modified hydrothermal method, which was further confirmed by HRTEM image of Fe$_3$O$_4$@TiO$_2$ NCs and Fe$_3$O$_4$@TiO$_2$@Ag NCs in Fig. 4f. After synthesis of Fe$_3$O$_4$@TiO$_2$ NCs, there were trace amount of Fe$_3$O$_4$ nanoparticals modified on the TiO$_2$ nanofibers. Meanwhile, Ag nanoparticles were found in size of about 4 nm uniformly in the HRTEM image of heterozygosis nanofiber. The interplanar spacing of 0.352 nm corresponds to the [110] plane of TiO$_2$, the 0.256 nm corresponds to the [311] plane of Fe$_3$O$_4$, while 0.226 nm correspond to the [111] plane of Ag in Fig. 4g. The pattern shows rings that may be indexed to the [311] and [440] lattice planes of Fe$_3$O$_4$ (JCPDS File No.19-0629),
[101], [440], [105] plans of TiO$_2$ (JCPDS card No. 37-0951), and [111] plane of Ag (JCPDS card no.04-0783). Electron mapping image were analyzed, the different color areas shown in parts h–j of Fig. 4 indicate Fe−, Ti−, and Ag-enriched areas of the sample, respectively, which indicate the coexistence of TiO$_2$ and Ag as well as Fe$_3$O$_4$ in the hollow cavities and heterozygosis nanofiber.

**Fig. 4** a) TEM image of Fe$_3$O$_4$@TiO$_2$@Ag NCs; b–e) elemental mapping of the Fe$_3$O$_4$@TiO$_2$@Ag NCs from the TEM images based on O (b), Fe (c), Ti (d) and Ag (e); f) Nanofibers enlarged portion of Fe$_3$O$_4$@TiO$_2$@Ag NCs, the inset on the left is nanofibers of Fe$_3$O$_4$@TiO$_2$ NCs; g) HRTEM image of TiO$_2$/Fe$_3$O$_4$/Ag heterojunction, the inset on the right is the selected area electron diffraction (SAED) pattern. h–j) elemental mapping of the TiO$_2$/Fe$_3$O$_4$/Ag nanofiber from TEM images based on Fe (h), Ti (i) and Ag (j).

### 3.2.2 Elemental compositions analysis with XRD and XPS

To prove the successful synthesis of Fe$_3$O$_4$@TiO$_2$@Ag heterozygosis, their elemental compositions and chemical status were analyzed by XRD and XPS. The change of crystal structures during the synthesis process of Fe$_3$O$_4$@TiO$_2$@Ag NCs was studied by XRD as in Fig. 5a. Wide angle XRD patterns show that the characteristic broad diffraction peaks correspond to the spinel Fe$_3$O$_4$, titanate, anatase TiO$_2$ and cubic phase Ag NPs in the composite. The specific XRD of Fe$_3$O$_4$...
is characterized by six peaks positioned at the 2θ values of 30.0°, 35.3°, 42.9°, 53.5°, 57.0° and 62.4°, which correspond to the [220], [311], [400], [422], [511], and [440] lattice planes of the cubic phase of Fe₃O₄ (JCPDS card No. 19-0629), respectively. After hydrothermal treatment, the peaks at 2θ values of 24.38°, 29.95° and 47.86° correspond to the reflections from the [110], [-501], [-314] planes and demonstrate the formation of the titanate phase (JCPDS card No. 37-0951), which yielded from the reaction of TiO₂ with the alkaline solution. It is possible that some oligomeric species of sodium titanate may be produced during NaOH etching. Although sodium titanate has a number of applications, its photocatalytic activity is considerably lower than that of anatase phase titania, and therefore, it is not a desirable phase in our synthesis. After acid-treatment and calcination, the patterns of the Fe₃O₄@TiO₂ NCs show several additional peaks compared with the patterns of Fe₃O₄/titanate NCs, which can be attributed to the anatase phase of TiO₂, whose photocatalytic activity is considerably high. The extra peaks located at 25.3°, 37.9°, 48.0° and 53.9° correspond to the reflections from the [101], [004], [200], and [105] planes of the anatase phase (JCPDS card no. 21-1272). After loading the Ag NPs on the surface of the Fe₃O₄@TiO₂ MS, several characteristic peaks are found at 2θ of 38°, 44°, 65° and 77°, which are ascribed to the [111], [200], [220] and [311] planes of face-centered cubic Ag phase (JCPDS card no.04-0783). These are in agreement with the SAED patterns as shown in Fig. 4g. The characteristic XRD patterns of Fe₃O₄@TiO₂@Ag NCs imply that the current system is suitable for the synthesis of anatase phase.

