

## Electronic Supplementary Information

### Magnetic Fe<sub>3</sub>O<sub>4</sub>@NiO Hierarchical Structures: Preparation and Their Excellent As(V) and Cr(VI)

#### Removal Capabilities

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#### Sorption experiments.

For the kinetic experiments, 50 mg of the Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres was added to 60mg/L (100 mL) As(V) and Cr(VI) solution under stirring at T=30°C. The pH 6.2 was adjusted by adding negligible volumes of NaOH (1-0.1M) or HCl (1-0.1M). Samples were withdrawn at appropriate time intervals and supernatant liquid was separated by centrifuging at 9000 rpm for 10 min, and atomic absorption spectrophotometer (Shimazu ICPE-9000) was used to measure the concentration of As(V) or Cr(VI) in the remaining solution.

To obtain the adsorption isotherms, 50 mg of the Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres were added to 100 mL (40~300 mg/L) As(V) and Cr(VI) solution under stirring at T=30°C. The pH 4 was adjusted by adding negligible volumes of NaOH (1-0.1M) or HCl (1-0.1M). After stirring for 4 h, the solid and liquid were separated immediately by centrifuging at 9000 rpm for 10 min and atomic absorption spectrophotometer (Shimazu ICPE-9000) was used to measure the concentration of As(V) or Cr(VI) in the remaining solution.

For pH experiment, Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres suspension and 300mg/L As(V) or Cr(VI) solutions were added to 10 mL polyethylene tubes to achieve the desired concentrations of different

components. The pH, ranging between 4 and 10, was adjusted by adding negligible volumes of NaOH (1-0.1M) or HCl (1-0.1M). After the mixture was oscillated for 24 h at T=30°C, the solid and liquid phases were separated by centrifugation at 9800 rpm for 10 min and atomic absorption spectrophotometer (Shimazu ICPE-9000) was used to measure the concentration of As(V) or Cr(VI) in the remaining solution

The Langmuir and Freundlich isotherm models are applied to simulate As(V) and Cr(VI) adsorption on Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres. The Langmuir model is expressed as:

$$q_e = \frac{bq_m C_e}{1 + bC_e}$$

The Freundlich isotherm model can be expressed by the following formula:

$$q_m = k_F C_e^n$$

where  $C_e$  is the equilibrium concentration of As(V) and Cr(VI) in the supernatant (mg/L);  $q_m$  is the amount of As(V) and Cr(VI) adsorbed per weight of Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres (mg/g) after adsorption equilibrium;  $q_m$  represents the maximum adsorption capacity of As(V) and Cr(VI) per weight of Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres composites (mg/g); and  $b$  is the Langmuir adsorption constant (L/mg). The Freundlich constant  $k_F$  is correlated to the relative adsorption capacity of the adsorbent (mg/g), and  $n$  is the adsorption intensity.

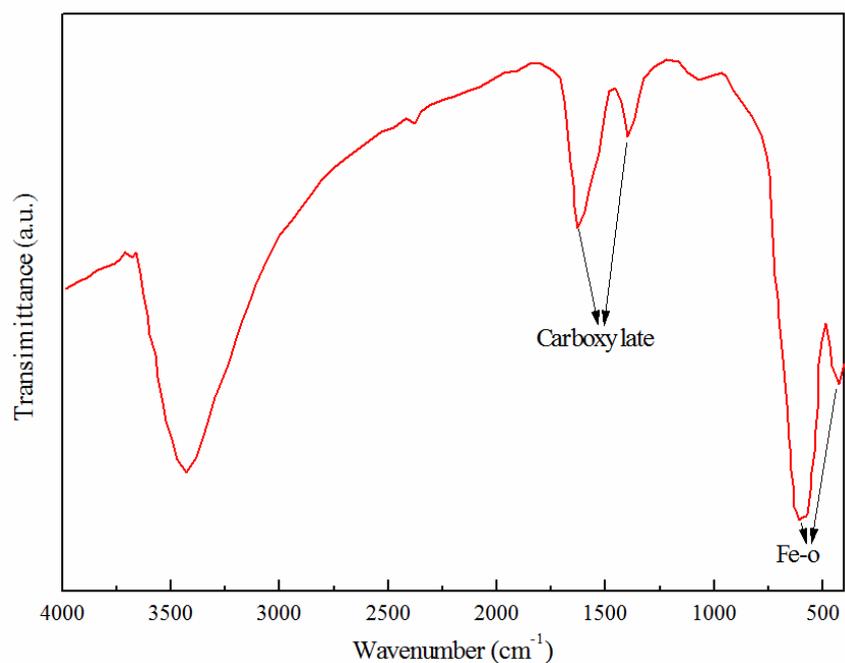


Figure S1. FT-IR spectrum of the Fe<sub>3</sub>O<sub>4</sub> microspheres. The bands at 1629 and 1397 cm<sup>-1</sup> are associated with carboxylate group. Typical bands assigned to the Fe-O stretching are visible at around 590 and 425 cm<sup>-1</sup>. This hydrophilic group offers the Fe<sub>3</sub>O<sub>4</sub> nanoparticles with high water solubility as well as good adsorbents.

