

## Electronic Supporting Information

### Magnetic nanoparticles coated with dithizone-modified chitosan for use in solid-phase extraction of copper(II)

Lei Zhang\*, Zhichao Xiong, Lingyi Zhang, Bohao Yu, Weibing Zhang\*

*Research Center of Analysis Test and Key Laboratory of Functional Materials Chemistry, East China University of Science and Technology, 200237 Shanghai, China*

*weibingzhang@ecust.edu.cn*

*leizhang595@126.com*

#### Contents

Experimental-----	2
Synthesis of magnetic nanoparticles coated with chitosan-----	2
Synthesis of bromoalkyl-dithizone-----	2
Preparation of magnetic nanoparticles coated with dithizone-modified chitosan-----	2
Figure S1 <sup>1</sup> H NMR and HRMS spectra of bromoalkyl-dithizone-----	3
Figure S2 SEM (a) and TEM (b) of magnetic nanoparticles coated with dithizone-modified chitosan-----	4
Figure S3 EDS of magnetic nanoparticles coated with chitosan (a) and magnetic nanoparticles coated with dithizone-modified chitosan (b)-----	5
Figure S4 Effect of pH on the adsorption efficiency of Cu <sup>2+</sup> -----	5
Table S1 Comparison between this method and literatures-----	6

### *Preparation of magnetic nanoparticles coated with chitosan*

The magnetic nanoparticles were prepared by conventional method[1]. Briefly, 2.7 g ferric trichloride hexahydrate was dissolved in ethylene glycol (100 mL) to form a clear orange yellow color solution and followed by the addition of anhydrous sodium acetate (7.2 g). The mixture was homogeneous mixed by ultrasonication. Then, the solution was sealed in a PTFE-lined autoclave and reacted at 200 °C for 8 h. The resulting magnetic nanoparticles were separated by external magnetic force and then rinsed with water and ethanol for 3 times each, dried at 50 °C in a vacuum overnight.

0.4 mL TEOS, 40 mL of water, 160 mL ethanol and 200 mg magnetic nanoparticles were mixed added to a three neck flask, adjusted to pH 4.5 by ammonium hydroxide, then the suspension was stirred for 10 h at room temperature. The Silica magnetic nanoparticles were isolated and washed several times with water and ethanol.

Then 200 mg of silica magnetic nanoparticles was into 100 mL of isopropanol. Sequentially, 2 mL of APTES was added dropwise to the mixture while it was mechanically stirred for 24 h at room temperature under nitrogen protection. The functionalized silica magnetic nanoparticles with amino groups were isolated and washed by the same method with silica magnetic nanoparticles.

The glutaraldehyde-activated magnetic nanoparticles were prepared by literature[2]. Silica magnetic nanoparticles with amino groups were dispersed into 100 mL of acetic acid/methanol (v/v, 1: 125), 4 mL of pentanedial was added, and the reaction was allowed to continue for 10 h at room temperature to generate the Schiff base. The product was isolated and washed several times with methanol.

Then, the glutaraldehyde-activated magnetic nanoparticles was added to 0.20 g chitosan of 100 mL with 1 % acetic acid solution. The reaction was allowed to continue for 10 h at room temperature, then 5 mL 10 % sodium borohydride was added to gain magnetic nanoparticles coated with chitosan.

