Magnetic mesoporous TiO$_2$ microspheres for sustainable arsenate removal from acidic environments†

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Carcinogenic arsenic pollution in ground water seriously threatens the health and lives of humans all over the world. It is highly desirable to fabricate new materials for sustainable arsenate removal with high capacities, stabilities and recyclabilities. In this study, we demonstrate that uniform magnetic core–shell structured Fe$_3$O$_4$@Resorcinol-Formaldehyde@mesoporous TiO$_2$ microspheres (denoted Fe$_3$O$_4$@RF@mTiO$_2$) can function as excellent adsorbents for the fast removal of arsenate (As$^{V}$) in acidic environments with very high efficiency. The mesoporous TiO$_2$ outer shell (50 nm in thickness) endows them with a high surface area of 337 m$^2$ g$^{-1}$ and a large pore volume of 0.42 cm$^3$ g$^{-1}$, thus resulting in a fast adsorption rate (1.16 g mg$^{-1}$ h$^{-1}$) and a high adsorption capacity (up to 139 mg g$^{-1}$) calculated using the Langmuir model at a pH of 3. The inner Fe$_3$O$_4$ core (130 nm in diameter) makes separation facile from wastewater using a magnet. Moreover, the hydrophobic properties of the RF interlayer (10 nm in thickness) are increased after calcination at 200 °C, and this can protect the inner Fe$_3$O$_4$ cores against etching from acid solutions over long cycles. In addition, the study of the As$^{V}$ adsorption mechanism on the core–shell mesoporous Fe$_3$O$_4$@RF@mTiO$_2$ microspheres shows the existence of electrostatic forces and surface complexation interactions between arsenate and partially crystallized TiO$_2$. Benefiting from all of these advantages, the multilayer magnetic core–shell structured design is expected to be a promising nanomaterial for long-term wastewater treatment.

1. Introduction

With the rapid development of industrialization, the environment and human health are strongly threatened by increasing concentrations of various heavy metal ions in groundwater.$^{1-3}$ Arsenic, as one of the most toxic and carcinogenic elements, can result in massive arsenic poisoning, and has been categorized as a class ‘A’ human carcinogen in the U. S. Environmental Protection Agency (USEPA) list of prioritized pollutants.$^{4-6}$ Therefore, efficient removal of arsenic species from aqueous solutions has become one of the most meaningful issues in water pollution control. To date, many efforts have been devoted to developing proper technologies for arsenic removal from contaminated water, including adsorption,$^{7-9}$ ion exchange,$^{10}$ membrane filtration,$^{11}$ chemical precipitation,$^{12}$ and electrochemical methods.$^{13}$ Obviously, adsorption technology stands out from all of the others because of its high removal efficiency, simple operation, and excellent disposal qualities.

To date, a large number of adsorbents have been used for arsenic removal, such as mesoporous carbon,$^{14-18}$ TiO$_2$,$^{19-21}$ Al$_2$O$_3$,$^{22}$ MnO$_2$,$^{23}$ CuO,$^{24}$ and so on. Among them, TiO$_2$-based nanomaterials are very promising due to their excellent properties, such as being environmentally friendly and low-cost, and their chemical stability.$^{25-27}$ In addition, arsenic pollutants generally exist as two kinds of species in natural water, i.e. arsenate As$^{V}$ and arsenite As$^{III}$, and As$^{III}$ is more toxic than As$^{V}$ owing to its stronger affinity for proteins.$^5$ It is worth noting that the more toxic As$^{III}$ can be easily oxidized to less toxic As$^{V}$ by TiO$_2$ under irradiation, which can be
adsorbed and removed easily.\textsuperscript{28,29} For example, Meichtry et al. investigated the photocatalytic oxidation process of As(III) to As(V) by TiO\textsubscript{2}, confirming the fast oxidation and good adsorption process.\textsuperscript{30} However, bulk crystallized TiO\textsubscript{2} materials generally possess low surface areas and few surface functional groups (e.g. \(-\text{OH}, \sim\text{COOH}\)), and as a result, low capacities have been reported.\textsuperscript{31} In comparison, nano-adsorbents, with distinct advantages including high surface areas, increased surface-to-volume ratios, short inter-particle diffusion distances, and versatile surface chemistry, often give rise to much better performances.\textsuperscript{32} Nevertheless, the separation and recycling of TiO\textsubscript{2} nano-adsorbents turn out to be another critical problem. The conventional separation processes including filtration and centrifugation are time- and energy-intensive and may result in the loss of adsorbents. In contrast, magnetic nano-adsorbents have recently been developed which benefit from facile and fast separation properties using a magnet. For example, Fe\textsubscript{3}O\textsubscript{4}-based nanocomposites have been widely used for the removal of heavy metal ions, exhibiting good arsenic removal performance and magnetic separation properties. For instance, iron oxide nanoparticle coated single-wall carbon nanotubes were used as As\textsuperscript{V} adsorbents, exhibiting a good As\textsuperscript{V} adsorption amount of 42.3 mg g\textsuperscript{-1}.\textsuperscript{33} However, they still suffer from the limitation of inferior protection of Fe\textsubscript{3}O\textsubscript{4} nanoparticles, thus leading to aggregation in aqueous media or dissolution under acidic conditions.\textsuperscript{34–38} It is urgent to fabricate new materials for sustainable arsenic removal with high capacities, stabilities and recyclabilities. Core–shell structured nanomaterials consisting of different components and functional compositions have attracted attention recently, as they are advantageous for the design of novel adsorbents for water treatment.\textsuperscript{39–41}