Compared with Fe₃O₄@TiO₂ NCs, new peaks of Ag were found in Fe₃O₄@TiO₂@Ag NCs in addition to the Ti, O, and C elements based on XPS survey spectra shown in Fig. 5b, and the surface concentration of C, O, Fe, Ti and Ag elements were 22.59 %, 56.62 %, 1.47 %, 18.22 %, 1.11% respectively. The samples contained Fe in Fig.5c, were confirmed by the binding energies of Fe
2p\textsubscript{3/2} and 2p\textsubscript{1/2} at \( \sim 710 \) eV and \( \sim 724 \) eV, respectively. These binding energies can be assigned to Fe\textsubscript{3}O\textsubscript{4}. Meanwhile, it showed the signals of Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} at \( \sim 458 \) eV and \( \sim 464 \) eV in Fig. 5d respectively, corresponding to TiO\textsubscript{2}. It can be observed that the surface concentration of O is relatively high, due to TiO\textsubscript{2} coating. Metallic Ag loading can be confirmed by the presence of the signals of Ag 3d\textsubscript{5/2} and Ag 3d\textsubscript{3/2} at 368.5 eV and 374.5 eV in Fe\textsubscript{3}O\textsubscript{4}@TiO\textsubscript{2}@AgNCs as shown in Fig. 5e respectively.
Fig. 5 a) XRD patterns of Fe$_3$O$_4$ MSs, Fe$_3$O$_4$/titanate NSs, Fe$_3$O$_4$@TiO$_2$ NCs and Fe$_3$O$_4$@TiO$_2$@Ag NCs; b) Survey scan of Fe$_3$O$_4$@TiO$_2$ NCs and Fe$_3$O$_4$@TiO$_2$@Ag NCs; c) Fe$2p$ high-resolution XPS spectra; d) Survey scan of Ti$2p$ high-resolution XPS spectra; e) Ag$3d$ high-resolution XPS spectrum of Fe$_3$O$_4$@TiO$_2$@Ag NCs; f) UV-vis absorption spectra of TiO$_2$, Fe$_3$O$_4$ MSs, Fe$_3$O$_4$@TiO$_2$ NCs and Fe$_3$O$_4$@TiO$_2$@Ag NCs; g) Kubelka-Munk plot for the estimation of the band-gap energies of TiO$_2$ and Fe$_3$O$_4$@TiO$_2$@Ag NCs; h) Schematic diagrams for the possible photocatalytic mechanism of Fe$_3$O$_4$@TiO$_2$@Ag NCs.

3.2.3 UV-vis diffuse reflectance spectra analysis

The UV-vis diffuse reflectance spectra for TiO$_2$, Fe$_3$O$_4$ MSs, Fe$_3$O$_4$@TiO$_2$ NCs and Fe$_3$O$_4$@TiO$_2$@Ag NCs were showed in Fig. 5f. The Fe$_3$O$_4$@TiO$_2$ NCs and Fe$_3$O$_4$@TiO$_2$@Ag NCs photocatalyst presented an enhanced adsorption in the visible region from 400 to 600nm. Pure TiO$_2$ had a broad intense adsorption in the UV region below 400 nm. The band-gap energy was calculated by the Kubelka-Munk (KM) method.$^{42}$ The band-gap energy value, $E_g$, was determined using the theory of optical adsorption for allowed direct transitions as in Eq. (2).

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$  \(2\)

