

**Simultaneous determination of chemical vapour generation forming elements (As, Bi, Sb, Se, Sn, Cd, Pt, Pd, Hg) and non chemical vapour forming (Cu, Cr, Mn, Zn, Co) by ICP-OES.**

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## **Supporting Information**

This supporting information contains the procedure of synthesis of [1,5-bis (2-pyridyl)-3-sulphophenyl methylene] thiocarbonohydrazide (PSTH) chemically bonded to magnetic nanoparticles (PSTH-MNPs), the instrumentation used for its characterization and the tables with the MS and XPS results.

## **Instrumentation**

Mass spectrum was obtained with a Trace DSQ Mass spectrometer from Thermo Electron Corporation (Massachusetts, USA), the sample was introduced by means of a DIP (direct introduction probe). IR Spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer (Perkin Elmer, Concord, Canada), samples were measured by using potassium bromide pellets, in which the concentrations for the samples were 2% (wt/wt) approximately. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Physical Electronics 5700 instrument with a MgK X-ray excitation source ( $h\nu = 1253.6$  eV); binding energies (BE) were determined with respect to the position of the Ca 2p peak at 346.5 eV. The residual pressure in the analysis chamber was maintained below  $10^{-9}$  Torr during data acquisition. Transmission and scanning electron microscopies (TEM, JEOL, JEM-1400 and SEM, JEOL, JFM 840) were used to observe the microstructures of the new functionalized MNPs.

## **Synthesis of chelating resin.**

The magnetic nanoparticles (MNPs) were prepared by the conventional co-precipitation method with minor modifications.<sup>1</sup> Thus, 11.68 g ferric chloride was dissolved in 200 mL highly purified water within a three neck flask. Under a nitrogen atmosphere, 4.30 g ferrous chloride was added with vigorous stirring at 85 °C. Then 20 mL 30% (vol/vol)  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added with further increased nitrogen passing rate and stirring speeds, and the orange-red clear solution became a black suspension immediately. The reaction was stopped after 30 min, and the obtained suspension was cooled down to room temperature naturally. The nanoparticles were sequentially washed with deionized water,  $0.02 \text{ mol L}^{-1}$  sodium chloride and ethanol for several times until the solution was clarified quickly in the external magnetic field. The cleaned nanoparticles were stored in ethanol at a concentration of  $40 \text{ g L}^{-1}$ . 8 mL TEOS, 60 mL of glycerol and 200 mL ethanol were mixed by ultrasonication in 500 mL large beaker, and adjusted to pH 4.5 by acetic acid–sodium acetate buffer solution. The mixture was added to a three neck flask, followed by adding the magnetite suspension prepared above. Then the suspension was stirred and heated to 60°C, refluxed for 2 h under a nitrogen atmosphere. After cooling to room temperature, the suspension was washed sequentially

with deionized water ( $3 \times 500$  mL) and methanol ( $3 \times 500$  mL). The silica magnetite composite was stored in methanol at a concentration of  $40 \text{ g L}^{-1}$ .

Following the Huang and Hu<sup>2</sup> procedure for the synthesis, the silica-coated magnetite (25 mL) prepared as described above was washed with ethanol ( $2 \times 100$  mL) and then diluted to 150 mL with 1% 3-aminopropyltriethoxysilane into 95% ethanol and  $16 \text{ mmol L}^{-1}$  acetic acid (pH 4.5). The solution was transferred to a 500 mL 3-necked round-bottom flask and then stirred and heated at  $60 \text{ }^\circ\text{C}$  for 2 h under a nitrogen atmosphere. After that, the resulting nanospheres (AP-MNPs) were washed with deionized water three times and twice with methanol, then dried into powders at room temperature under vacuum.