Herein, uniform magnetic core–shell structured Fe\textsubscript{3}O\textsubscript{4}@Resorcinol-Formaldehyde@mesoporous TiO\textsubscript{2} microspheres (Fe\textsubscript{3}O\textsubscript{4}@RF@mTiO\textsubscript{2}) are fabricated, in which RF acts as a protective layer and the mesoporous TiO\textsubscript{2} contributes to the effective adsorption in acidic media. The new multilayer core–shell structured microspheres with a uniform size of 250 nm were synthesized \emph{via} a facile successive sol–gel coating method. After calcination at 200 °C, the mesoporous TiO\textsubscript{2} shells can be partially crystallized with a uniform thickness (~50 nm). The resultant Fe\textsubscript{3}O\textsubscript{4}@RF@mTiO\textsubscript{2} microspheres still have a high surface area (~337 m\textsuperscript{2} g\textsuperscript{-1}) and pore volume (~0.42 cm\textsuperscript{3} g\textsuperscript{-1}), providing more active sites for the adsorption. In addition, increased hydrophobic properties can be endowed to the RF interlayer, which can effectively maintain the magnetic properties of Fe\textsubscript{3}O\textsubscript{4} nanoparticles under acidic conditions after long adsorption cycles. As a result, the obtained uniform Fe\textsubscript{3}O\textsubscript{4}@RF@mTiO\textsubscript{2} microspheres exhibit excellent arsenate removal behaviour with a fast adsorption rate (1.16 g mg\textsuperscript{-1} h\textsuperscript{-1}), high adsorption capacities (up to 138.6 mg g\textsuperscript{-1}), and perfect recycling performance at pH 3. Finally, the existence of electrostatic forces and surface coordination complexation interactions between arsenate and TiO\textsubscript{2} was disclosed.

2. Experimental section

2.1 Materials

FeCl\textsubscript{3}, H\textsubscript{2}O\textsubscript{2}, trisodium citrate, sodium acetate, tetrabutyl titanate (TBOT), sodium hydroxide, resorcinol, formaldehyde, and the solvents of ethylene glycol and ethanol were purchased from Shanghai Chemical Corp. Concentrated ammonia solution (28 wt%) was purchased from Aldrich. Commercial TiO\textsubscript{2} was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. All chemicals were used without further purification, and deionized water was used for all syntheses.

2.2 Synthesis of magnetite Fe\textsubscript{3}O\textsubscript{4} nanoparticles

The magnetite Fe\textsubscript{3}O\textsubscript{4} nanoparticles were prepared through a modified solvothermal reaction.\textsuperscript{42} Typically, 3.25 g of FeCl\textsubscript{3}, 6H\textsubscript{2}O and 1.3 g of trisodium citrate were dissolved in 100 mL of ethylene glycol under magnetic stirring until a clear solution formed. Then, 6.0 g of sodium acetate was added, and the mixed solution was stirred for another 24 h. The mixed solution was transferred and sealed in a Teflon-lined stainless-steel autoclave (100 mL in capacity). The autoclave was heated at 200 °C for 10 h, and then allowed to cool down to room temperature. The resultant black solid product was washed and separated three times assisted by a magnet, decantation, and redispersion in ethanol, and was finally dispersed into 30 mL of ethanol for further use.