Where $A$ is a constant relative to the material, $h\nu$ is the discrete photon energy, and $\alpha$ is the adsorption coefficient for the characterization of optical absorption edge energy and could be calculated from the diffuse reflectance data using the KM method. The $E_g$ value can be obtained by extrapolating a linear fit of $(\alpha h\nu)^2$ against $h\nu$ to zero. It is observed that the band-gap energy of pure TiO$_2$ is from 3.0eV to 3.2eV, while the Fe$_3$O$_4$@TiO$_2$@Ag NCs presents even lower band energy with the values of 1.5eV as shown in Fig. 5g. It has been reported by Kamat,$^{43}$ that the electrons can be transferred from the excited TiO$_2$ to the metallic nanoparticles that work as co-catalysts until the two systems attain an equilibrium. When Fe$_3$O$_4$ cocatalyst and Ag nanoparticles are
simultaneously deposited on the surface of $\text{Fe}_3\text{O}_4@\text{TiO}_2@\text{Ag}$ NCs, it is clearly found that the photocatalytic performance of resulting $\text{TiO}_2/\text{Fe}_3\text{O}_4/\text{Ag}$ heterojunction has been further improved, which can be well explained by the synergistic effect of Fe (III) and Ag nanoparticles.\textsuperscript{44,45} The loading of Ag nanoparticles leads to the production of more photogenerated charges in $\text{TiO}_2/\text{Fe}_3\text{O}_4/\text{Ag}$ heterojunction via LSPR absorption of Ag nanoparticles, and enhances band-gap absorption of $\text{TiO}_2$, while the Fe(III) cocatalyst provides as active sites for oxygen reduction by the effective transfer of photogenerated electrons to oxygen(Fig.5h).\textsuperscript{44-46} The electron accumulation increases the Fermi level of the heterojunction to more negative potentials; the resultant Fermi level of the composite shifts closer to the conduction band of the semiconductor. Therefore the involved edge energy $E_g$ in the electron transfer from $\text{TiO}_2$ to the heterojunction is lower than bare $\text{TiO}_2$, which provide strong visible-light sensitization. As a result, enhanced photocatalytic activity is realized in $\text{Fe}_3\text{O}_4@\text{TiO}_2@\text{Ag}$ NCs.

3.2.4 $\text{N}_2$ adsorption/desorption isotherms

Fig. 6 a) Nitrogen adsorption-desorption isotherms and the corresponding Barrett–Joyner–Halenda (BJH) pore
diameter distribution curve (inset) of Fe₃O₄ MSs, Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs; b) Magnetization curves of the Fe₃O₄ MSs, Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs, respectively. The inset is a photograph before and after magnetic separation.

Fig. 6a exhibits the N₂ adsorption/desorption isotherms and pore diameter distribution curves of Fe₃O₄ MSs, Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs. The isotherms of Fe₃O₄ are type III, showing little or no pore on the Fe₃O₄ surface morphology. The average pore diameter obtained via the BJH method from the adsorption branch is 4.733 nm. The surface area and the total pore volume are 46.039 m² g⁻¹ and 0.4571 cm³ g⁻¹. The isotherms of Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs are type-IV with H₂ hysteresis loops, suggesting mesoporous characteristic. The average pore diameter obtained via the BJH method from the adsorption branch is 9.057 nm, the surface area and the total pore volume are 125.349 m² g⁻¹ and 0.4434 cm³ g⁻¹, respectively. After coating with Ag nanoparticles, the surface area is increased to 131.175 m² g⁻¹, while the average pore diameter and total pore volume decrease to 6.821 nm and 0.399 cm³ g⁻¹, respectively.

2.2.5 Magnetic behavior

Fig. 6b shows the magnetic hysteresis loops of Fe₃O₄ MSs, Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs at room temperature. As can be seen, they exhibit superparamagnetic behavior, little hysteresis, remanence and coercivity, as the particles were composed of ultrafine magnetite nanocrystals. The magnetization of Fe₃O₄ MSs, Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs is about 40.1 emu·g⁻¹, 34.5 and 26.5 emu·g⁻¹, respectively. The decrease in magnetization is mainly due to the density decrease of Fe₃O₄ in the obtained composites after being...
coated with TiO$_2$ and Ag. However, the Fe$_3$O$_4$@TiO$_2$@Ag NCs still show strong magnetization, which suggests their suitability for magnetic separation. The superparamagnetic characteristic and high magnetization facilitate catalyst recovery from catalytic system via an external magnetic field as in Fig. 5b inset.

3.3 Photocatalytic Activities

3.3.1 Photocatalytic degradation of AMP

**Fig. 7** a) The ball-and-stick mode of AMP; b) Schematic illustration of the adsorption, degradation and recyclable process of Fe$_3$O$_4$@TiO$_2$@Ag NSs; c) Adsorption of AMP in dark and photocatalytic degradation of AMP under UV light; d) Photocatalytic degradation of AMP under visible light. [AMP]$_0$ = 20 mg L$^{-1}$ and [Photocatalysts] = 1 mg L$^{-1}$.

