Facile Synthesis of Magnetic Hierarchical Copper Silicate Hollow Nanotubes for Efficient Adsorption and Removal of Hemoglobin

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Experimental Section

Materials

$AgNO_3$ was purchased from Shanghai Reagent Factory. PVP (Mn=40000)was purchased from Yonghua Chemical Technology co., Ltd. (Jiangsu.China). Iron(III) acetylacetonate ($Fe(acac)_3$, 99%) was from energy chemical. Triethylene glycol (TREG, 99%) and glycerol was purchased from SCRC. TEOS, Nickel(II) Chloride hexahydrate, Copper(II) Chloride Dihydrate, Magnesium sulfate anhydrous, ammonia chloride were purchased from Aladdin Co., Ltd(shanghai). Other reagents used were analytical grade.

Preparation of magnetic silver nanowires

Fe_3O_4-coated Ag NWs were synthesized according to our previously work. Briefly, 10 mL Ag NWs(10 mg/mL) ethanol solution and 30 mL triethylene glycol add to the flask, and the mixture was then heated to 95°C to remove ethanol. After the ethanol was removed completely, 150 mg of the iron precursor $Fe(acac)_3$ and 30 mL triethylene glycol were added to the flask. The solution was sonicated for 5 min. Finally, the resulting mixture was then heated to 278 °C under vigorous stirring and N_2 protection and kept at reflux for 30 min. After cooling to room temperature, 60 mL ethanol was added to dilute the solution. The obtained composites was centrifuged at 4000 rpm for several times until the centrifugal supernatant fluid was colorless transparent and dried in vacuum.

Preparation of SiO_2 coated magnetic silver nanowires

For coating of the silica shell on the Ag NWs/Fe_3O_4 surface, a certain amount of synthesized 2 mL of the Ag NWs/Fe_3O_4 ethanol solution were dispersed in a mixture of 38 mL ethanol, 10 mL water and 1.5 mL aqueous ammonia in a round bottomed flask. Finally, 600 uL TEOS was added slowly with gentle stirring(320 rpm) at room temperature for 10 h. The resulting product was collected via a magnet and washed with deionized water and ethanol for 3 times to remove by-products. And finally the composites were dried in a vacuum at 60°C for 24 h.

Synthesis of magnetic hierarchical copper silicate hollow nanotube.

Magnetic copper silicate hollow nanotubes were fabricated through a simple hydrothermal process. In a typical synthesis copper(II) chloride dihydrate (1.6 mmol), ammonia chloride (16 mmol), and $NH_3{\cdot}H_2O$ (1.5 mL,

28%) were added under stirring to 40 mL of distilled water, and the mixture solution and the as-made Fe_3O_4@ SiO_2 nanotube (80 mg/30 mL) were transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 140°C for 10 h. After the autoclave was cooled to room temperature, the resulting products were collected by magnetic separation and washed with deionized water and absolute ethanol for several times. The final products were dried under vacuum at 60°C for 12 h. The magnetic hierarchical nickel silicate and magnesium silicate hollow nanotubes were prepared under a similar experimental process by varying the corresponding reactants(as shown in Table S1)

Table.S1

	$CuCl_2$	$NiCl_2$	$MgSO_4$	$NH_3{\cdot}H_2O$	NH_4Cl
1	●			●	●
2		●		●	●
3			●	●	●
4	●				

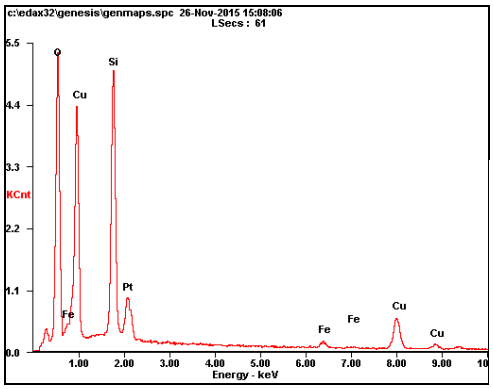
The adsorption experiment for small molecules(MB).

