Low-Cost Synthesis of Flowerlike $\alpha$-Fe$_2$O$_3$ Nanostructures for Heavy Metal Ion Removal: Adsorption Property and Mechanism

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ABSTRACT: Flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures were synthesized via a template-free microwave-assisted solvothermal method. All chemicals used were low-cost compounds and environmentally benign. These flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures had high surface area and abundant hydroxyl on their surface. When tested as an adsorbent for arsenic and chromium removal, the flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures showed excellent adsorption properties. The adsorption mechanism for AsV and CrVI onto flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures was elucidated by X-ray photoelectron spectroscopy and synchrotron-based X-ray absorption near edge structure analysis. The results suggested that ion exchange between surface hydroxyl groups and AsV or CrVI species was accounted for by the adsorption. With maximum capacities of 51 and 30 mg g$^{-1}$ for AsV and CrVI, respectively, these low-cost flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures are an attractive adsorbent for the removal of AsV and CrVI from water.

1. INTRODUCTION

Recently, the exploitation of iron oxide nanomaterials for heavy metal ion removal has attracted attention because of their demonstrated excellent adsorption capacities and environmentally benign nature. Among various morphologies of $\alpha$-Fe$_2$O$_3$ nanomaterials, three-dimensional (3D) flowerlike nanostructures composed of hierarchically assembled nanosized building blocks, with the total size in the micrometer scale, have several advantages for adsorption, such as high surface area, easy mass transformation, and easy separation. However, it is quite expensive to produce flowerlike $\alpha$-Fe$_2$O$_3$ nanomaterials using a popular ethylene glycol (EG)-mediated process. In our previous study, flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures were prepared through heating iron chloride and urea in EG at 180 °C for several hours, using tetrabutylammonium bromide (TBAB) as the surfactant, followed by calcination. This EG-mediated method is a simple and reliable synthetic method to produce hierarchically self-assembled flowerlike $\alpha$-Fe$_2$O$_3$ architectures but consumes EG and TBAB because it may be even more expensive to recycle them, making it difficult to use flowerlike $\alpha$-Fe$_2$O$_3$ in practical water treatment. Thus, it is very desirable to develop a low-cost method to produce flowerlike $\alpha$-Fe$_2$O$_3$ nanomaterials. In general, the material cost can be lowered using low-cost raw materials, shortening the heating time, and recycling unused materials.

In addition, the adsorption mechanisms of flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures for heavy metal ions, such as AsV and CrVI, were believed to involve electrostatic attraction and/or ion exchange. However, how ion exchange occurred, i.e., what species are involved in the process, and how heavy metal ions are bound to the adsorbent remain not very clear. For the rational design of materials, such knowledge is also needed. In this study, we developed a surfactant-free microwave-assisted solvothermal method to prepare flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures. All chemicals (FeCl$_3$·6H$_2$O and urea as reaction materials and ethanol as the solvent and can be recycled) used were low-cost and environmentally benign. The reaction time was less than 30 min with microwave heating. These make this route a rapid, reliable, and easily scaled-up method. These flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures had a large surface area (130 m$^2$ g$^{-1}$) and abundant surface hydroxyl groups and showed excellent adsorption properties for AsV and CrVI. The maximum adsorption capacities for AsV and CrVI were 51 and 30 mg g$^{-1}$, respectively. These values were nearly 170 times higher than that of the commercial bulk $\alpha$-Fe$_2$O$_3$. The high surface area as well as abundant surface hydroxyl groups accounted for the excellent adsorption properties of flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures. X-ray photoelectron spectroscopy (XPS) and synchrotron-based X-ray absorption near edge structure (XANES) analysis showed unambiguous evidence to support an ion-exchange adsorption mechanism between hydroxyl on the surface of flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures and AsV and CrVI species in the solution during adsorption.

