Electronic Supplementary Information

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

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Fig. S1 The TEM image of the magnetite Fe₃O₄ nanoparticles prepared by a modified solvothermal reaction by aging a glycol solution of FeCl₃·6H₂O (3.25 g), trisodium citrate (1.3 g), and sodium acetate (6.0 g) at 200 °C for 10 h.
Fig. S2 SEM (a) and TEM (b) images of the core-shell structured Fe$_3$O$_4$@mTiO$_2$ microspheres prepared through the versatile kinetics-controlled coating method followed by calcining at 200 °C for 3 h in air.
The nitrogen adsorption/desorption isotherms (a) and the corresponding pore size distribution curves (b) of the as-made Fe$_3$O$_4$@RF@mTiO$_2$ and calcined Fe$_3$O$_4$@RF@mTiO$_2$ microspheres. The as-made Fe$_3$O$_4$@RF@mTiO$_2$ microspheres were obtained by the successive sol–gel coating method and the versatile kinetics-controlled coating method. The Fe$_3$O$_4$@RF@mTiO$_2$ microspheres were fabricated by calcining the as-made Fe$_3$O$_4$@RF@mTiO$_2$ microspheres at 200 °C for 3 h in air.
Fig. S4 The influence of pH values on As$^\text{V}$ adsorption for the core-shell structured Fe$_3$O$_4$@RF@mTiO$_2$ and Fe$_3$O$_4$@mTiO$_2$ microspheres. The adsorption amounts of Fe$_3$O$_4$@RF@mTiO$_2$ and Fe$_3$O$_4$@mTiO$_2$ nano-adsorbents decreased with the increase of the pH values. The Fe$_3$O$_4$@RF@mTiO$_2$ and Fe$_3$O$_4$@mTiO$_2$ microspheres were fabricated by calcining the corresponding as-made Fe$_3$O$_4$@RF@mTiO$_2$ and as-made Fe$_3$O$_4$@mTiO$_2$ microspheres at 200 °C for 3 h in air, respectively.
Fig. S5 The concentration of iron ions in the residual solution after As\(^{3+}\) adsorption by the Fe\(_3\)O\(_4\)@RF@mTiO\(_2\) and Fe\(_3\)O\(_4\)@mTiO\(_2\) microspheres within different pH values (the initial arsenate concentration was 5 mg·L\(^{-1}\)). The Fe\(_3\)O\(_4\)@RF@mTiO\(_2\) and Fe\(_3\)O\(_4\)@mTiO\(_2\) microspheres were fabricated by calcining the corresponding as-made Fe\(_3\)O\(_4\)@RF@mTiO\(_2\) and as-made Fe\(_3\)O\(_4\)@mTiO\(_2\) microspheres at 200 °C for 3 h in air, respectively.
Fig. S6 The magnetic hysteresis loops of the multilayer core-shell structured Fe$_3$O$_4$@RF@mTiO$_2$ microspheres before As$^V$ adsorption and after five As$^V$ adsorption cycles.
Fig. S7 Adsorption isotherms of As$^\text{V}$ on the multilayer core-shell Fe$_3$O$_4$@RF@mTiO$_2$ microspheres, commercial TiO$_2$, and Fe$_3$O$_4$@RF-200 microspheres at 25 °C, suggesting the better As$^\text{V}$ adsorption performance than the commercial TiO$_2$ and Fe$_3$O$_4$@RF-200 microspheres. Typically, 20 mg of adsorbents were dissolved into 20 mL of As$^\text{V}$ solution with different concentrations (1–350 mg·L$^{-1}$). The Fe$_3$O$_4$@RF-200 microspheres were produced by calcining the Fe$_3$O$_4$@RF microspheres at 200 °C in air for 3 h.
Fig. S8 The optical photos of (a) 20 mg of the Fe$_3$O$_4$@RF@mTiO$_2$ microspheres dispersed in 20 mL of deionized water by ultrasound and (b) separated by a magnet after 10 minutes.
Fig. S9 The $\text{As}^{\text{V}}$ desorption curves of the $\text{Fe}_3\text{O}_4@\text{RF}@\text{mTiO}_2$ microspheres. The desorption processes were conducted by using 0.5 M NaOH solution.
Fig. S10 Effect of ion strength on As$^\text{V}$ adsorption by the multilayer Fe$_3$O$_4$@RF@mTiO$_2$ microspheres. The increased concentration of NaCl induces a competition effect with As$^\text{V}$ removal, suggesting an electrostatic interaction between As$^\text{V}$ and TiO$_2$ shells. The multilayer Fe$_3$O$_4$@RF@mTiO$_2$ microspheres were fabricated by calcining the as-made Fe$_3$O$_4$@RF@mTiO$_2$ microspheres at 200 °C for 3 h in air.
Fig. S11 (a) XPS wide scan spectra of the multilayer Fe$_3$O$_4$@RF@mTiO$_2$ microspheres before and after As$^{V}$ adsorption. (b) High resolution As3d spectrum of the Fe$_3$O$_4$@RF@mTiO$_2$ microspheres after As$^{V}$ adsorption, indicating the presence of As$^{V}$ on the surface of the microspheres after adsorption. The multilayer Fe$_3$O$_4$@RF@mTiO$_2$ microspheres were fabricated by calcining the as-made Fe$_3$O$_4$@RF@mTiO$_2$ microspheres at 200 °C for 3 h in air.
Fig. S12 Ti2p spectra of the multilayer Fe₃O₄@RF@mTiO₂ microspheres before and after arsenate adsorption. It can be found that the intensity of Ti2p bands slightly decreases after arsenate adsorption, which can be ascribed to the formation of surface coordination complex, thus shielding the surface exposure of Ti. The multilayer Fe₃O₄@RF@mTiO₂ microspheres were fabricated by calcining the as-made Fe₃O₄@RF@mTiO₂ microspheres at 200 °C for 3 h in air.
Table S1 Textural properties of the core-shell structured Fe₃O₄@RF@mTiO₂ and Fe₃O₄@mTiO₂ microspheres, their maximum adsorption capacities (q<sub>max</sub>), and the rate constants of the pseudo-second-order model.

<table>
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<th>Samples</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt; (m&lt;sup&gt;2&lt;/sup&gt;·g&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>V&lt;sub&gt;t&lt;/sub&gt; (cm&lt;sup&gt;3&lt;/sup&gt;·g&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Pore size (nm)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>q&lt;sub&gt;max&lt;/sub&gt; (mg·g&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</th>
<th>k (g·mg&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;f&lt;/sup&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;2&lt;/sup&gt;</th>
<th>g</th>
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<tr>
<td>Fe₃O₄@RF@mTiO₂</td>
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<td>0.996</td>
<td>1.37</td>
<td>0.999</td>
<td></td>
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</tbody>
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<sup>a</sup>, S<sub>BET</sub> represents BET specific surface area obtained from N₂ adsorption data in the p/p<sub>0</sub> range from 0.05 to 0.20; <sup>b</sup>, V<sub>t</sub> represents the total pore volume calculated from the adsorbed amount at p/p<sub>0</sub> = 0.99; <sup>c</sup>, Pore size is determined by using the Barrett-Joyner-Halenda (BJH) model; <sup>d</sup>, q<sub>max</sub> is the maximum adsorption capacity obtained by fitting with Langmuir model; <sup>e</sup>, R<sub>1</sub> represents correlation coefficient related to the Langmuir mode; <sup>f</sup>, k is the rate constant related to the pseudo-second-order rate mode; <sup>g</sup>, R<sub>2</sub> represents correlation coefficient related to the pseudo–second–order rate mode.