The functionalization of aminopropyl silica coated MNPs is describe in Fig. 1 (1-4). For the synthesis of 2-benzoil (3-sulphophenyl) pyridine (1), a 2.0 g mass of 2-benzoilpyridine was dissolved in 20 mL concentrated sulphuric acid at  $0 \text{ }^\circ\text{C}$ . The solution was refluxed for 2 h, and then cooled and mixed with 180 mL of ether. The mixture was then cooled in a refrigerator and the product, 2-benzoil (3-sulphophenyl) pyridine, was filtered, washed with ether, recrystallised from ethanol:water (1:1) and dried. Then, 5.0 g AP-MNPs were mixed with 100 mL of 3% (vol/vol) diglutaric aldehyde in deionised water and the reaction mixture was refluxed for 4 h (2). The solid obtained (GlutAP- MNPs) was filtered off, washed with de-ionised water and mixed with 1.5 g of thiocarbonohydrazide previously dissolved in 100 mL of de-ionised water; five drops of glacial acetic acid were added. After boiling and refluxing for 24 h, the corresponding derivative (TCHGlutAP- MNPs) was obtained (3). After that, the TCHGlutAP-MNPs obtained, was mixed with 2% (wt/vol) 2-benzoil (3-sulphophenyl) pyridine in ethanol/water 40/30 (4). After refluxing for 24 h, the resulting product (PSTH-MNPs) was filtered off, washed with ethanol and dried in an oven at  $50^\circ\text{C}$ .

## References

- 1 X.Q. Liu, Z.Y. Ma, J.M. Xing, H.Z. Liu, *J. Magn. Magn. Mater.*, 2004, **270**, 1.
- 2 C. Z. Huang, B. Hu. *Spectrochimica Acta Part B*, 2008, **63**, 437.

Table 1. Identification of some peaks of mass spectrum for PSTH-MNPs

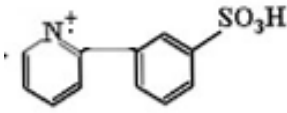
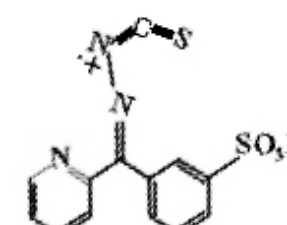
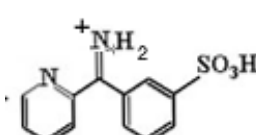
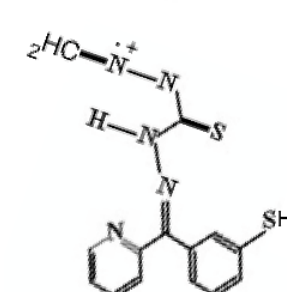
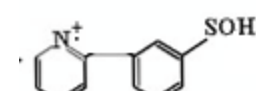
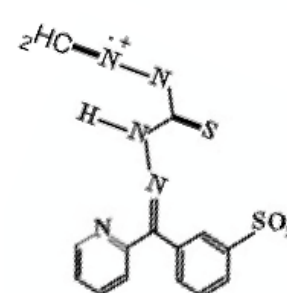
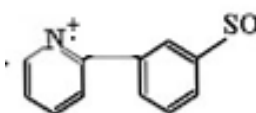
Peak / m/z	Attributions	Peak / m/z	Attributions
64	SO <sub>2</sub>	235	
81	-SO <sub>3</sub> H (sulphonic group)	272	
183		316	
203		362	
219			

Table 2. Concentration of different element in AP-MNPs and PSTH-MNPs determined by XPS.

Element	Concentration /%	Concentration /%
	AP-MNPs	PSTH-MNPs
C	12.12	20.86
O	58.87	50.02
Fe	16.63	21.80
N	0.52	2.44
S	0.00	2.62
Si	11.85	2.26

## **Figure captions**

Figure 1. Schematic diagram of the PSTH-MNPs synthesis.

Figure 2. TEM micrographs at various scales of AP-MNPs (A) scale bar represents 90 nm and (C) 30 nm, and of PSTH-MNPs (B) scale bar represents 90 nm and (D) 30nm.