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2. EXPERIMENTAL SECTION

2.1. Preparation of Flowerlike α-Fe2O3 Nanostructures. All of the materials, including iron(III) chloride hexahydrate (FeCl3·6H2O), urea, and ethanol, were used as received from Beijing Chemicals Co. (Beijing, China). In a typical procedure, 5 mmol of FeCl3·6H2O and 7.5 mmol of urea were dissolved in 100 mL of anhydrous ethanol (99%), and then 40 mL of reaction solution was poured into a Teflon-lined autoclave with a volume of 70 mL. The autoclave was sealed and placed in a programmable microwave oven (MDS-6, Shanghai Sino-Microwave Chemistry Technology Co., Ltd.). The oven was heated to 150 °C in 2 min by microwave irradiation and then kept at that temperature for another 30 min under microwave heating. After cooling to room temperature, precipitates were collected as α-Fe2O3 by centrifugation, washed with ethanol 5 times, and then dried at 80 °C for 3 h.

2.2. Characterizations. X-ray diffraction (XRD) patterns were preformed on a Rigaku D/max-2500 diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 200 mA. The morphology and microstructures of the samples were characterized by field emission scanning electron microscopy (FE-SEM, JEOL 6701F), transmission electron microscopy (TEM, JEOL 1011), and high-resolution transmission electron microscopy (HR-TEM) (FEI Tecnai F20). The nitrogen adsorption–desorption isotherms were measured on a Quantachrome Autosorb AS-1 instrument. The pore size distributions were derived from the desorption branches using the Barrett–Joyner–Halenda (BJH) model. XPS data were obtained with an ESCALab220-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Fourier transform infrared (FTIR) spectroscopy was characterized on Bruker Tensor 27. Samples were dried before characterization by an infrared lamp to remove the adsorbed water. Synchrotron-based XANES experiments were performed on the soft X-ray magnetic circular dichroism (SXMCD) station at the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The samples were loaded in an ultrahigh-vacuum chamber at a vacuum of 3 × 10−10 Pa. All spectra were acquired in the total electron yield (TEY) mode with an experimental resolution of 0.2 eV at room temperature.

2.3. Heavy Metal Ion Adsorption. Solutions with different concentrations of As(V) and Cr(VI) were prepared using Na2HAsO4·7H2O and K2Cr2O7 as the sources of heavy metal ions, respectively. The pH value was adjusted to 3 using HCl (2 M). For the adsorption isothermal study, 20 mg of adsorbent was added to 30 mL solutions with a Cr VI initial concentration of 25 mg L−1, while 20 mg of adsorbent was added to 30 mL solutions with a Cr(VI) initial concentration of 25 mg L−1. After a specified time, the solid and liquid were separated immediately and analyzed by inductively coupled plasma–optical emission spectroscopy (Shimazu ICPE-9000) to measure the concentration of metal ions in the remaining solution. For the adsorption isothermal study, 20 mg of adsorbent was added to 50 mL of solution with different concentrations under stirring for 12 h at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterizations of Flowerlike α-Fe2O3 Nanostructures. Flowerlike α-Fe2O3 nanostructures were produced using iron chloride and urea as raw materials and ethanol as the solvent. All chemicals used were low-cost chemicals and environmentally benign. Unlike previously reported EG-mediated methods for flowerlike nanostructures,3,10–12 no organic template or organic metal compounds were used. In addition, notably, α-Fe2O3 nanostructures were directly produced without calcinations. In the EG-mediated process, iron-alkoxide-type compounds were first produced and then converted into iron oxide by calcination, which is time-consuming and costly.3

The typical SEM image of the obtained sample was shown in Figure 1a. They were composed of many uniform, flowerlike architectures approximately 0.8–1 μm in diameter. The flowerlike α-Fe2O3 nanostructures in this study were composed of hundreds of small petals, making the surface of the overall structure uniform. This is quite different from the one in our previous study, which was composed of a large but small number of petal-like leaves.3 A high-magnification SEM image (Figure 1b) revealed that the entire structure were built of many nanopetals and connected to each other to form 3D flowerlike structures. The TEM image (Figure 1c) further confirmed the hierarchical flowerlike structures. Nanoparticles were self-assembled to form nanopetals, which were then self-assembled to form flowerlike nanostructures. A representative high-resolution TEM (HR-TEM) image taken from α-Fe2O3 nanoparticles was shown in Figure 1d. Lattice fringes from nanoparticles were clearly visible, with a spacing of 0.252 nm, corresponding to the spacing of the (110) planes of α-Fe2O3.

