

Supporting Information

Simple cyanide sensing probe based on Ag/Fe₃O₄ nanoparticles

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Experimental and Reagents

A Perkin Elmer (LS50B) luminescence spectrometer was used for recording the Rayleigh spectra and measuring the intensities at a given wavelength. A single beam UV-mini-WPA spectrophotometer was used for recording absorption spectra. Thermal Field Emission Scanning Electron Microscope (JEOL JSM-7600F) and Transmission Electron Microscope (JEOL, JEM-2100 Electron Microscope) were used for preparation of FESEM and TEM images and EDX measurements as well. The crystal structure of the synthesized materials was determined by an X-ray diffractometer (XRD) (38066 RIVA, d/G.Via M. Misone, 11/D (TN) ITALY) at ambient temperature. A Metrohm model 713 pH-meter was used for adjustment of the pH and a 40 kHz universal 35 ultrasonic cleaner water bath (RoHS, Korea) was used. All the reagents were of analytical grade by high purity from Merck Company (Darmstadt, Germany) and doubly distilled water was used throughout the experiment.

Experimental procedure

Preparation of Fe₃O₄ Nanoparticles and their Characterizations

Magnetic (Fe₃O₄) NPs were synthesized according to the alkaline precipitation of ferric and ferrous iron salts from their acidic aqueous solutions. As observed in Field Emission Scanning Electron Microscopy (FESEM) and X-ray diffraction (XRD) (Fig. S1), the prepared particles

possess an average diameter below 20 nm and crystallite size of 15 nm from Scherrer equation calculations. Transmission Electron Microscopy (TEM) also confirmed the size of nanoparticles (The TEM and EDX results are shown in the main article (Fig 1)).

Preparation of Ag/Fe₃O₄ Nanoparticles

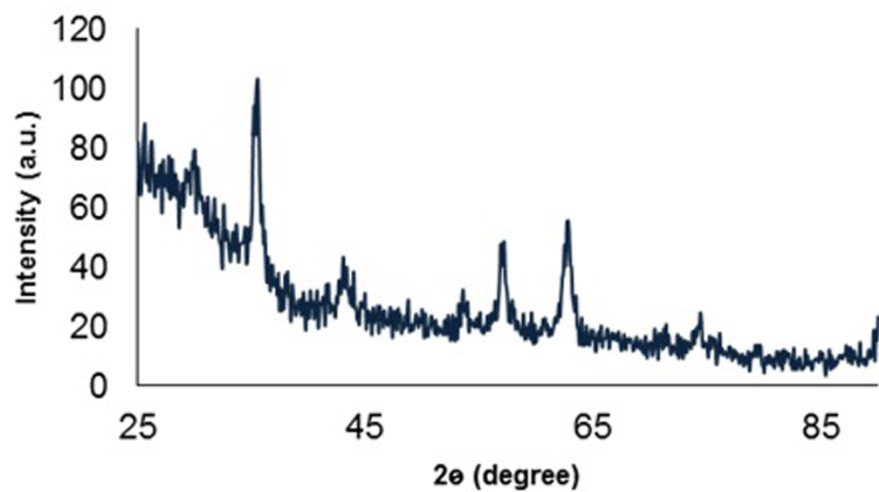
Coating of Fe₃O₄ NPs by silver, utilizing glucose as a mild reducing agent, resulted in the formation of Ag/Fe₃O₄ nanostructures consisting of small as-prepared Fe₃O₄ nanoparticle aggregates in addition with Ag NPs (Fig S1, S2 and Fig. 1). The molar ratio of Fe₃O₄ to AgNO₃ to glucose was chosen at 1:2:1 and the solution was sonicated for 15 min and then heated in a water bath for 1 h with slow stirring. As the black Fe₃O₄ particles became brownish in color, silver-iron oxide particles were separated and collected with a magnet. After the particles were separated, the decanted supernatant liquid was fully transparent.