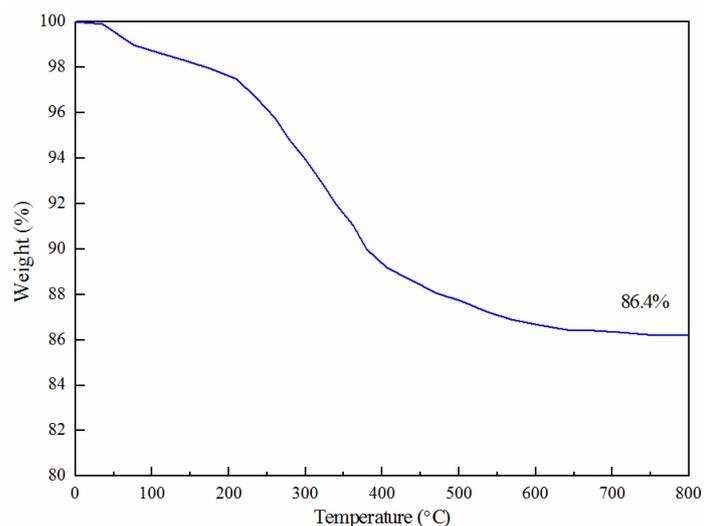


Figure S2 TGA thermogram curve of Fe<sub>3</sub>O<sub>4</sub>

To further confirm the presence of carboxylate groups on the magnetic particles, thermogravimetric analysis was performed. The weight loss increases with an increase of the amount of sodium citrate, which further confirmed that the weight loss in the formulations is due to the modification of the carboxylate groups.

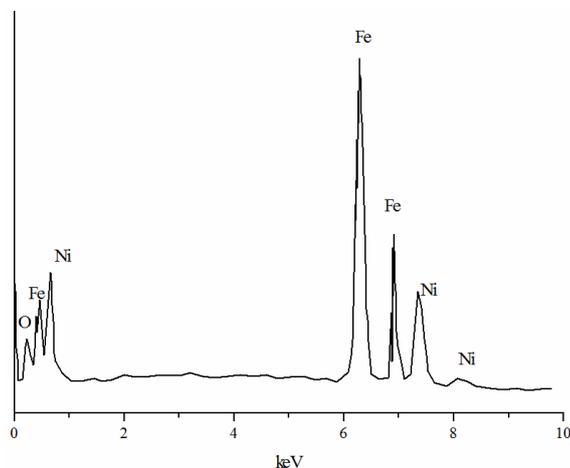


Figure. S3 The EDS spectrum of Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres

EDS result originated from the point scan confirms the presence of Ni, Fe, and O in Fe<sub>3</sub>O<sub>4</sub>@NiO nanocomposites, indicating the successful attachment of the nickel oxide shell and well-retained magnetite phase.

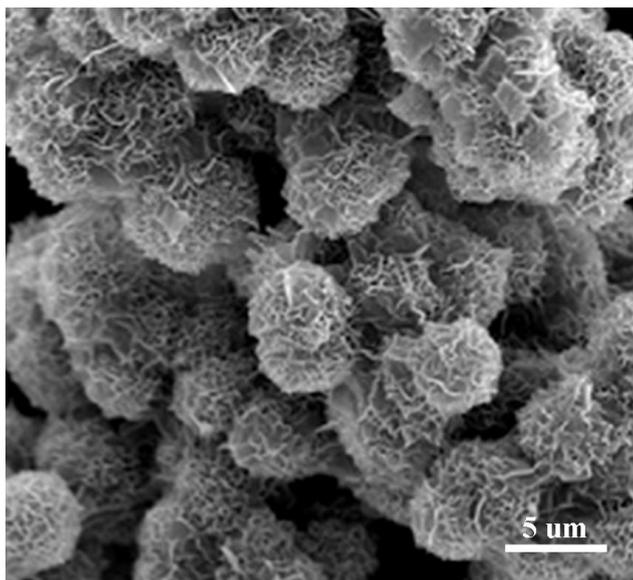


Figure S4. SEM image of the as-synthesized NiO hierarchical microspheres for 8 h.