As a common penicillin-class veterinary and human antibiotic, ampicillin (AMP) was chosen as the model organic pollutant because antibiotic contaminants, as bio-refractory organics, show the
adverse effects on human, animal, and indigenous microbial communities as in Fig. 7a. Photocatalytic performances of Fe₃O₄ NSs, Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs were comparatively evaluated by measuring the degradation of AMP aqueous solution under ultraviolet and visible irradiation. Fig. 7b shows the schematic illustration of the adsorption, degradation and recyclable process of Fe₃O₄@TiO₂@Ag NCs. It can be seen that the degradation rates increase with the increase of irradiation time for all samples as in Fig. 7c, d.

As showed in Fig. 7c, it is clearly observed that the Fe₃O₄@TiO₂ NSs displays a good photocatalytic effect, and the decoration of Fe₃O₄@TiO₂ NCs with Ag nanoparticles is an effective way to achieve higher catalytic efficiency, since the Ag loaded samples show higher photocatalytic activity than that with Fe₃O₄@TiO₂ NCs only. After 180min of ultraviolet irradiation, the degradation rates reach 90.6% for Fe₃O₄@TiO₂@Ag NSs, while 69.4% for Fe₃O₄@TiO₂ NCs; and after 360min, the degradation rates reach 98.7% for the Fe₃O₄@TiO₂@Ag NCs, while 77.0% for Fe₃O₄@TiO₂ NCs. The dependences of adsorption rates with time in dark are also revealed in Fig. 6c, they all reach the absorption equilibrium after 180min, which further confirms that there is no significant difference of mesoporous characteristic between Fe₃O₄@TiO₂ NCs and Fe₃O₄@TiO₂@Ag NCs.

Fig. 7d shows the photocatalytic activity of different catalysts evaluated by the degradation of AMP under visible light irradiation. The relative photocatalytic activity of the catalysts for AMP degradation follows the order: Fe₃O₄@TiO₂@Ag NCs > Fe₃O₄@TiO₂ NCs > Fe₃O₄ MSs. In the absence of catalysts, there was a slight photodegradation of AMP. Under 360min visible light irradiation, the degradation rate of Fe₃O₄@TiO₂@Ag NCs is above 91.5%, while that of Fe₃O₄@TiO₂ MCs is 78%, and 29% the Fe₃O₄ MSs. The results indicate that Fe₃O₄@TiO₂@Ag
NCs has a better photocatalytic activity under visible light for the decomposition of AMP. The higher activity is due to the enhanced photocatalytic activity as analyzed before. The observed photocatalytic performance is better than that of most reported nanostructures, especially for visible photocatalytic activity, which has been summarized in Table 1.
<table>
<thead>
<tr>
<th>Catalyst used and amount</th>
<th>Conc. and volume</th>
<th>Light</th>
<th>Time(min)</th>
<th>Degradation%</th>
<th>BET($m^2g^{-1}$)</th>
<th>Magnetic properties(emu)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$@TiO$_2$@Ag (1mg mL$^{-1}$)</td>
<td>20mg L$^{-1}$</td>
<td>8W*3, 180(UV)</td>
<td>90.7(UV)</td>
<td>131.175</td>
<td>19.376</td>
<td>our work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AMP</td>
<td>UV/Vis</td>
<td>360(Vis)</td>
<td>92.1(Vis)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$@TiO$_2$@Au (50mg)</td>
<td>2.0 *10$^{-5}$M, 150mL</td>
<td>500W</td>
<td>50</td>
<td>100</td>
<td>50-60</td>
<td>26.5</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>R6G</td>
<td>UV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$_2$O/TiO$_2$ (40mg)</td>
<td>10$^{-5}$M,40mL</td>
<td>40W</td>
<td>15,30</td>
<td>93,100</td>
<td>57.9</td>
<td>_____</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>UV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclodextrin-Fe$_3$O$_4$@TiO$_2$ (1 mg mL$^{-1}$)</td>
<td>20 mg L$^{-1}$</td>
<td>Hg Light</td>
<td>180</td>
<td>95</td>
<td>_____</td>
<td>28</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>BPA</td>
<td>UV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$@rGO@TiO$_2$ (1.5g L$^{-1}$)</td>
<td>10 mg L$^{-1}$</td>
<td>300 W</td>
<td>150</td>
<td>~90</td>
<td>_____</td>
<td>34.202</td>
<td>50</td>
</tr>
</tbody>
</table>

| MB | UV |

Table 1. Performance of Photocatalytic Activity in Literature
2.3.2 Photocatalytic degradation products analysis

