



# Novel synthesis and application of FePt/CuInS<sub>2</sub> magneto-optical core-shell nanostructures in copper ions sensing



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## ABSTRACT

In this study, the FePt core, CuInS<sub>2</sub> shell and FePt/CuInS<sub>2</sub> core-shell nanostructures were successfully synthesized using Polyol process. Temperature and field dependence magnetization behavior of as-synthesized FePt and FePt/CuInS<sub>2</sub> showed super paramagnetic and ferromagnetic behavior at 300 K, respectively. The blocking temperature ( $T_B$ ) estimating by the peak in ZFC curve was about 26 K for FePt and this peak was absences for FePt/CuInS<sub>2</sub> NSs, which indicates ferromagnetic regime. To design novel sensor for Cu<sup>+2</sup> ions, a glassy carbon electrode was fabricated with FePt/CuInS<sub>2</sub> core shell NSs and multi walled carbon nanotubes (MWCNT). Using cyclic voltammetry, the electrochemical behavior of Cu<sup>+2</sup> ions was studied at FePt/CuInS<sub>2</sub> core-shell/MWCNT@GCE and compared with responses on bare GCE and MWCNT@GCE. Finally, this electrode was used for construction of the calibration curve in linear range from 12.5–575.0 nmol L<sup>-1</sup> Cu<sup>+2</sup> with a detection limit of 0.14 nmol L<sup>-1</sup>.

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## 1. Introduction

Copper, a very important element for hematopoiesis, metabolism, growth, and immune system [1], has important functions in various biological processes [2]. However, exposure to high levels of copper can cause gastrointestinal disturbance and even liver or kidney damage [3,4]. Copper ions ranging from low ppb to ppt levels can be quantitatively analyzed using conventional methods including colorimetric [5,6], high performance liquid chromatography (HPLC) [7], inductively coupled plasma-mass spectrometry (ICP-MS) [8], and flame atomic absorption spectrophotometer (FAAS) [9]. HPLC and ICP-MS provide a low detection limit down to ppt (part per million) concentrations of copper ions, but require trained technicians for instrument operation as well as collection and transportation of environmental samples for the analysis in the laboratory. The use of electrochemical sensing platforms for copper ion analysis offering portability can be great alternatives to the above conventional methods. Electrochemical sensors utilizing various types of

working electrodes such as commonly used gold electrodes [10,11], Pt ultra microelectrode arrays [12], as well as carbon based electrodes [13,14] have been reported in conjunction with linear sweep or stripping voltammetry.

According to our knowledge, no report has been published on determination of Cu<sup>+2</sup> using core-shell nanostructures based electrochemical sensors. In present work, in order to improve the catalytic activity of CuIn<sub>2</sub>S<sub>4</sub> nanoparticles, we report the synthesis of core-shell FePt-CuIn<sub>2</sub>S<sub>4</sub> composite by a novel solvothermal method. This preparation method can effectively make CuIn<sub>2</sub>S<sub>4</sub> nanoparticles distribute on the surface of FePt. Therefore, the purpose of this study was; (i) Polyol synthesis of FePt-CuInS<sub>2</sub> core-shell nanostructures and its characterization; and in continuation, (ii) application of FePt-CuInS<sub>2</sub> core-shell/MWCNT@GCE as a novel sensor for Cu<sup>+2</sup> ions in phosphate buffer solution.

## 2. Experimental

### 2.1. Materials and physical measurements

Platinum (II) acetylacetonate (97%), tris (acetylacetonato) iron (III) (99.9%), Indium (III) Nitrate Pentahydrate, In(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (99.9%), anhydrous ethyl alcohol and hexane were purchased

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from Merck and 1,2-hexadecanediol (90%), oleic acid (99%) and oleyl amine (70%), Thioacetamide (TAA, >99%) and Copper acetyl acetonate hydrate – powder  $\text{Cu}(\text{acac})_2$  (99.9%) purchased from Sigma–Aldrich. All the chemicals used without further purification.