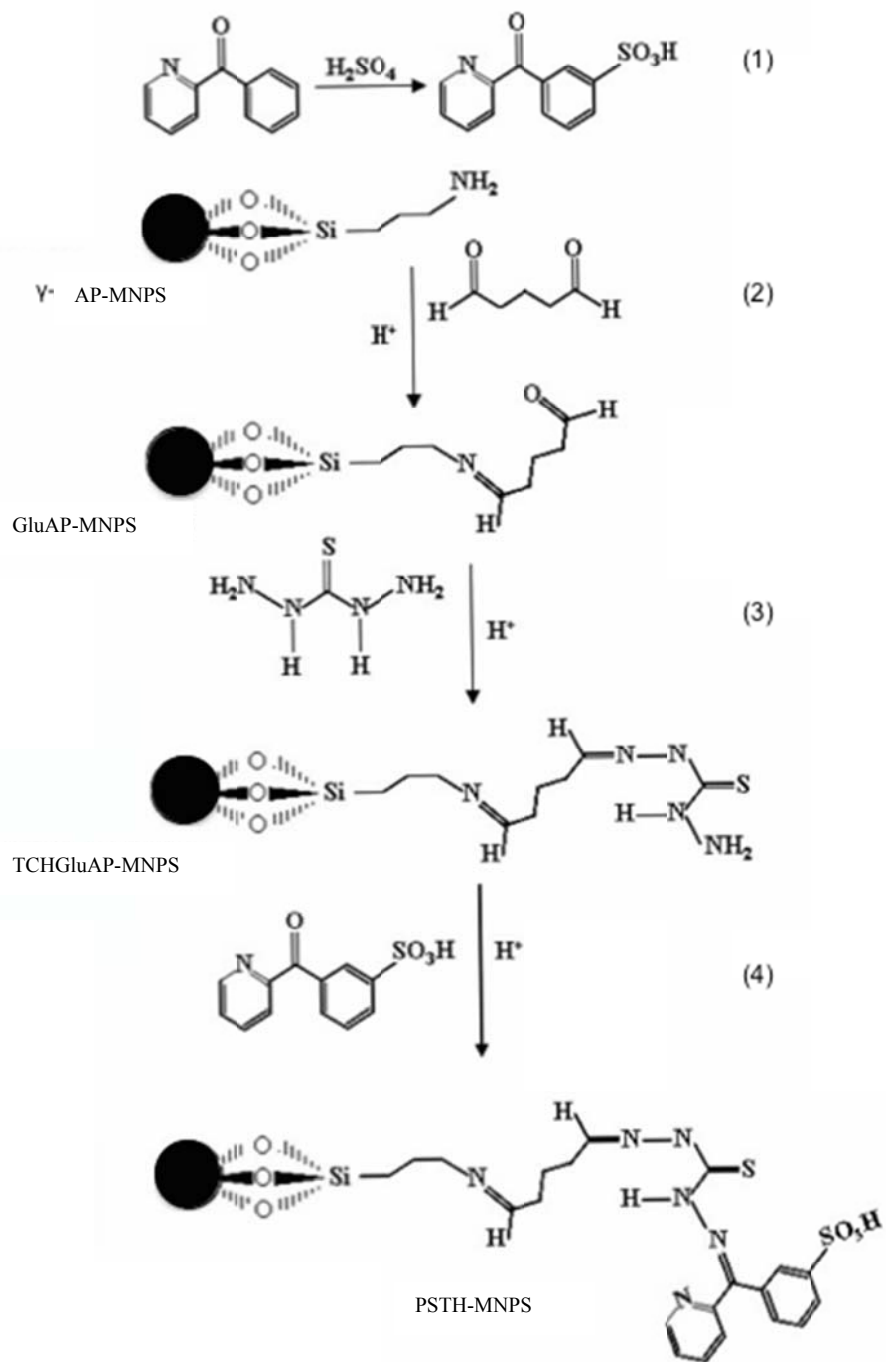


Figure 1