2.3 Synthesis of core–shell structured Fe\textsubscript{3}O\textsubscript{4}@RF microspheres

The core–shell structured Fe\textsubscript{3}O\textsubscript{4}@RF microspheres were prepared using a modified sol–gel coating method. Firstly, 4.0 mL of ethanolic solution of the Fe\textsubscript{3}O\textsubscript{4} nanoparticles obtained above and 3.2 mL of concentrated ammonia solution were added into a three-necked flask which contained 80 mL of water and 160 mL of ethanol. The mixed solution was treated with ultrasound for 30 min and further mechanical stirring for 30 min. Then, 0.23 g of resorcinol was added into the solution. After stirring for 30 min, 0.4 mL of formaldehyde was dropped in. Finally, the reaction was allowed to proceed under mechanical stirring at 30 °C for 6 h. The final products were collected using a magnet and washed with water and ethanol three times, respectively. The Fe\textsubscript{3}O\textsubscript{4}@RF microspheres were re-dispersed into 30 mL of ethanol. The Fe\textsubscript{3}O\textsubscript{4}@RF-200 microspheres were obtained by calcining the Fe\textsubscript{3}O\textsubscript{4}@RF microspheres at 200 °C in air for 3 h.

2.4 Synthesis of core–shell structured Fe\textsubscript{3}O\textsubscript{4}@RF@mTiO\textsubscript{2} microspheres

The multilayer core–shell structured mesoporous Fe\textsubscript{3}O\textsubscript{4}@RF@mTiO\textsubscript{2} microspheres were first fabricated using the extended kinetics-controlled coating method.\textsuperscript{42} Typically, 12 mL of the above ethanolic solution of Fe\textsubscript{3}O\textsubscript{4}@RF was mixed with 88 mL of ethanol. Then, 0.4 mL of concentrated ammonia solution (28 wt%) was added. The solution was treated with ultrasound for 10 min and further mechanical stirring for 30 min. Then, 0.75 mL of TBOT was added into the
solution and the reaction was allowed to proceed for 24 h at 45 °C under continuous mechanical stirring. The resultant products were collected by utilizing a magnet, followed by washing with ethanol three times. After being dried at 60 °C for 24 h, the as-made Fe3O4@RF@mTiO2 solid samples were calcined at 200 °C in air for 3 h to obtain the final product, Fe3O4@RF@mTiO2 microspheres.

2.5 Synthesis of core–shell structured Fe3O4@mTiO2 microspheres

The method to fabricate the core–shell structured Fe3O4@mTiO2 microspheres was similar to that for the multilayered Fe3O4@RF@mTiO2 microspheres. Before coating the amorphous TiO2 outer layers, a thin SiO2 layer was decorated onto the surface of the magnetite Fe3O4 nanoparticles. Typically, 8.0 mL of the above ethanolic solution of Fe3O4 nanoparticles was mixed with 120 mL of ethanol, 18 mL of water and 3 mL of concentrated ammonia solution (28 wt%) with ultrasound treatment for 10 min and further mechanical stirring for 30 min. Then, 0.3 mL of TEOS was added into the solution. The reaction was allowed to proceed under continuous mechanical stirring at room temperature for 20 min. The products were collected by centrifuging, followed by washing with ethanol three times. Then, the samples were redispersed into 9 mL of ethanol. The TiO2 coating process followed was similar to the synthesis of the multilayer core–shell structured Fe3O4@RF@mTiO2 microspheres (here, 3.0 mL of ethanolic solution of the Fe3O4 nanoparticles modified with a thin SiO2 layer and 97 mL of ethanol was used). The final Fe3O4@mTiO2 microspheres were produced by calcining the as-made Fe3O4@mTiO2 at 200 °C in air for 3 h.

2.6 Arsenate adsorption

Arsenate adsorption experiments were conducted in batch mode at 25 °C. Typically, 20 mg of absorbents was dissolved into 20 mL of AsV solutions of different concentrations (1–350 mg L−1). Then, the solution was treated with ultrasound for 10 min, followed by shaking at 25 °C for 6 h to achieve adsorption equilibrium. The sorbent was separated from the solution using a magnet, and the concentration of arsenate in the residual solution was measured using ICP-AES analysis. The pH of the solution was adjusted by adding different amounts of 0.1 M HCl and NaOH solutions.

