Supporting Information:

Removal of Multifold Heavy Metal Contaminations in Drinking Water by Porous Magnetic Fe$_2$O$_3$@AlOOH Superstructure

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Experimental Section

Materials: All chemical reagents used in this experiment were of analytical grade. Pb(NO$_3$)$_2$, Na$_2$HAsO$_4$·7H$_2$O, K$_2$Cr$_2$O$_7$, FeSO$_4$·7H$_2$O, Mg(CH$_3$COO)$_2$·4H$_2$O, Na$_2$CO$_3$, Al(NO$_3$)$_3$·9H$_2$O, HCl, NaOH, ethanol and ethylene glycol were procured commercially and were used as received without further purification.

Synthesis of urchin-like hierarchical Fe$_2$O$_3$@AlO(OH): The urchin-like hierarchical γ-FeOOH was fabricated using one-pot solvothermal method. Specifically, 0.5561 g of FeSO$_4$·7H$_2$O and 0.4289 g of Mg(CH$_3$COO)$_2$·4H$_2$O were dissolved in Milli-Q water (100 mL) under vigorous stirring for 30 min at room temperature. And then, the solution was heated to 90 °C with continuously stirred for additional 1 h in round bottom flask (250 mL). After that, the mixture was filtered through a PTFE membrane (pore size: 0.22 μm), and washed with double-distilled water and ethanol several times. The obtained products were dried in a vacuum oven at 70 °C for 12 h. In order to prepare porous magnetic α, γ-Fe$_2$O$_3$, the vacuum-dried powders were calcined at 350 °C for 4 h using a ramp rate of 5 °C ·min^{-1} in the flow of nitrogen (purity: ≥ 99.99%).

The γ-AlO(OH)-coated α, γ-Fe$_2$O$_3$ were prepared by *in situ* chemical precipitation method in accordance with the following procedure. The obtained α, γ-Fe$_2$O$_3$ (100 mg) and Al(NO$_3$)$_3$·9H$_2$O (360.7 mg) were dispersed in 120 mL ethylene glycol-H$_2$O (v/v = 1:5) through an ultrasonic treatment process for 30 min. Subsequently, 244.6 mg Na$_2$CO$_3$ dissolved in 20 mL deionized water was added to the fully dispersed solution with ultrasonic vibrations for another 30 min. The mixture was then vigorous stirred for 5 h at room temperature. Final products were collected by a PTFE membrane, washing with deionized water and ethanol for several times to remove any possible ionic remnants, followed by drying overnight in a vacuum oven at 70 °C. The γ-AlO(OH) was also prepared according to the same procedure but without α, γ-Fe$_2$O$_3$ added. All chemical reagents used in this study were analytical grade and were used without further purification.

Synthesis of FeOOH using K$_2$CO$_3$ as alkaline source: 0.5561 g of FeSO$_4$·7H$_2$O and 0.2120 g of Na$_2$CO$_3$ were dissolved in Milli-Q water (100 mL) under vigorous stirring for 30 min at room temperature. And then, the solution was heated to 90 °C with continuously stirred for additional 1 h in round bottom flask (250 mL). After that, the mixture was filtered through a PTFE membrane (pore size: 0.22 μm), and washed with double-distilled water and ethanol several times. The obtained products were dried in a vacuum oven at 70 °C for 12 h.

Toxic heavy metal ions removal: The solution containing different concentrations of Pb(II), As(V) and Cr(VI) with 10, 20, 50, 100 and 200 mg·L^{-1} were prepared using Pb(NO$_3$)$_2$, Na$_2$HAsO$_4$·7H$_2$O and K$_2$Cr$_2$O$_7$ as the sources of heavy metal ions, respectively. The pH value of the Na$_2$HAsO$_4$ and K$_2$Cr$_2$O$_7$ solutions was adjusted to 4 with hydrochloric acid (0.2 M) prior to the adsorption experiments to ensure species of As(V) and Cr (VI) as negative

charged anions. The time-dependant curves were preformed with the initial ion concentration for 10 mg·L^{-1} and sample dose for 20 mg/100 mL. At predetermined time intervals, 5 mL supernatant solutions were pipetted and filtered through 0.22 μm PTFE membranes. For the adsorption isotherms, 5 mg of the urchin-like Fe_2O_3@AlO(OH) was added to 25 mL of the above solution under stirring at room temperature. After 12 h, the samples were separated through 0.22 μm PTFE membrane and analyzed by inductively coupled plasma-optical emission spectroscopy (Shimazu ICPE-9000) to measure the concentration of metal ions in the remaining solution. The adsorption capacity of the adsorbents was calculated according to the following equation (1):[1]

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 and C_e represent the initial and equilibrium concentrations (mg·L^{-1}), respectively. V is the volume of the solution (mL), and m is the amount of adsorbent (mg).