Methylene blue(MB) was used as the model small molecules to evaluate the high uptake capacity of the magnetic HCNTs. The as-prepared magnetic hierarchical copper silicate nanotubes(1mg) were mixed with 30 mL MB solutions of different concentrations (1, 3, 5, 6, and 10 mg L^{-1}) at room temperature. The above mixed solution was ultrasonicated for 3 min and stirred for 6 hours to ensure adsorption equilibrium. After reached the adsorption equilibrium the magnetic hierarchical copper silicate nanotubes were separated from aqueous solution by using a magnet. The top solution was moved to a quartz cuvette with optical length of 10 mm for the absorbance measurement. A UV-Vis spectrophotometer was used to determine the concentration of MB solution.

Characterization

The morphology and the size of the synthesized samples were characterized by scanning electron microscope (SEM, Hitachi S-8000, Japan) in a secondary electron scattering mode at 5 kV or 1 kV and transmission electron microscope (TEM)[JEOL 2010]. X-Ray powder diffraction (XRD) patterns of the products were recorded with a Rigaku D/max-γB diffractometer equipped with a rotating anode and a Cu Kα source (l = 0.154 nm). And the magnetic characterization of the hierarchical copper silicate hollow nanotubes were carried out using a vibrating

specimen magnetometer. Brunauer–Emmett–Teller (BET) surface area was measured on a Micromeritics Asap 2460 analyzer at 77.4 K. The dye concentrations were determined by a UV-vis spectrophotometer (UV-1601, Shimadzu, Japan).



Element	Wt%	At%
OK	10.64	24.28
SiK	33.07	43.01
FeK	04.30	02.81
CuK	51.99	29.89
Matrix	Correction	ZAF

Fig. S1 The EDX spectrum of the magnetic HCNTs composites

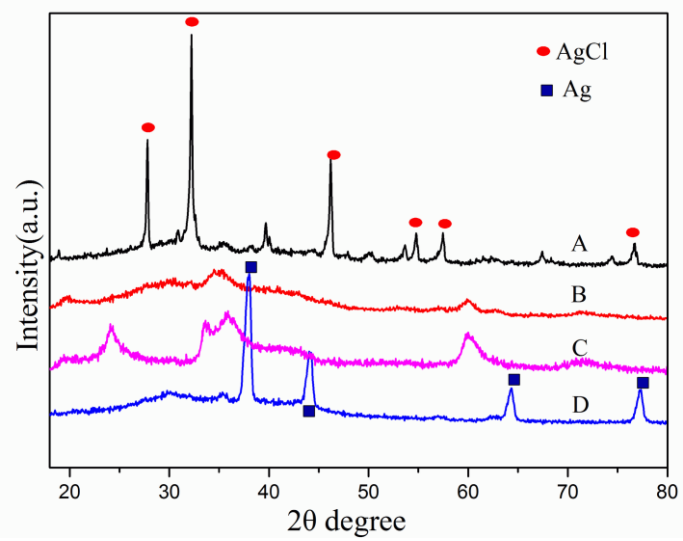


Fig. S2 X-Ray diffraction patterns of the as-prepared products of SiO_2/Fe_3O_4/AgNWs and $CuCl_2$ in H_2O(A), SiO_2/Fe_3O_4/AgNWs and $MgSO_4$ in NH_3-NH_4Cl buffer(B), SiO_2/Fe_3O_4/AgNWs and $NiCl_2$ in NH_3-NH_4Cl buffer (C), SiO_2/Fe_3O_4/AgNWs composites(D)

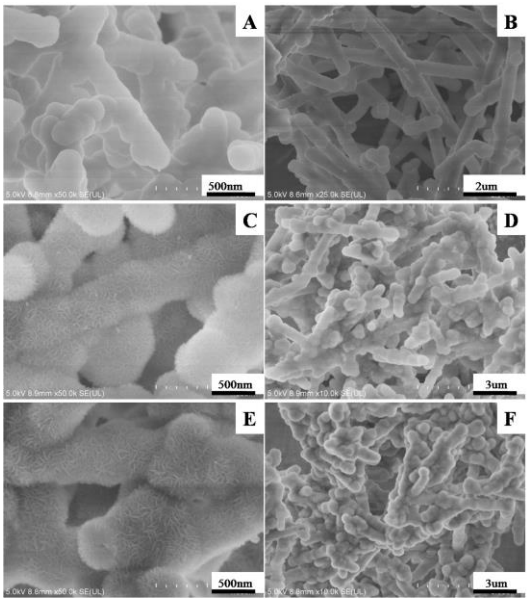


Fig. S3 The as-prepared products of SiO_2/Fe_3O_4/AgNWs and $CuCl_2$ in H_2O(A,B), SiO_2/Fe_3O_4/AgNWs and $MgCl_2$ in NH_3-NH_4Cl buffer(C,D), SiO_2/Fe_3O_4/AgNWs and $NiCl_2$ in NH_3-NH_4Cl buffer (E,F)