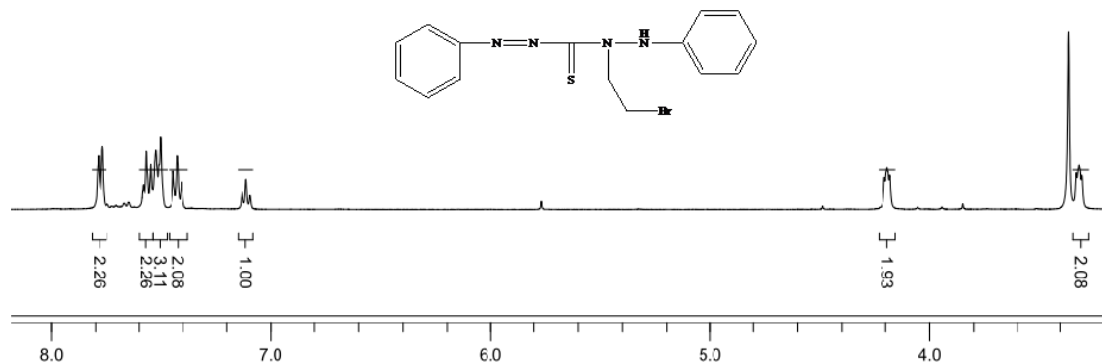
### *Synthesis of bromoalkyl-dithizone*

In order to modified the magnetic nanoparticles coated with chitosan, the ligand of bromoalkyl-dithizone was synthesis. Dithizone (0.12 g) which was solution by acetonitrile (15 mL), then, was added dropwise to a solution of 1,2-dibromoethane (5 ml) solution with potassium carbonate (0.20 g) at 60 °C. The mixture was allowed to stir at room temperature overnight. Upon completion, the precipitation was filtered, acetonitrile was removed under reduced pressure, the bromoalkyl-dithizone was obtained as a darkly solid.

### *Preparation of magnetic nanoparticles coated with dithizone-modified chitosan*

0.2 g bromoalkyl-dithizone was dissolved by 30 mL dimethylformamide solution. Then, the magnetic nanoparticles coated with chitosan (0.20 g) were added into bromoalkyl-dithizone solution with potassium carbonate (0.20 g). The reaction was mechanically stirred at 60 °C for 10 h. The product was washed by ethanol and water and dried at 50°C in a vacuum overnight.

The chemical structures of bromoalkyl-dithizone was characterization by NMR and ESI spectra (Fig. S1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.80 (d, 2H), 7.58 (t, 3H), 7.50 (d, 2H), 7.42 (d, 2H), 7.16 (t, 1H), 5.80 (s, 1H), 4.20 (t, 2H), 3.25 (t, 2H), ESI (HR): m/z 363.0206 (M+H)<sup>+</sup>, calculated 363.0279 for (M+H)<sup>+</sup>.



Monoisotopic Mass, Even Electron Ions  
19 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:  
C: 0-15 H: 0-16 N: 0-4 S: 0-1 Br: 0-1

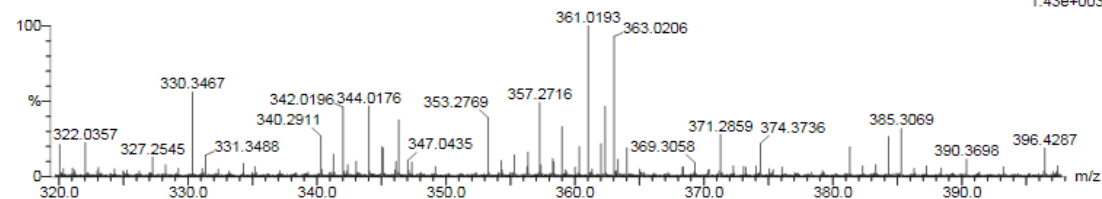
WB-ZHANG

ECUST institute of Fine Chem

24-Mar-2014

ZWB-ZL-1 208 (1.373) Cm (208:222)