Characterization: The morphology and microstructures of the samples were characterized by field emission scanning electron microscopy (FE-SEM, JEOL 6701F), transmission electron microscopy (TEM, JEOL 2010). X-ray diffraction (XRD) patterns were preformed on a Rigaku D/max-2500 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation. Fourier transform infrared spectrometry (FT-IR, Thermo Fisher Scientific) was employed to analyze the surface chemical composition. Thermal gravity measurement was made on a TGA/STA409 PC module with a rising temperature rate of 10 °C min^{-1} from 50 to 1000 °C under continuous N_2 flow. ^{27}Al solid-state NMR spectra were recorded at 104.2 MHz with a pulse width of 0.33 μs on a Bruker Avance 400 solid-state

spectrometer by using an aluminum sulfate liquid solution as a reference. The specific surface areas of the as-prepared products were measured on a Quantachrome Autosorb AS-1 instrument, and the pore size distributions were derived from the desorption branches of the isotherm with the Barrett-Joyner-Halenda (BJH) model. The magnetic properties of the magnetic nanocomposites were investigated using a vibrating sample magnetometer with an applied field of between -10000 and 10000 Oe at room temperature. pH value was measured using pH meter (Thermo Scientific, Model: 410p-13).
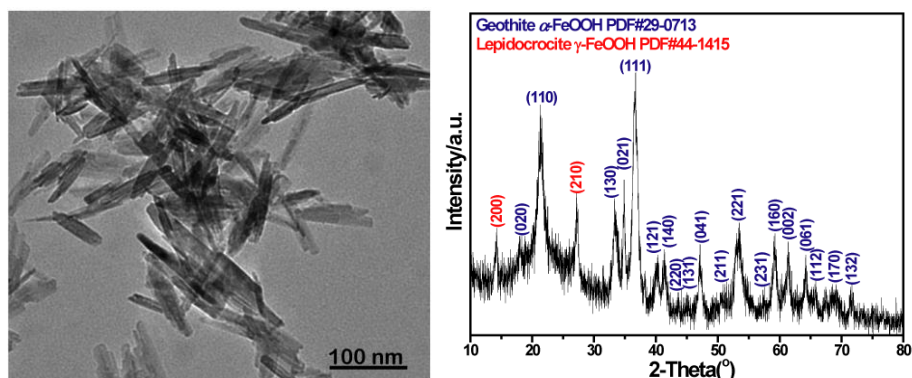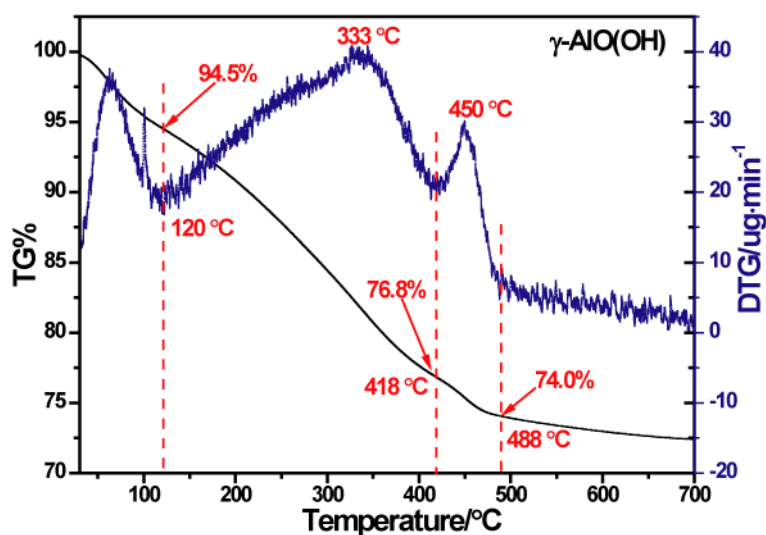

γ-FeOOH

α, γ- Fe_2O_3

$Fe_2O_3@AlO(OH)$

Fig. S1 TEM image (left) and XRD result (right) of FeOOH prepared by Na_2CO_3 as alkaline source.