The powder XRD pattern of the typical sample obtained was shown in Figure 2a. The diffraction peaks can be indexed to the hexagonal phase of α-Fe2O3 [Joint Committee on Powder Diffraction Standards (JCPDS) 80-2377], which was in good agreement with the HR-TEM result. The energy-dispersive spectrometry (EDS) spectrum also showed that only Fe and O elements existed in the sample (see Figure S1 of the Supporting Information).

The surface area and pore size distribution of flowerlike α-Fe2O3 nanostructures were tested by nitrogen adsorption–desorption (Figure 2b). The Brunauer–Emmett–Teller (BET) surface area of flowerlike α-Fe2O3 nanostructures was calculated to be 130 m2 g−1. This was a very high surface area for iron oxide hierarchical flowerlike nanostructures. Such a surface area value is equivalent to α-Fe2O3 nanoparticles of 4.4 nm based on the equivalent average particle size calculation.13,14 There was a sharp pore distribution with an average diameter of 3.7 nm obtained by the BJH method. These pores were likely due to the void space of self-assembled nanoparticles.

The yield of flowerlike α-Fe2O3 nanostructures was nearly 100% based on the amount of FeCl3·6H2O. The crystal water in FeCl3·6H2O was actually an essential part of the following reaction sequences. Both hydrolysis of urea and formation of Fe(OH)3 need water, and the concentration of water
determined the rate of these two steps. Flowerlike nanostructures could be produced only within a narrow range of the water content. When anhydrous FeCl₃ was used instead of FeCl₃·6H₂O, only irregular aggregate particles were obtained (see Figure S2a of the Supporting Information). When the water content exceeded 0.5%, only aggregated nanoparticles were obtained again (see Figure S2b of the Supporting Information).

The role of urea was to provide steady but low concentrations of the OH⁻ group for Fe³⁺ to form Fe(OH)₃. On the basis of the following reaction sequences, the stoichiometric ratio of urea and FeCl₃·6H₂O should be 1:1.5 (mole ratio). In this study, we found that, as long as the amount of urea was no less than the stoichiometric requirement, flowerlike α-Fe₂O₃ nanostructures were produced. Thus, the simplest and lowest cost recipe was to use a stoichiometric amount of urea and FeCl₃·6H₂O.

$$\text{CO(NH₂)₂} + \text{H}_2\text{O} \rightarrow 2\text{NH₃} + \text{CO}_2$$

$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}^{4⁺} + \text{OH}⁻$$

$$\text{Fe}^{3⁺} + 3\text{OH}^- \rightarrow \text{Fe(OH)}₃$$

$$\text{NH}^{4⁺} + \text{Cl}^- \rightarrow \text{NH}_4\text{Cl}$$

Ethanol was not consumed during the synthesis. It could be recycled after fast distillation to remove the ammonia-related species, which somehow led to irregular-shaped particles if ethanol was directly reused. As shown in Figure S2c of the Supporting Information, the morphology of the flowerlike α-Fe₂O₃ nanostructures obtained from recycled ethanol was the same as that using fresh ethanol.

3.2. Heavy Metal Ion Adsorption Property. Clean water, especially free of highly toxic heavy metal ions, is vital to people’s health. Considerable attention has been paid to the water treatment in recent years. Among all of the heavy metal ion removal methods, the adsorption technique is perhaps the most extensively adopted method because of its simplicity and low cost. Nanomaterial sorbents showed higher adsorption properties than bulk materials because of the nanosize effects. This may provide an efficient way to help solve the water problem. Because of their 3D hierarchical and porous structure, we expected that these flowerlike α-Fe₂O₃ nanostructures would be useful in heavy metal ion adsorption. In addition, the large surface area may be beneficial for mass transformation and adsorption. Because the total size of flowerlike α-Fe₂O₃ nanostructures was in micrometers, the separation would be fairly easy.