22:59:17  
1: TOF MS ES+  
1.43e+003

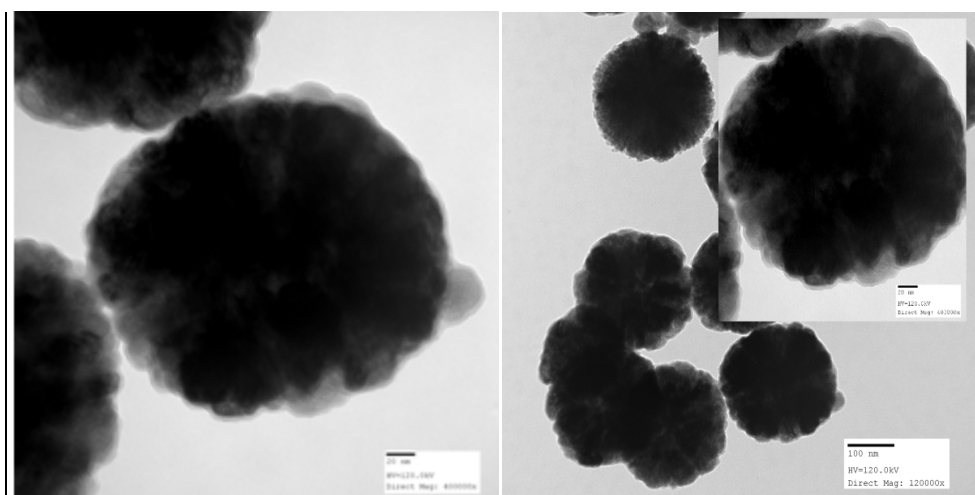
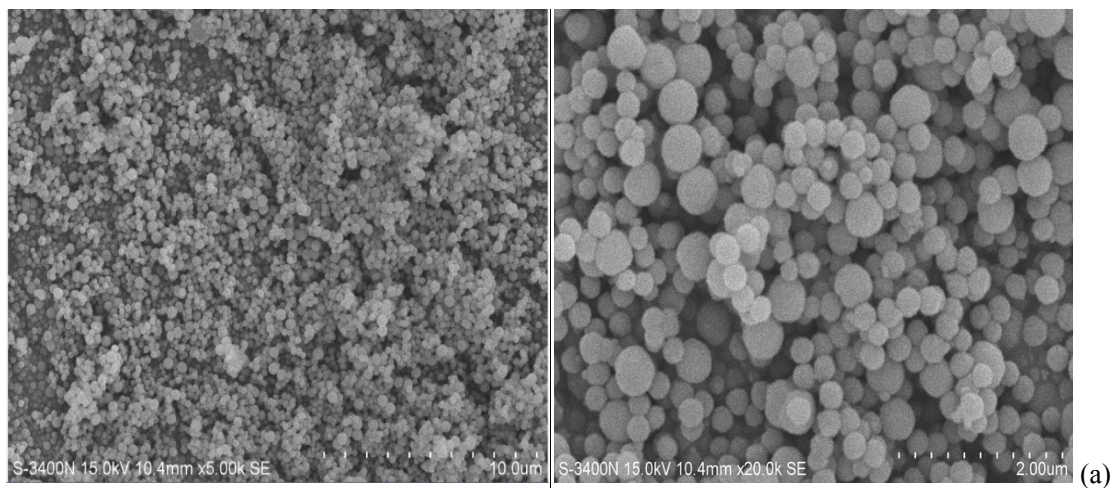


Minimum:  
Maximum:

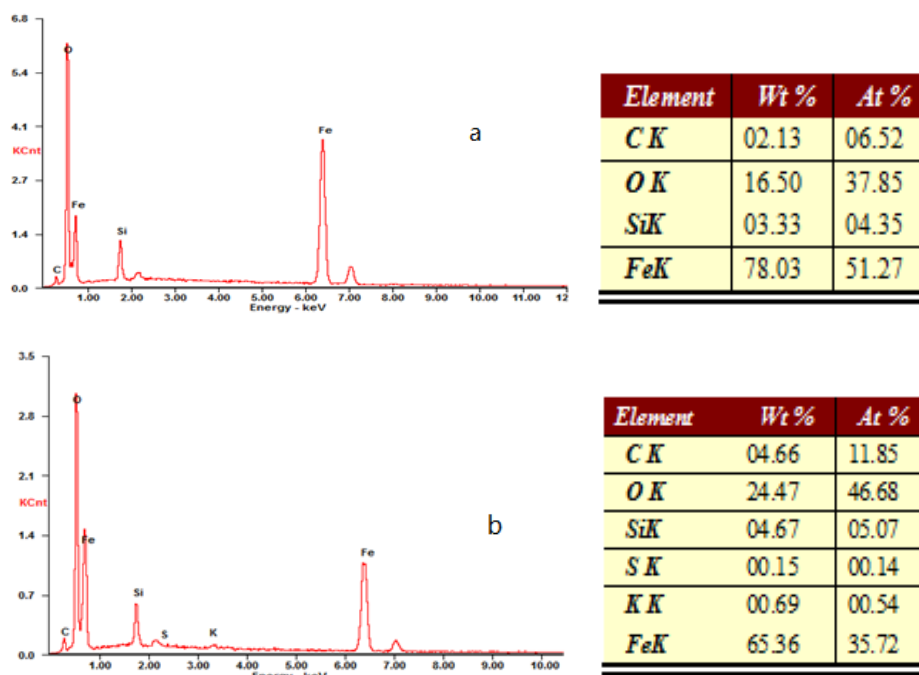
30.0 50.0 -1.5  
100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
363.0206	363.0279	-7.3	-20.1	9.5	176.2	0.0	C15 H16 N4 S Br