The adsorption kinetic curves were obtained as follows. The sample (20 mg) was dissolved into the AsV solution (20 mL) with a concentration of 5.0 mg L−1 and treated with ultrasound for 10 min. After shaking at 25 °C for a certain time (1–24 h), the solution was quickly separated using a magnet to analyze the corresponding concentration of AsV using ICP-AES, so that the time-dependent adsorption capacity was obtained.

The adsorption isotherms were fitted using the Langmuir model (eqn (1)), where qe represents the equilibrium adsorption capacity (mg g−1), ce is the concentration after equilibration, b is the Langmuir constant which is associated with adsorption affinity, and a represents the saturated adsorption capacity (mg g−1).

\[ q_e = \frac{abc_e}{1 + bc} \] (1)

The adsorption kinetics data could be fitted into a pseudo-second-order rate kinetic model (eqn (2)), in which \( q_t \) represents the adsorption amount of AsV at a time of t, \( k_2 \) is the rate constant of the pseudo-second-order model (g mg−1 h−1) and \( q_e \) is the equilibrium adsorption capacity (mg g−1).

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} \] (2)

The cycling experiments were conducted as follows. Firstly, 100 mg of the multilayer mesoporous Fe3O4@RF@mTiO2 microspheres was dissolved into 100 mL of an AsV aqueous solution with a concentration of 5 mg L−1 and treated with ultrasound for 10 min. After adsorbing for 6 h with shaking at 25 °C, the solution was then quickly separated using a magnet. The separated precipitate was dispersed in 100 mL of NaOH solution (0.5 M) for 24 h for ion exchange. Then, the adsorbent was washed with water until the pH value of the separated solution reached ∼7. After the ion exchange treatment, the sample was then reused for AsV adsorption.

Controlled adsorption experiments were also performed using 20 mg of commercial TiO2 and Fe3O4@RF-200 microspheres as adsorbents under otherwise identical conditions.

2.7 Measurements and characterization

Transmission electron microscopy (TEM) measurements were collected on a JEOL JEM-2100 F microscope (Japan), operating at 200 kV. The samples were suspended in ethanol and then supported on a Cu grid. The crystalline phase of the products was measured using powder X-ray diffraction (XRD, D8 Diffractometer with Ni-filtered Cu Kα radiation, Bruker, Germany). The diffractometer was set at 40 kV working voltage and 40 mA working current, scanning from 10–80° in 2θ with a step of 0.02° and a scan-step time of 4 s. Nitrogen sorption isotherms were obtained at 77 K using a Quantachrome Autosorb-1-MP instrument (Quantachrome, USA). Before measurements were taken, all samples were pretreated under vacuum at 180 °C for 6 h. The specific surface areas were calculated using the standard Brunauer–Emmett–Teller (BET) method using the adsorption data in a relative pressure range from 0.05 to 0.20. The pore size distribution was derived from the adsorption branch, using the Barrett–Joyner–Halenda (BJH) model. The total pore volume \( V_p \) was calculated from the adsorbed amount at \( p/p_0 = 0.99 \). Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to measure the concentration of AsV in the residual solution and the desorbed solution. To conduct the XPS analysis, the precipitate of Fe3O4@RF@mTiO2 after AsV adsorption was collected using a magnet and dried in a vacuum oven at 60 °C for 24 h.
3. Results and discussion