**Fig. 8.** Photocatalytic degradation of Ampicillin by Fe$_3$O$_4$@TiO$_2$@Ag NCs. a) LC-MS chromatograms for different visible irradiation times at the pH of 7. Ampicillin and byproducts with different retention times are also indicated; b) Evolution of photodegradation products of Ampicillin vs irradiation time; c) TOC and concentration changes of APM solution along different treatment times. [AMP] $0 = 20$ mg L$^{-1}$ and [Photocatalysts] = 1 mg L$^{-1}$. d) The molecular species corresponding to the different m/z ions.
The intermediate products of AMP photocatalytic degradation by Fe$_3$O$_4$@TiO$_2$@Ag NCs at different periods of exposure to light were investigated by LC-MS analysis with methanol/water as the eluent. The chromatograms for the degradation of AMP within seven different UV exposure times are shown in Fig. 8a. The products at different retention times were mass-analyzed in the positive ion mode, and their evolutions with irradiation time are displayed in Fig. 8b. The seven main product ions depicted in the degradation of AMP are $m/z$ 368, 333, 324, 307, 289, 184 and 124. The Ampicillin parent ($m/z$=350, retention time=5.3 min) observed in the chromatograms at short exposure times is identified. After 300 min of UV exposure, this cannot be observed any more in the chromatograms. Ions with molecular weights of $m/z$ 368 and 333 observed in Fig. 7b recorded after 60 min irradiation suggest that the first step in the photocatalytic degradation is the reaction of hydroxyl radicals with the side chain C-N bond of AMP. It has been illustrated that there are two potential pathways for the formation of AMP byproducts observed in solutions mixed with Fe$_3$O$_4$@TiO$_2$@Ag NCs (pH=7). Path 1 starts with the formation of penicilloic acid, is followed by decarboxylation, possibly via the attachment of primary COO$^-$ group or carboxylic acid moiety formed by opening beta-lactam ring. Path 2 begins with the de-ammonification of parent AMP, yielding a byproduct of $m/z = 333$. Subsequent decarboxylation ($m/z = 289$), followed by hydrolysis, would also yield the species of $m/z = 307$. It has been further discovered in our study that the amount of byproduct $m/z = 123$, increases significantly after 4 h photocatalytic degradation.

Antibiotic concentration decrease cannot reflect the mineralization extent of organic species because of the formation of some intermediates during the photocatalytic degradation process, which could also result in the decrease of antibiotic concentration. The mineralization effects of Fe$_3$O$_4$@TiO$_2$@Ag NCs for AMP were further studied by recording the TOC contents of AMP.
solution as well as the mass concentration at different times as in Fig. 7c. After treatment with Fe$_3$O$_4$@TiO$_2$@Ag NCs for 720 min, AMP concentration decreased about 99%, while TOC removal rate was less than 46%, which indicates that complete mineralization was a relatively slow process compared with the degradation of AMP molecules. So, longer treatment time would be required to obtain proper TOC removal efficiency.

3.3.3 Recycled performances

![Graph showing efficiency variation of Fe$_3$O$_4$@TiO$_2$@Ag NCs for photocatalytic degradation of Ampicillin with cycling under UV light.](image)

**Fig. 9 a)** Efficiency variation of the Fe$_3$O$_4$@TiO$_2$@Ag NCs for the photocatalytic degradation of Ampicillin with cycling under UV light. [AMP]$_0$ = 20 mg L$^{-1}$ and [Photocatalysts] = 1 mg L$^{-1}$; **b)** HRTEM image of Fe$_3$O$_4$@TiO$_2$@Ag NCs after six cycles

Important considerations for the application of photocatalytic nanomaterials in water remediation are their separation and reusability. The photocatalytic efficiency of the Fe$_3$O$_4$@TiO$_2$@Ag NCs for multiple usages was investigated. The Fe$_3$O$_4$@TiO$_2$@Ag NCs, which were magnetically separated from the dispersion after the photocatalytic degradation of AMP, were reused for the photodegradation of a freshly prepared AMP solution as in Fig. 7b. As mentioned
earlier in the experiments, the AMP concentrations were determined by liquid chromatography and the visible exposure time was 360 min. The Fe₃O₄@TiO₂@Ag NCs were again magnetically separated and the experiments repeated. The results of photodegradation studies are shown in Fig. 9a. It can be seen that the efficiency of the Fe₃O₄@TiO₂@Ag NCs for the photocatalytic degradation of AMP still maintains 95% efficiency, even after 5 cycles. The HRTEM image of the Fe₃O₄@TiO₂@Ag NCs, which had been used for five times shown in Fig. 9b, also proves the stability of synthesized catalysts.