**Fig. S2** TG and DTG curves of γ-AlO(OH).

Fig. S2 shows the TG-DTG profiles of the synthesized γ-AlO(OH). The weight loss between 30 and 120 °C in the TG curve, accompanied with an endothermic peak around 120 °C, could be attributed to the loss of surface adsorbed water.[2] The weight loss between 120 and 418 °C on the TG curve, accompanied with a strong exothermic peak around 333 °C, is mainly due to the γ-AlO(OH) tardily decomposed to γ-Al_2O_3. The mass loss of the γ-AlO(OH) at 120-418 °C of ca. 17.7 % is due to the removal of structural water and the surface –OH groups from γ-AlO(OH), which is higher than that of the theoretical value of

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15% on going from γ-AlO(OH) to γ-Al$_2$O$_3$.[3] A sharp exothermic peak appears on the DTG

curve of around 450 °C may be caused by the decomposition of carbonate ions adsorbed on

the surface of γ-AlO(OH), whose existence has been confirmed by XPS and FT-IR

spectroscopy.
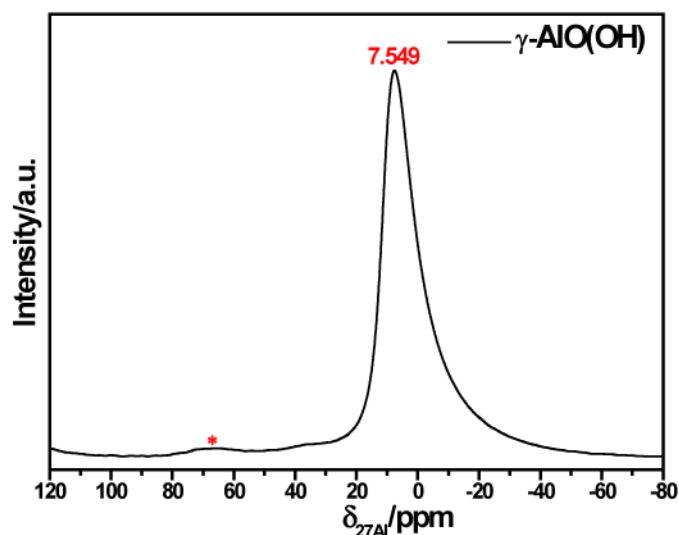
Fig. S3 ^{27}Al MAS NMR spectra of prepared γ-AlO(OH).

Solid-state ^{27}Al MAS NMR spectra of the pure AlO(OH) s shown in Fig. S3, which has

been used extensively to study the properties of glasses, zeolites, ceramics and cements, etc.[4]

Under certain conditions, solid-state NMR spectra can yield valuable information about

chemical bonding and molecular structure that may be unavailable from solution NMR

spectroscopy. The spectrum from the sample shows a single peak at 7.549 ppm,

corresponding to boehmite γ-AlO(OH), which has been widely reported possessing a signal

with chemical shift in the range 4~9 ppm.[5] Meanwhile, It has been clearly confirmed that