Optical properties of NPs

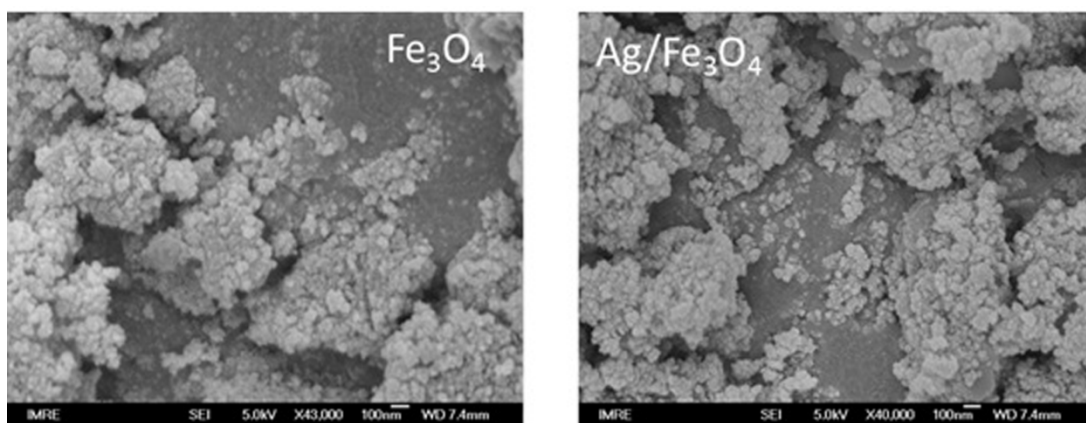
UV–Vis absorbance spectra of the solutions were measured for each sample of 5.0×10^{-1} mg L⁻¹ nanoparticles and 1.4×10^{-4} mg L⁻¹ of cyanide (Fig. S3). The absorption intensity of Fe₃O₄ spectrum decreased with the increase in the wavelength in the range 220–600 nm and no obvious absorption peak was observed. When silver was deposited in the nanostructure, attached to the Fe₃O₄ nanoparticle, the absorption peak maximum at around 400 nm was appeared which is characteristic for Ag NPs. This peak confirms the presence of silver in the particles and is due to the silver surface plasmon resonance band.

Enhancement effect

Ag NPs and iron oxide both in the nanostructure, amplify the signals and enhance the sensitivity and selectivity of the cyanide probe (Fig. S4)



a



b

Fig. S1. XRD pattern of magnetite (Fe_3O_4) (a) and FESEM images of Fe_3O_4 and $\text{Ag}/\text{Fe}_3\text{O}_4$ nanoparticles (b).

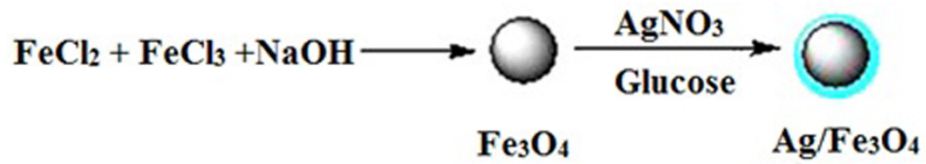


Fig S2. Schematic illustration of the Ag/Fe₃O₄ magnetic nanoparticles formation.

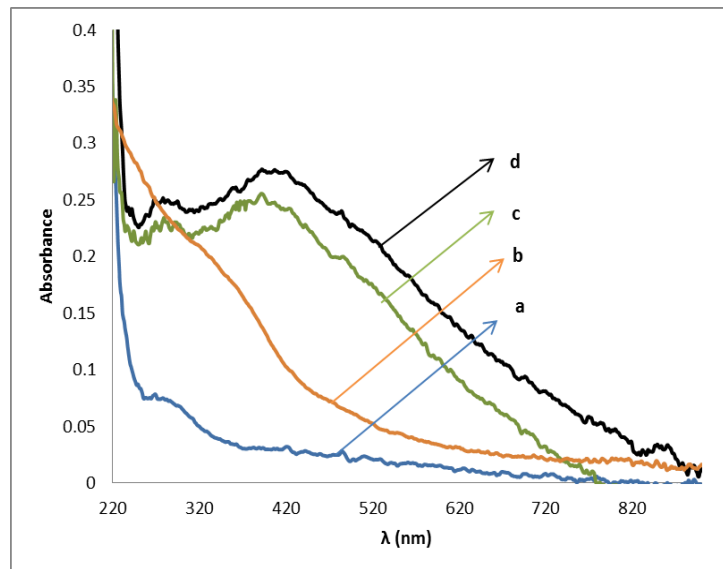


Fig. S3. UV-Vis absorption spectra of CN (a), Fe₃O₄ nanoparticles (b), Ag/Fe₃O₄ nanoparticles (c), CN with Ag/Fe₃O₄ nanoparticles (d).