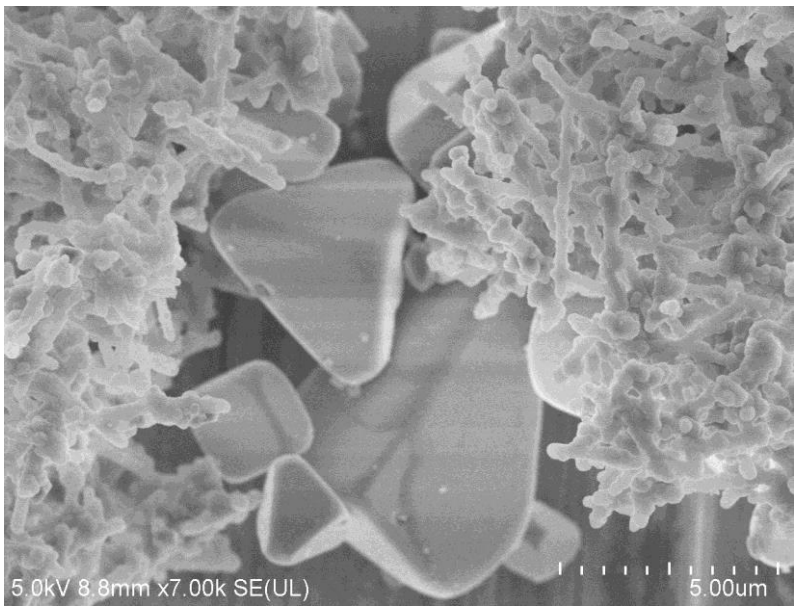


Fig. S4 The SEM images of as-prepared product SiO_2/Fe_3O_4/Ag NWs composites reacted with $CuCl_2$ in purified water

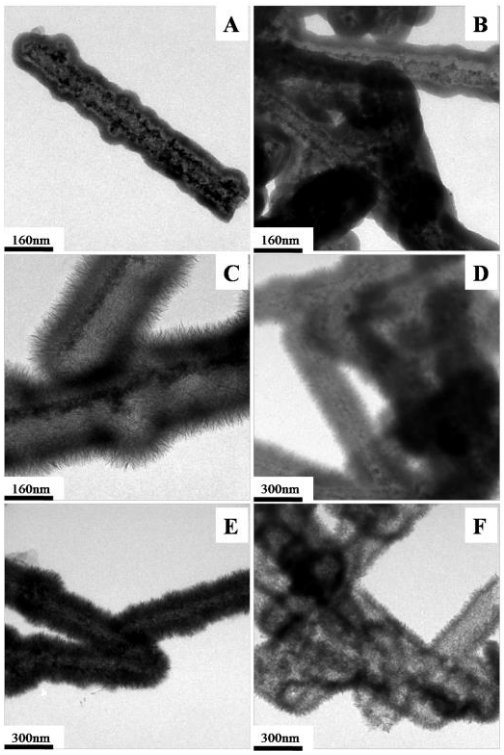


Fig. S5 The as-prepared products of SiO_2/Fe_3O_4/Ag NWs and $CuCl_2$ in H_2O (A, B), SiO_2/Fe_3O_4/Ag NWs and $MgCl_2$ in NH_3-NH_4Cl buffer (C, D), SiO_2/Fe_3O_4/Ag NWs and $NiCl_2$ in NH_3-NH_4Cl buffer (E, F)