For characterization of as-synthesized nanostructures, X-ray diffraction (XRD) patterns were recorded by a Philips-X'PertPro, X-ray diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation at scan range of  $10 < 2\theta < 80$ . Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were obtained on a Philips EM208S transmission electron microscope with an accelerating voltage of 200 kV. The UV–vis diffuse reflectance spectrum of the samples was recorded by an Ava Spec-2048TEC spectrometer. Also, the magnetization measurements were carried out using a vibrating sample magnetometer (PPMS equipped with a 9 T superconducting magnet).

For sensor-related experiments, all electrochemical experiments were carried out using an Auto lab potentiostat-galvanostat PGSTAT 35 (Eco chemie Utrecht, Netherlands), equipped with the General Purpose Electrochemical System (GPES 4.9, 006) software. The measurements were carried out in a 25 ml single compartment three-electrode glass cell with  $\text{Ag}/\text{AgCl}$  as a reference electrode, a platinum wire as counter electrode and a glassy carbon electrode (GCE) as working electrode. All the potentials are given against the  $\text{Ag}/\text{AgCl}$  (3.0 M KCl). A digital pH meter (Metrohm model 691) was used when preparing buffer solutions that served as the supporting electrolyte in the voltammetric experiments. An ultrasound bath (Bandelin Sonorex, Germany) at a constant frequency of 35 kHz was used during experiments. All experiments were carried out at an ambient temperature of  $25 \pm 0.1^\circ\text{C}$ .

## 2.2. Synthesis of FePt core nanoparticles

The FePt nanoparticles as a core were synthesized using polyol method under standard air less process in accordance with the following command: initial precursors containing iron (III) acetyl acetonate (0.50 mmol), platinum (II) acetyl acetonate (0.25 mmol), 1, 2-hexadecanediol (2.5 mmol), oleic acid (5.0 mmol), oleyl amine (5.0 mmol) were mixed in 10 ml benzyl ether and magnetically stirred for 20 min under a flow of  $\text{N}_2$  atmosphere. Then the mixture was heated to boiling benzyl ether at a rate of approximately  $5^\circ\text{C}/\text{min}$  and kept at this temperature for 15 min. After completion of the growth of nanoparticles, the heat source was separated from the reaction vessel to the mixture to cool at room temperature. The resulting black nanoparticles were isolated by adding 40 ml of ethanol and centrifugation (8000 rpm for 10 min). Then, the ethanol impurities separated and black precipitation was dispersed in 10 ml hexane in the presence of oleic acid and oleyl amine. In order to completely remove of extra impurities, the centrifugation (8000 rpm, 10 min) was repeated twice. Finally, the FePt core nanoparticles were dispersed with the stabilizer in hexane.

## 2.3. Synthesis of $\text{CuInS}_2$ shell nanostructures

For synthesis of  $\text{CuInS}_2$  nanostructures as a shell, firstly based on stoichiometry, TAA (300 mg),  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (600 mg),  $\text{Cu}(\text{acac})_2$  (85 mg), 1, 2 hexadecanediol (365 mg), oleic acid (2400  $\mu\text{l}$ ), oleyl amine (2550  $\mu\text{l}$ ) were mixed in 10 ml benzyl ether and magnetically stirred under a flow of  $\text{N}_2$  atmosphere for 20 min at room temperature. Then, the resulting compound was heated from  $100^\circ\text{C}$  to boiling point of benzyl ether ( $300^\circ\text{C}$ ) at a rate of approximately  $5^\circ\text{C}/\text{min}$ . After the reaction, the reaction vessel was removed from the heat source to the mixture to cool at room temperature. Then, the resulting nanostructures were filtrated and separated by adding 40 ml of ethanol and centrifugation in 8000 rpm for 10 min. Finally, the nanostructures were dried in a vacuum oven at a temperature of  $70^\circ\text{C}$  for two hours.