Uniform magnetite Fe₃O₄ nanoparticles with an average diameter of ∼130 nm can be prepared using a solvothermal strategy as reported previously (Fig. S1†). The resultant magnetite nanoparticle surface was modified with plentiful citrate groups, and thus they could be easily coated with a RF polymer layer. The TEM image (Fig. 1a) shows that the mono-dispersed Fe₃O₄@RF nanoparticles were synthesized with a dense RF layer of ∼10 nm in thickness. Subsequently, a layer of amorphous TiO₂ can be deposited on the surfaces of the core–shell Fe₃O₄@RF nanoparticles through the versatile kinetics-controlled sol–gel coating process. It can be clearly seen that the as-made Fe₃O₄@RF@mTiO₂ microspheres possess porous TiO₂ shells (Fig. 1b). After the calcination at 200 °C, uniform Fe₃O₄@RF@mTiO₂ microspheres with a diameter of around 250 nm and highly porous shells can be retained (Fig. 1c and d). The high-resolution TEM (HRTEM) image (Fig. 1e) shows that the TiO₂ shells are partially crystallized with a d-spacing of ∼0.35 nm, which can be matched well to the (101) crystalline plane of anatase TiO₂. The low crystallinity of the multilayer core–shell Fe₃O₄@RF@mTiO₂ microspheres is mainly due to the low calcination temperature, which can be further proved by the selected-area electron diffraction (SAED) pattern (Fig. 1f). As a control, uniform Fe₃O₄@mTiO₂ microspheres were synthesized under similar conditions without the inner RF layer (Fig. S2†).

The nitrogen adsorption/desorption isotherms of the core–shell structured Fe₃O₄@RF@mTiO₂ and Fe₃O₄@mTiO₂ microspheres show characteristic type IV curves, indicating a uniform mesoporous structure of TiO₂ shells (Fig. 2a). The BET surface area and pore volume of the Fe₃O₄@RF@mTiO₂ microspheres are calculated to be ∼337 m² g⁻¹ and 0.42 cm³ g⁻¹ (Table S1†), which are almost the same as those of the Fe₃O₄@mTiO₂ microspheres without RF layers (351 m² g⁻¹ and 0.38 cm³ g⁻¹). This suggests that the introduction of the RF interlayer has little influence on the porous structures, implying a dense RF layer. The corresponding pore size distribution (PSD) curves (Fig. 2b) clearly show uniform pore sizes of ∼3.0 and 2.7 nm for the Fe₃O₄@RF@mTiO₂ and Fe₃O₄@mTiO₂ microspheres, respectively. In addition, N₂ sorption isotherms of the as-made Fe₃O₄@RF@mTiO₂ microspheres before the calcination show typical type IV curves as well (Fig. S3†). The specific surface area of as-made Fe₃O₄@RF@mTiO₂ is about 386 m² g⁻¹, which is slightly higher than that of Fe₃O₄@RF@mTiO₂ microspheres. This results from the densification of the TiO₂ shell networks and partial growth of nanocrystals during the calcination process.

XRD patterns of the core–shell structured Fe₃O₄@RF@mTiO₂ and Fe₃O₄@mTiO₂ microspheres only show the characteristic diffraction peaks that can be well assigned to magnetite Fe₃O₄. No obvious diffraction peaks of anatase TiO₂ were detected due to their poor crystallinity (Fig. 2c). Magnetic characterization shows that the saturation magnetization value of the multilayer core–shell Fe₃O₄@RF@mTiO₂ (15 emu g⁻¹) is smaller than that of the Fe₃O₄@mTiO₂ microspheres without the RF layer (20 emu g⁻¹) owing to the shielding effect of the interlayer (Fig. 2d). Moreover, no remanence was detected for these microspheres, suggesting their superparamagnetic features.

![Fig. 1](image1.png)
![Fig. 2](image2.png)
Herein, the well-designed Fe₃O₄@RF@mTiO₂ microspheres are demonstrated as As⁵⁺ adsorbents, with Fe₃O₄@mTiO₂ microspheres as a control. The pH values of the contaminated water are quite important for As⁵⁺ adsorption, which has been firstly studied. When the multilayer core–shell Fe₃O₄@RF@mTiO₂ microspheres are used as the adsorbents, the removal capacity decreases from 5.96 to 2.80 mg g⁻¹ as the pH value increases from 2.0 to 13.0 with an initial arsenate concentration of 5 mg L⁻¹ (Fig. S4†), suggesting that an acidic environment is helpful for As⁵⁺ removal. A similar phenomenon is also observed in the core–shell Fe₃O₄@mTiO₂ microspheres without an RF layer.