3.4 Photocatalytic Antibacterial Characteristics

As showed in Fig. 10, the antimicrobial activity of Fe₃O₄@TiO₂@Ag NCs was assessed by the diameter of inhibition zone (DIZ) test with *S. aureus* (G⁺), *E. coli* (G⁻) and *Asper. Niger* (pathomycete) as the representative microorganisms. Robust growth of *S. aureus*, *E. coli* and *Asper. Niger* was vividly observed in control experiments. The *S. aureus*, *E. coli* and *Asper. Niger*, approximately 10⁴ CFU mL⁻¹, were spread on the surface of an LB or YPD plate. Same as the control, Fe₃O₄@TiO₂ NCs and filter paper had no considerable antibacterial activity under visible
light, indicating that these material are not toxic to the microorganisms. Under visible light, Fe$_3$O$_4$@TiO$_2$ NCs did not show antimicrobial activities because TiO$_2$ could not be activated by visible light. Unlike the former case, the Fe$_3$O$_4$@TiO$_2$@Ag NCs showed a palpable DIZ value, indicating significant antibacterial activity against *S. aureus*, *E. coli* and *Asper. Niger*. The average DIZ values for *S. aureus* and *Asper. Niger* are 14 mm and 10 nm respectively, while the corresponding value for *E. coli* is merely 20 mm. It suggests that Fe$_3$O$_4$@TiO$_2$@Ag NCs have more effective contact biocidal property for *E. coli*. It can be hence predicated that excellent biocidal function of Fe$_3$O$_4$@TiO$_2$@Ag NCs is derived from Ag species and oxidative stress caused by photo-generated reactive radicals.

3. Conclusion

In summary, the sea urchin-like Fe$_3$O$_4$@TiO$_2$@Ag nanocomposites were successfully fabricated by controllable synthesis. It has been illustrated that a Fe$_3$O$_4$ core and a nanofiber shell of TiO$_2$/Ag nanoheterojunctions exist in sea urchin-like yolk-shell Fe$_3$O$_4$@TiO$_2$@Ag nanocomposites. These nanocomposites possess tunable cavity size, adjustable shell layers with various morphologies nanofibers, high structural stability and large specific surface area. The Ag nanoparticles of approximately 1 nm in diameter were loaded both on the TiO$_2$ nanofibers and inside the cavities of sea urchin-like Fe$_3$O$_4$@TiO$_2$ nanocomposites uniformly. Furthermore, the Fe$_3$O$_4$ magnetic core facilitates the convenient recovery of the catalyst by applying an external magnetic field. Sea urchin-like Fe$_3$O$_4$@TiO$_2$@Ag NCs displays excellent activities under UV and visible light and recycling properties in the catalytic reduction of organic molecules, such as Ampicillin, and it presents excellent broad-spectrum antibiosis under visible-light irradiation. It can be expected that the modified hydrothermal strategy combine with a calcination strategy provides a
very powerful method for controlling the morphology and porosity of sea urchin-like Fe$_3$O$_4$@TiO$_2$@Ag nanocomposites and for improving photocatalytic activity. Moreover, it should be point that the platform can decorate a variety of heavy metal nanoparticles material has certain novelty.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors express their thanks for the supports from the National Natural Science Foundation of China (21525625), the National Basic Research Program (973 Program) of China (2014CB745100), the (863) High Technology Project (2013AA020302), the Project sponsored by SRF for ROCS, SEM (LXJJ2012-001), the Chinese Universities Scientific Fund (JD1417).

References

3. J. Tang, Z. Huo, S. Brittman, H. Gao, P. Yang, Nat. Nanotechnol. 2011, 6, 568; W. Zhou, T. Li,  
   J.Wang, Y. Qu, K. Pan, Y. Xie, G. Tian, L. Wang, Z. Ren, B. Jiang, H. Fu, Nano Res. 2014, 7, 731;  


37 J. W. Peterson, L. J. Petrasky, M. D. Seymour, R. S. Burkhart, A. B. Schuiling, *Chemosphere* 2012, **87**(8), 911.