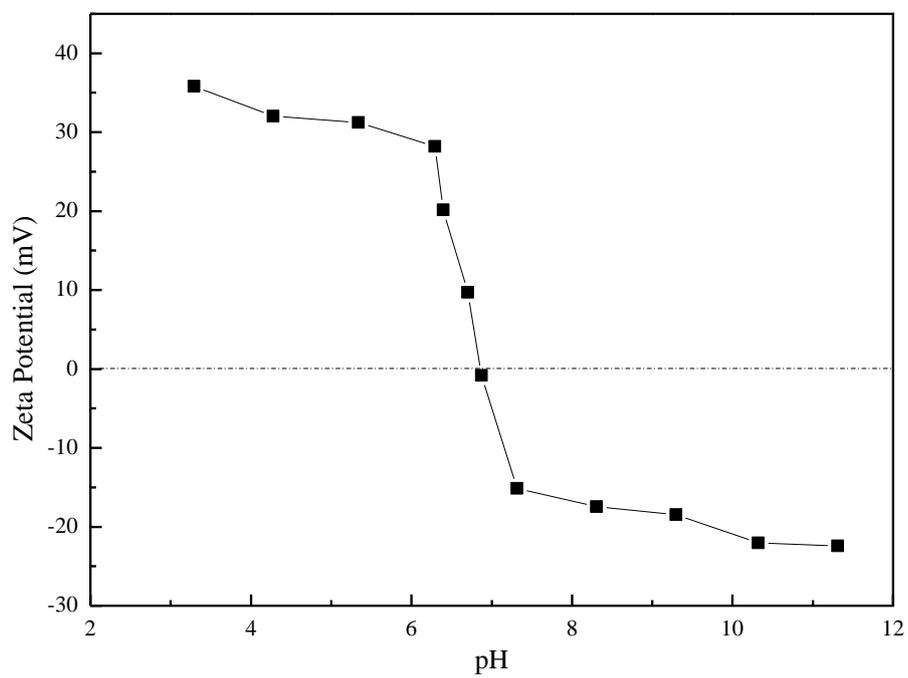


Figure S5. Zeta potentials of Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres as different pH values.

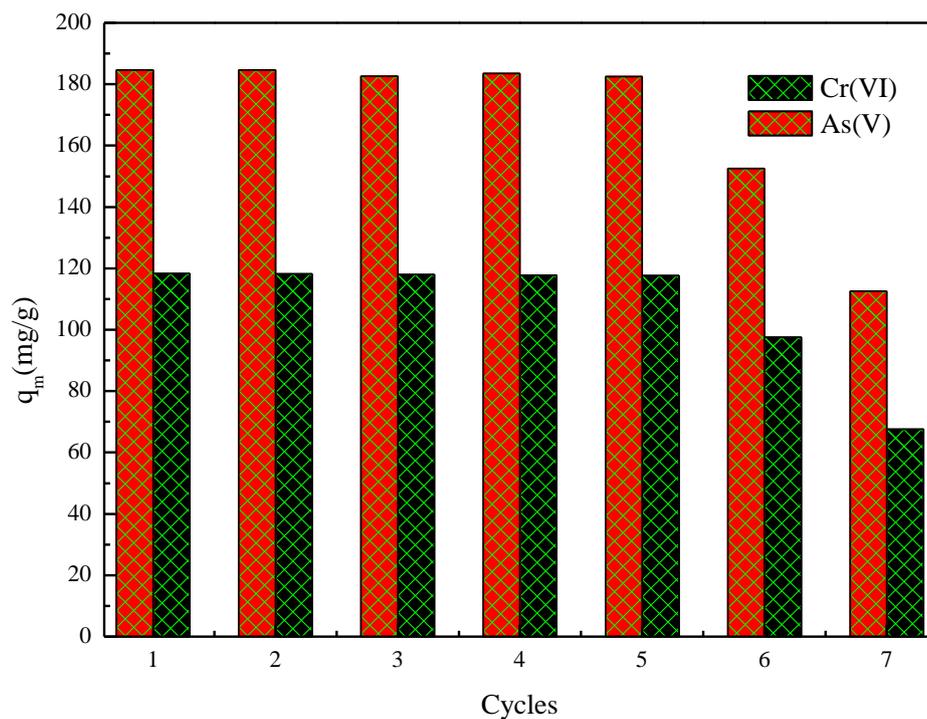


Figure S6. Five cycles of the adsorption process of Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres structures.

Table S1. Kinetics parameters for As(V) and Cr(VI) removal on Fe<sub>3</sub>O<sub>4</sub>@NiO hierarchical microspheres

	Second-Order Kinetic					
	K(g/(mg·min))		q <sub>e</sub> (mg/g)		R <sup>2</sup>	
	As(V)	Cr(VI)	As(V)	Cr(VI)	As(V)	Cr(VI)
Fe <sub>3</sub> O <sub>4</sub> @NiO	6.41×10 <sup>-4</sup>	2.31×10 <sup>-3</sup>	95.87	142.86	0.999	0.999