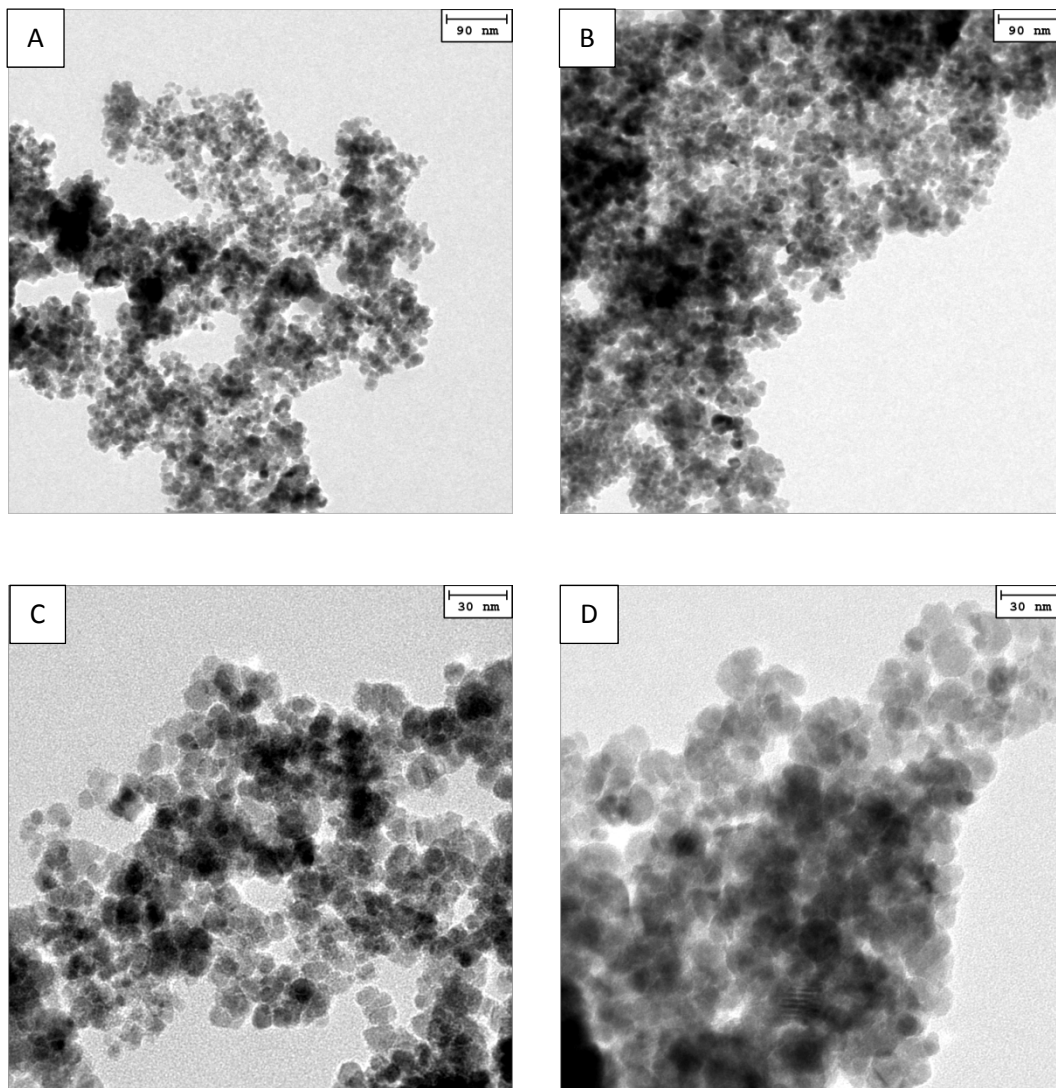


Figure 2