boehmite γ-AlO(OH) contains only octahedrally coordinated aluminium.[6]
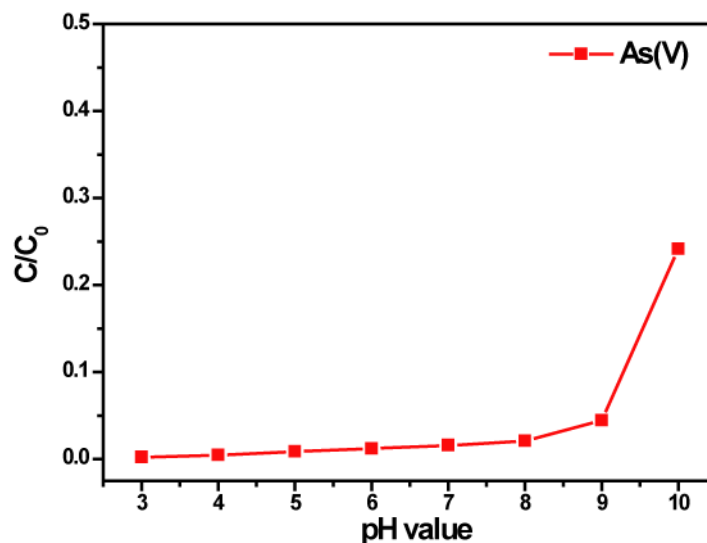
Fig. S4. Adsorption efficiencies of As(V) by $Fe_2O_3@AlO(OH)$ as a function of pH. Experiments were conducted at pH 3~10, with 5 mg samples stirring for 12 h. Initial arsenic concentration: 5 mg·L^{-1}, sample volume: 25 mL.
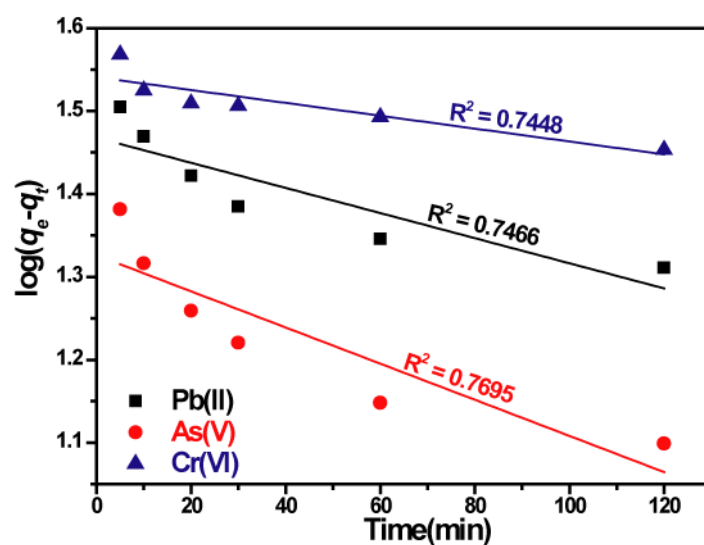
Fig. S5 Adsorption kinetics based on the pseudo-first-order kinetic model on the adsorption of Pb(II), As(V) and Cr(VI) ions onto the $Fe_2O_3@AlO(OH)$, the initial ion concentration is 10 mg·L^{-1} and sample dose is 20 mg/100 mL.

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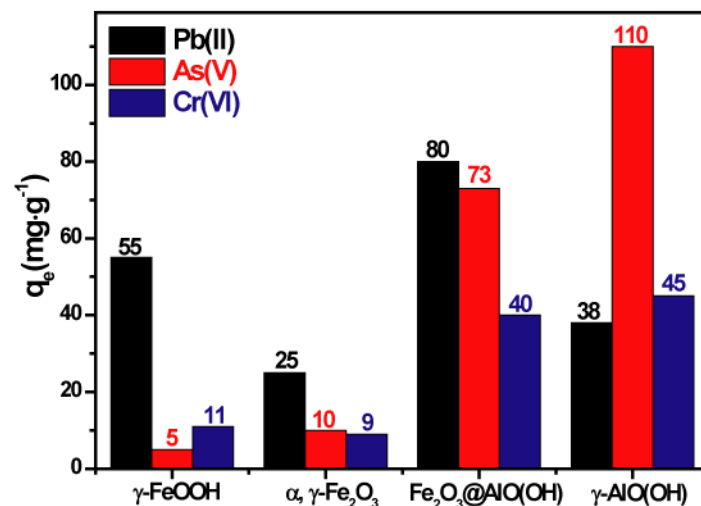
Fig. S6 Different samples as sorbents for Pb(II), As(V) and Cr(VI) ions removal.

Table S1 Summary of As(V), Cr(VI) and Pb(II) maximum adsorption capacities (q_m) on various adsorbents.

Sorbents	As(V): q_m (mg.g^{-1})	Cr(VI): q_m (mg.g^{-1})	Pb(II): q_m (mg.g^{-1})	BET (m^2.g^{-1})
Fe$_2$O$_3$@Al(OH)CO$_3$ (this study)	75.3	41.3	89.2	320.8
Urchin-like α-FeOOH hollow spheres [7]	58	--	80	96.9
Chrysanthemum-likeα-FeOOH [8]	66.2	--	103	120.8
Ceria Hollow Nanospheres [9]	22.4	15.4	9.2	72
3D Flowerlike Fe$_2$O$_3$ Nanostructures [10]	7.6	5.4	--	40
Flowerlike α-Fe$_2$O$_3$ [11]	51	30	--	130
Mesoporous Zr-Ti Oxide [12]	--	29.46	--	413
Mesoporous Titania Beads [13]	--	11.5	--	144
Fe@Fe$_2$O$_3$Core-Shell Nanowires [14]	--	7.78	--	31.1
hierarchicalSiO$_2$@γ-AlOOH spheres	--	~4.5	--	139.5
γ-AlOOH(Boehmite)@SiO$_2$/Fe$_3$O$_4$ [15]	--	--	214.59	28.6

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