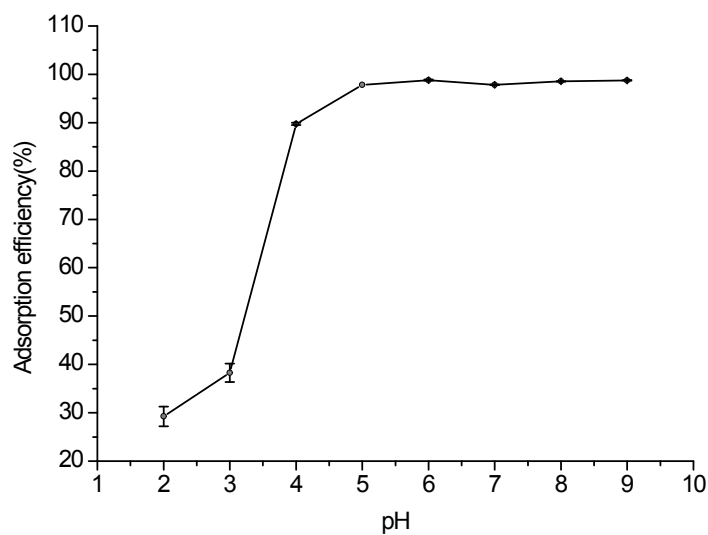
**Figure S1** <sup>1</sup>H NMR and HRMS spectra of *bromoalkyl-dithizone*



(b)  
**Figure S2** SEM (a) and TEM (b) of magnetic nanoparticles coated with dithizone-modified chitosan



**Figure S3** EDS of magnetic nanoparticles coated with chitosan (a) and magnetic nanoparticles coated with dithizone-modified chitosan (b)



**Figure S4** Effect of pH on the adsorption efficiency of  $\text{Cu}^{2+}$  condition : initial concentration: 4 mL  $100 \mu\text{g L}^{-1}$ , amount of adsorbent: 5 mg, extraction time : 10 min

**Table S1** Comparison between this method and literatures<sup>a</sup>Dithizone nanoporous fructose<sup>b</sup>Maximum adsorption capacity

Adsorbent	Detector	Detection limit ( $\mu\text{g L}^{-1}$ )	Calibration range( $\mu\text{g L}^{-1}$ )	MAC <sup>b</sup> (mg g <sup>-1</sup> )	Ref
Dithizone modified silica gel	FAAS	0.2	0.5–120	0.76	3
Dithizone-np-F <sup>a</sup>	FAAS	0.15	0.5–100	81	4
Fe <sub>3</sub> O <sub>4</sub> /IRMOF-3	ETAAS	0.073	0.1–10	2.4	5
Modified Fe <sub>3</sub> O <sub>4</sub> nanoparticle	ICP-OES	0.011	0.1–100	20.5	6
Dithizone modified chitosan coated magnetic nanoparticles	GFAAS	0.18	0.0-10	210	This work

[1] Zhichao Xiong, Weibing Zhang Chem. Commun.(2013)49:9284–9286

[2] Hua Li, Guowang Xu Anal. Chem.(2013)85:11585–11592

[3] Hong-Mei Yu, Hua Song Talanta(2011)85:625–630

[4] Mohammad Behbahani Microchim Acta(2013) 180:911-920

[5] Yang Wang, Jing Xie Microchimica Acta(2014) 181: 949-956

[6] Guihong Cheng, Bin Hu Talanta (2012)88:507–515