## 2.4. Synthesis of FePt-CuInS<sub>2</sub> core-shell nanostructures

The process for synthesis of FePt-  $\text{CuInS}_2$  core-shell nanostructures was as following: based on stoichiometry, a controlled amount of TAA (300 mg),  $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (600 mg) and  $\text{Cu}(\text{acac})_2$  (85 mg) was dissolved in a mixture of 10 ml benzyl ether, 1,2 hexadecanediol (365 mg), oleic acid (2400  $\mu\text{l}$ ), oleyl amine (2550  $\mu\text{l}$ ) which the result were mixed in and magnetically stirred under a flow of  $\text{N}_2$  atmosphere for 20 min at room temperature. Then, the synthesized FePt core nanoparticles dissolved in 10 ml hexane was added to the reaction vessel to be mixed with other ingredients, which the result were mixed in and magnetically stirred under a flow of  $\text{N}_2$  atmosphere for 20 min at room temperature. For hexane evaporation, the reaction vessel was heated from room temperature to  $100^\circ\text{C}$  for 20 min. Then, the mixture was heated from  $100^\circ\text{C}$  to boiling point of benzyl ether ( $300^\circ\text{C}$ ) at a rate of approximately  $5^\circ\text{C}/\text{min}$ . After the reaction, the heat source was removed from mixture to cool at room temperature. The core-shell nanostructures were filtrated and separated by adding 40 ml of ethanol and centrifugation in 8000 rpm for 10 min. At final, the obtained nanostructures dissolved in a mixture of oleic acid and oleyl amine in the presence of Hexane (10 ml) were centrifuged to separate impurities from synthesized nanoparticles.

## 2.5. Fabrication of FePt-CuInS<sub>2</sub>/MWCNT@GCE as $\text{Cu}^{2+}$ sensor

For designing a  $\text{Cu}^{2+}$  sensor, at the first, a GCE was further polished with 0.05 mm alumina powder on a polishing micro cloth for several minutes. Then, it was cleaned in an ethanol/water solution (50%, v/v) in the ultrasonic bath and rinsed thoroughly with doubly distilled water prior to modification. To increase sensitivity in  $\text{Cu}^{2+}$  ions sensing, the MWCNTs were used as basis modifier at GCE. So, after preparing of the stable suspension of MWCNTs through ultrasonication of MWCNTs in dimethyl formamide (DMF) solution (dispersion of 1.0 mg MWCNTs in 10.0 ml of DMF), 20  $\mu\text{l}$  of the stable MWCNT suspension was dropped onto the surface of GCE and it was dried in a hot air flow at  $50^\circ\text{C}$ . After immobilization of MWCNTs, 5  $\mu\text{l}$  of the fine dispersed solution of the FePt/ $\text{CuInS}_2$  nanoparticles in dimethyl formamide (DMF) was dropped onto the surface of MWCNT@GCE. The modified electrode was dried in a hot air flow at  $50^\circ\text{C}$  and applied for electrochemical experiments to sense  $\text{Cu}^{2+}$  ions.

## 3. Results and discussions

### 3.1. Morphologically characterization of FePt core and FePt-CuInS<sub>2</sub> core-shell nanostructures

Fig. 1a shows the TEM image of as-synthesized FePt core NPs made at the first step. According to Fig. 1b, average diameter of FePt core particles ( $\langle d \rangle$ ) based on log-normal fitting was about 4.2 nm with the standard deviation ( $\sigma$ ) of size particle about 0.36 nm. The particles were self-assembled mono-dispersed with spherical shape in narrow size distribution ( $\sigma/\langle d \rangle$ ) of 0.09. Inset photography shows HRTEM image of FePt NPs, which are crystalline.

The morphology and structural features of mono-dispersed FePt/ $\text{CuInS}_2$  magneto-optical core-shell Nanostructures were also investigated by TEM. The large area TEM image shows FePt/ $\text{CuInS}_2$  core-shell Nanostructures consist of small and irregular nanoparticles, and these nanoparticles interconnect to generate abundant holes (Fig. 2a and b with different magnification). High-resolution TEM (HRTEM) image shows the irregular interconnected nanostructures consist of ca. 4 nm seeds (Fig. 2c). Selected area electron diffraction (SAED) pattern displays a successive dotted pattern (inset in Fig. 2c) demonstrating FePt/ $\text{CuInS}_2$  core-shell Nanostruc-

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