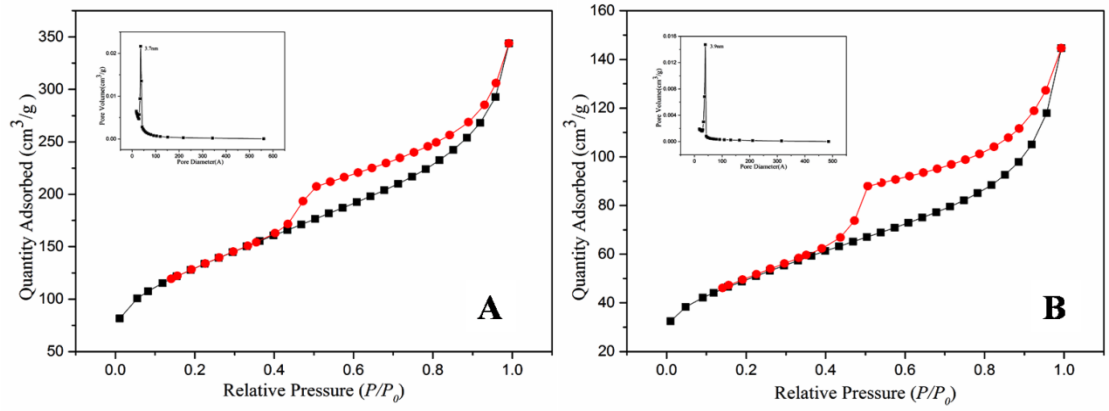


Fig. S6. Nitrogen adsorption–desorption isotherm of the as-prepared magnetic hierarchical magnesium silicate nanotube(A), magnetic hierarchical nickel silicate nanotube (B).

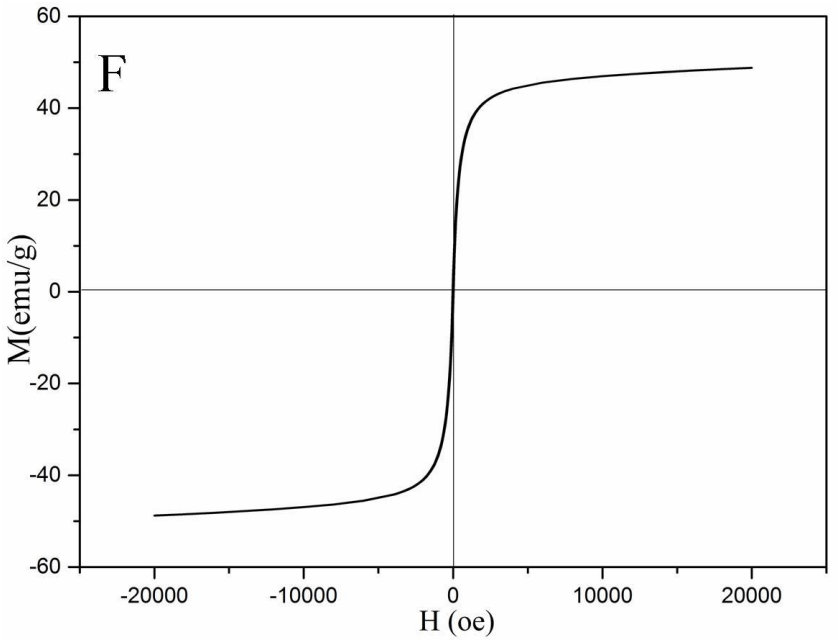


Fig. S7 Magnetic hysteresis curves measured at RT Fe_3O_4(without the addition of Ag NWs)(47.8 emu g^{-1})

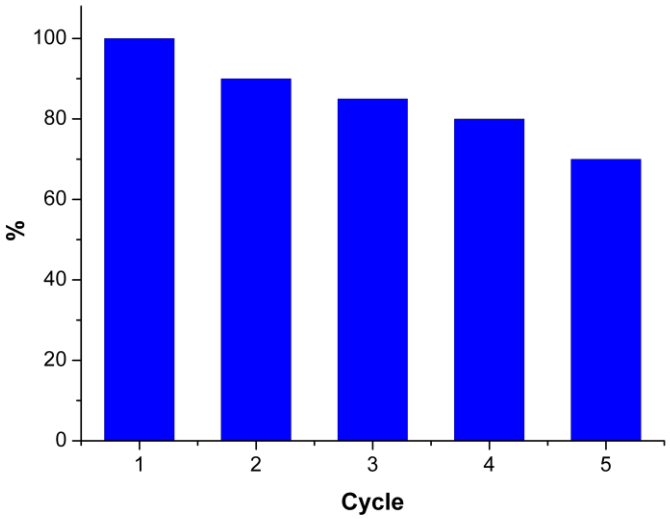


Fig. S8 Reusability of magnetic hierarchical copper silicate hollow through the adsorption–regeneration cycle for BHb.