TEM images of the core–shell structured Fe₃O₄@mTiO₂ and multilayer Fe₃O₄@RF@mTiO₂ microspheres within five adsorption cycles (pH = 3) are shown in Fig. 3. It can be clearly observed that the inner cores of the Fe₃O₄@mTiO₂ microspheres without the RF layer disappear gradually to generate a cavity after five adsorption cycles. For the multilayer Fe₃O₄@RF@mTiO₂ microspheres, the structure is almost unchanged, suggesting that the inner Fe₃O₄ cores can be well-protected by the RF interlayer. In addition, the iron ion concentration was also explored in the residual solution after As⁵⁺ adsorption at different pH values. For Fe₃O₄@mTiO₂, the concentration of the iron ions increases with the decreased pH values (Fig. S5†), while for the sample Fe₃O₄@RF@mTiO₂, the iron ion concentration is almost zero within a pH range of 2–13, further proving the protective role of the RF interlayer. The magnetization value of the Fe₃O₄@RF@mTiO₂ slightly decreases after five adsorption cycles, which can be ascribed to the surface oxidation upon cycling (Fig. S6†).

In order to study the removal rate of As⁵⁺ from aqueous solutions (pH = 3), kinetics measurements were obtained. It can be seen that almost 90% of As⁵⁺ with an initial arsenate concentration of 5 mg L⁻¹ is removed by the multilayer Fe₃O₄@RF@mTiO₂ microspheres in the first hour, implying their fast adsorption rates (Fig. 4a). However, the adsorption rate becomes slow after two hours. The kinetic process indicates that 6 hours are sufficient for complete As⁵⁺ removal by the Fe₃O₄@RF@mTiO₂ adsorbents. Moreover, the adsorption kinetic data can be well fitted by a pseudo-second-order model (Fig. 4b). The Fe₃O₄@RF@mTiO₂ microspheres exhibit a fast adsorption rate of 1.16 g mg⁻¹ h⁻¹ (Table S1†).

Adsorption isotherms (Fig. 4c) show that the Fe₃O₄@RF@mTiO₂ and Fe₃O₄@mTiO₂ microspheres possess unprecedented saturation capacities of ~138.6 and 143.2 mg g⁻¹ towards As⁵⁺ (calculated from the Langmuir model, and the corresponding correlation indices are shown in Table S1†), and exhibit better performances than most of the reported TiO₂-based nano-adsorbents.⁴³,⁴⁴ The relatively lower adsorption amount of the multilayer Fe₃O₄@RF@mTiO₂ compared to the core–shell Fe₃O₄@mTiO₂ may be due to the presence of the RF interlayer which blocks the adsorption contribution of
inner Fe₃O₄ cores. The adsorption isotherms of As⁵⁺ on these microspheres can be well fitted to the Langmuir model with linear coefficient $R^2$ values close to 1, indicating that monolayer adsorption occurs (Table S1†). To further prove the advantage of Fe₃O₄@RF@mTiO₂ for the removal of As⁵⁺, the adsorption capacities of Fe₃O₄@RF-200 and commercial TiO₂ were compared (Fig. S7†). The adsorption isotherms show that the multilayer Fe₃O₄@RF@mTiO₂ can adsorb more As⁵⁺ no matter whether the initial concentration is low or high, which is far superior to Fe₃O₄@RF-200 microspheres and the commercial TiO₂. The results highlight the primary contribution of the mesoporous TiO₂ shells to the As⁵⁺ adsorption. Moreover, the magnetic core–shell structured nano-adsorbent can be easily separated using a magnet and thus effectively recycled (Fig. S8†). The adsorbed As⁵⁺ can be effectively desorbed from the Fe₃O₄@RF@mTiO₂ microspheres using 0.5 M NaOH solution (Fig. S9†). After five cycles, the adsorption capacity can still be maintained with a negligible decrease (Fig. 4d), which can be attributed to the incomplete 100% desorption effect (Fig. S9†).

In addition, we explored the influence of ionic strengths on As⁵⁺ removal behaviours by adding various concentrations of NaCl. The increased concentration of NaCl induces a competition effect with As⁵⁺ removal (Fig. S10†), suggesting an electrostatic interaction between As⁵⁺ and the TiO₂ shells. XPS measurements were performed to further demonstrate the possible adsorption mechanism (Fig. S11†). Four obvious peaks of arsenic (As 3d, 3p, LMMb, and LMMa bands) can be clearly observed in the wide-scan spectra of the Fe₃O₄@RF@mTiO₂ microspheres after the adsorption, indicating the presence of As⁵⁺ on the surfaces of the microspheres. The As 3d peak is located at 45.20 eV, which can be assigned to As⁵⁺–O (Fig. S11b†). Moreover, it can be found that the intensity of the Ti 2p peaks slightly decreases after arsenate adsorption (Fig. S12†), which can be ascribed to the formation of surface coordination complexes, thus shielding the surface exposure of Ti.