Arsenic and chromium are two typical toxic heavy metal ions in water resources, one from natural causes and the other from industrial emissions, and their efficient removal is of great
importance. Figure 3a showed the adsorption rates of As\textsuperscript{V} and Cr\textsuperscript{VI} ions with an initial concentration of 25 mg L\textsuperscript{−1} on the flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructure samples. The adsorption processes were very fast during the first 30 min, and the equilibrium were established after 3 h. To further investigate the adsorption property, adsorption isotherms were obtained with different initial concentrations ranging from 10 to 200 mg L\textsuperscript{−1}, as shown in Figure 3b. Experimental data were fitted well with the Langmuir adsorption model, from which the maximum adsorption capacity could be calculated.\textsuperscript{11,23} The maximum adsorption capacity of flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructures was 51 mg g\textsuperscript{−1} for As\textsuperscript{V} and 30 mg g\textsuperscript{−1} for Cr\textsuperscript{VI}. These values were much higher than those flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{5} flowerlike CeO\textsubscript{2}\textsuperscript{10} and hollow CeO\textsubscript{2} nanostructures\textsuperscript{11} in our previous studies and nearly about 170 times higher than that of commercial bulk \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}, as shown in Table 1. In addition, TEM images showed that the morphology of flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructures was not changed after adsorption of As\textsuperscript{V} and Cr\textsuperscript{VI} ions (see Figure S3 of the Supporting Information).

![Figure 4. EDS spectra of flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} after adsorption of heavy metal ions: (a) As\textsuperscript{V} adsorption and (b) Cr\textsuperscript{VI} adsorption (peak breaks were attributed to Si).](image)

**Table 1. BET Surface Area and Maximum Adsorption Capacity for As\textsuperscript{V} and Cr\textsuperscript{VI} at the Same Experimental Conditions**

<table>
<thead>
<tr>
<th>adsorbent sample</th>
<th>BET surface area (m\textsuperscript{2} g\textsuperscript{−1})</th>
<th>maximum adsorption capacity</th>
<th>As\textsuperscript{V} (mg g\textsuperscript{−1})</th>
<th>Cr\textsuperscript{VI} (mg g\textsuperscript{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>flowerlike (\alpha)-Fe\textsubscript{2}O\textsubscript{3} (this study)</td>
<td>130</td>
<td>51</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>CeO\textsubscript{2} hollow nanospheres\textsuperscript{11}</td>
<td>72</td>
<td>22.4</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>flowerlike CeO\textsubscript{2}\textsuperscript{10}</td>
<td>34</td>
<td>14.4</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>flowerlike (\alpha)-Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{5}</td>
<td>40</td>
<td>7.6</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>commercial (\alpha)-Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{11}</td>
<td>2</td>
<td>0.3</td>
<td>0.37</td>
<td></td>
</tr>
</tbody>
</table>

XPS was used to characterize the surface states of flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructures before and after adsorption of heavy metal ions. Figure 5a showed full-range XPS spectra of flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructures before and after As\textsuperscript{V} and Cr\textsuperscript{VI} adsorption. As and Cr information appeared after As\textsuperscript{V} and Cr\textsuperscript{VI} were adsorbed on flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructures. The As 3d spectrum after As\textsuperscript{V} adsorption (see Figure S5a of the Supporting Information) showed a peak located at 45.4 eV, which should be attributed to As\textsuperscript{V}–O bonding.\textsuperscript{24} The Cr 2p spectrum after Cr\textsuperscript{VI} adsorption (see Figure S5b of the Supporting Information) showed two peaks located at 579.5 and 588.7 eV, which can be attributed to Cr 2p\textsubscript{3/2}–O and Cr 2p\textsubscript{1/2}–O bonding, respectively.\textsuperscript{25} All of these results indicated that As\textsuperscript{V} and Cr\textsuperscript{VI} were adsorbed on the surface of flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} nanostructures.

A high-resolution O 1s XPS spectrum of flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} (Figure 5b) can be deconvoluted into peaks located at 530.0 and 531.5 eV, which can be attributed to oxygen in the lattice, i.e., oxygen atoms that were bound to only iron atoms (Fe–O), and oxygen atoms on the surface, i.e., oxygen atoms in surface hydroxyl groups (H–O), respectively. The peak intensity of H–O species was significantly higher than that of Fe–O, confirming that there were many hydroxyl groups on the surface of fresh flowerlike \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}. However, the binding energy of the O 1s shifts to low energy after As\textsuperscript{V} and Cr\textsuperscript{VI} adsorption, as shown in panels c and d of Figure 5, respectively. The intensity of the H–O peak became lower than that of the
Fe–O peak after As or Cr adsorption, suggesting that hydroxyl groups have exchanged with H$_2$AsO$_4$$^-$ or Cr$_2$O$_7^{2-}$/HCrO$_4$$^-$ species.