The remarkable As⁵⁺ adsorption ability and magnetic separation performance in acid solutions (pH = 3) can be ascribed to the following aspects (Fig. 5). Firstly, the mesoporous TiO₂ shells provide more active sites for As⁵⁺ adsorption due to the high specific surface area derived from the low calcination temperature (200 °C), which is beneficial for increasing the adsorption amount. In addition, the porous structure facilitates the diffusion of nano-adsorbates, improving the adsorption rate and efficiency. As a result, a high adsorption amount of 138.6 mg g⁻¹ and a fast adsorption rate of 1.16 g mg⁻¹ h⁻¹ can be obtained for the multilayer Fe₃O₄@RF@mTiO₂ nano-adsorbents. Secondly, the perfect adsorption performance of the multilayer Fe₃O₄@RF@mTiO₂ microspheres under low pH conditions can be ascribed to the fact that a large number of OH radicals attached on the surfaces of TiO₂ shells are easily protonated in an acidic environment. In the meantime, As⁵⁺ predominantly exists in the forms of H₂AsO₄⁻ and HAsO₄²⁻ when pH values are in the range of 2–7. Thus, an electrostatic attraction between the negative oxyanions and positively charged surfaces of TiO₂ shells is formed, thus improving the removal amount of As⁵⁺ under acidic conditions compared to that in the basic solution. In addition, combined with our analyses and previous reports, the formation of surface coordination complexes can also contribute to the interaction of the partially crystallized TiO₂ shells and As⁵⁺ species. Finally, the continuous magnetic response properties after several cycles are attributed to the presence of the RF interlayer. For the core–shell structured Fe₃O₄@mTiO₂ microspheres, owing to the porous TiO₂ shells, H⁺ can easily make contact and react...

**Fig. 5** Schematic illustration for the adsorption processes for As⁵⁺ in an acid aqueous solution of the core–shell structured Fe₃O₄@RF@mTiO₂ and Fe₃O₄@mTiO₂ microspheres.
with the inner Fe₃O₄ cores, resulting in a gradual decomposition of the cores. Comparatively, the dense RF interlayers with increased hydrophobic properties due to the calcination process in Fe₃O₄@RF@mTiO₂ microspheres can effectively prevent H⁺ from etching the Fe₃O₄ cores. Thus, the sandwich-like structure can be well-retained after several cycles. In consequence, the uniform magnetic Fe₃O₄@RF@mTiO₂ microspheres display outstanding As V removal performance and perfect magnetic response properties, and it is believed that the nanocomposites are a type of ideal nanomaterial for arsenate removal.

4. Conclusions
In summary, a facile synthesis of magnetic multilayer core–shell structured Fe₃O₄@RF@mTiO₂ microspheres with high specific surface areas (337 m² g⁻¹) and pore volumes (0.42 cm³ g⁻¹) has been demonstrated. The microspheres with uniform diameters of 250 nm consisted of a magnetite Fe₃O₄ core of ~130 nm in diameter, a dense RF interlayer with a thickness of ~10 nm, and a mesoporous TiO₂ shell with a thickness of ~50 nm. The obtained magnetic mesoporous TiO₂-based microspheres supply a huge number of active adsorption sites for the removal of arsenate. Thus, the nanocomposites exhibit very superior arsenate removal performance with a high adsorption capacity (up to 138.6 mg g⁻¹) and a fast adsorption rate (1.16 g mg⁻¹ h⁻¹) which can be well fitted by a pseudo-second-order model. In addition, the adsorbent exhibits better adsorption performance in acid solutions than in basic solutions. Vitaly, benefiting from the good protective role of the RF interlayers, the nanocomposites can be easily separated using a magnet, and exhibit high cycling stability even under acidic conditions. Finally, the investigation of the mechanism proves the existence of electrostatic forces and surface coordination complex interactions between arsenate and partial crystallized TiO₂, which are responsible for the excellent As V adsorption performance in acidic environments. It is believed that the multilayer core–shell structured design can find more applications in areas of energy storage and conversion, environmental remediation, waste water treatment, and catalysis.

Conflicts of interest
There are no conflicts to declare.

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