The FTIR spectra of the samples after As$^V$ and Cr$^{VI}$ adsorption were acquired, as shown in Figure 6. The peak from hydroxyl groups of flowerlike α-Fe$_2$O$_3$ nanostructures at around 3430 cm$^{-1}$ decreased after As$^V$ and Cr$^{VI}$ adsorption. This was consistent with XPS results. In addition, new peaks at 813 and 790 cm$^{-1}$ appeared for flowerlike α-Fe$_2$O$_3$ nanostructures after As$^V$ and Cr$^{VI}$ adsorption, which can be attributed to stretching vibrations of As–O and Cr–O, respectively.$^{25,26}$

For a better understanding of the evolution of oxygen species during adsorption, synchrotron-based XANES spectra were obtained, which provided a much higher energy resolution and, consequently, deeper insight into the adsorption processes. Figure 7 showed the normalized O K-edge XANES spectra of flowerlike α-Fe$_2$O$_3$ nanostructures before and after adsorbing heavy metal ions. All of these spectra showed a pair of well-resolved resonance peaks in the pre-edge region around 530 eV, which originated from the transitions of hybridized Fe(3d)–O(2p) states with $t_{2g}$ and $e_g$ orbital symmetry, respectively.$^{27,28}$ The O K-edge spectra are sensitive to the chemical environment of the oxygen atoms. In comparison to pure flowerlike α-Fe$_2$O$_3$, As$^V$, or Cr$^{VI}$-saturated samples showed a substantial decrease of the relative ratio of $t_{2g}$ to $e_g$. The $e_g$ orbital is sensitive to the ligands linked to O atoms.$^{29}$ The $e_g$ peak intensity increased when H–O groups were replaced by H$_2$AsO$_4$$^-$ or Cr$_2$O$_7^{2-}$/HCrO$_4$$^-$ species, so that the ratio of $t_{2g}$/$e_g$ decreased when flowerlike α-Fe$_2$O$_3$ adsorbed As$^V$ or Cr$^{VI}$. On the basis of the above XPS and XANES results, we concluded that the adsorption mechanism of flowerlike α-Fe$_2$O$_3$ nanostructures for As$^V$ and Cr$^{VI}$ was ion exchange between hydroxyl groups and H$_2$AsO$_4$$^-$ or Cr$_2$O$_7^{2-}$/HCrO$_4$$^-$ species. Hydroxyl groups played critical roles for adsorption.
4. CONCLUSION

We produced flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures using a low-cost template-free microwave-assisted solvothermal method. These flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures had a high surface area and abundant hydroxyl on the surface and showed excellent adsorption properties for As$^{V}$ and Cr$^{VI}$. The adsorption mechanism for As$^{V}$ and Cr$^{VI}$ on flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures was confirmed as ion exchange between hydroxyl on the $\alpha$-Fe$_2$O$_3$ surface and As$^{V}$ and Cr$^{VI}$ species. Because of the advantages, such as low cost, high surface area, and high adsorption capacity, such flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures were an attractive adsorbent for the removal of both As$^{V}$ and Cr$^{VI}$ from water.

ASSOCIATED CONTENT

Supporting Information
EDS spectrum of flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures (Figure S1), SEM images of samples obtained under different conditions (Figure S2), TEM images of flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures after As$^{V}$ and Cr$^{VI}$ adsorption (Figure S3), element mapping of flowerlike $\alpha$-Fe$_2$O$_3$ after As$^{V}$ and Cr$^{VI}$ adsorption (Figure S4), and As 3d and Cr 2p XPS spectra of flowerlike $\alpha$-Fe$_2$O$_3$ nanostructures after As$^{V}$ and Cr$^{VI}$ adsorption (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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