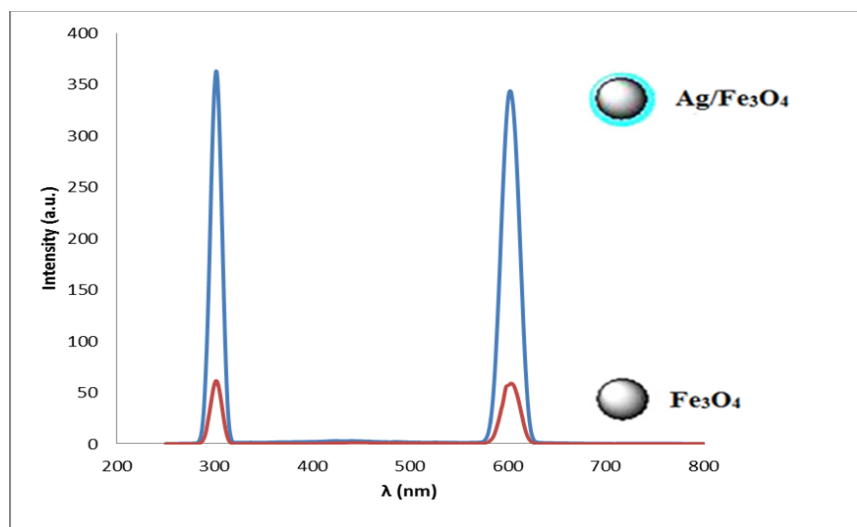


Fig. S4. The compared Rayleigh (at 313 and 625 nm) scattering of $6.0 \times 10^{-1} \text{ mg L}^{-1}$ bare and Ag coated magnetic nanoparticles suspensions based on excitation at 300 nm.

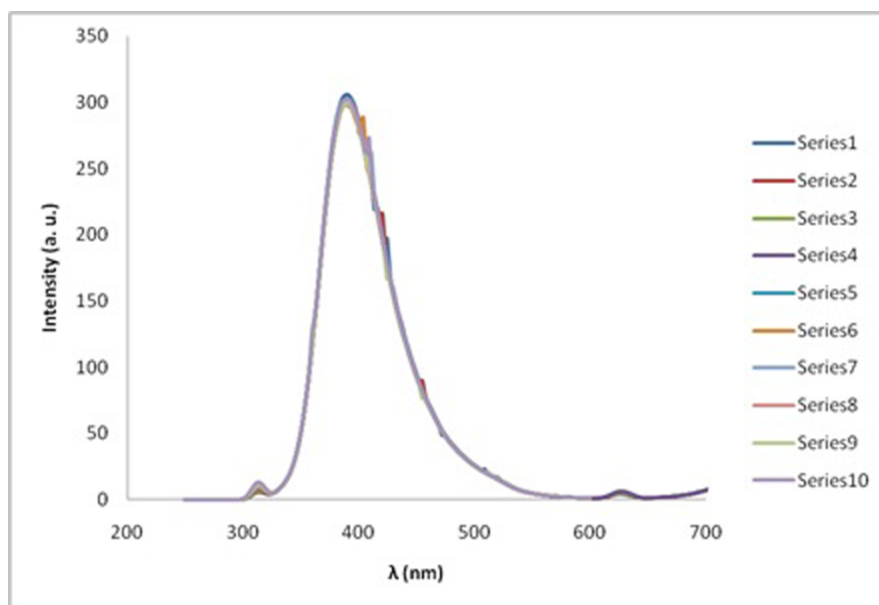


Fig. S5. The Rayleigh (at 313 and 625 nm) scattering and Fluorescence peak (at 405 nm) of Ag nanoparticles by the addition of increasing amount of cyanide based on excitation at 300 nm.

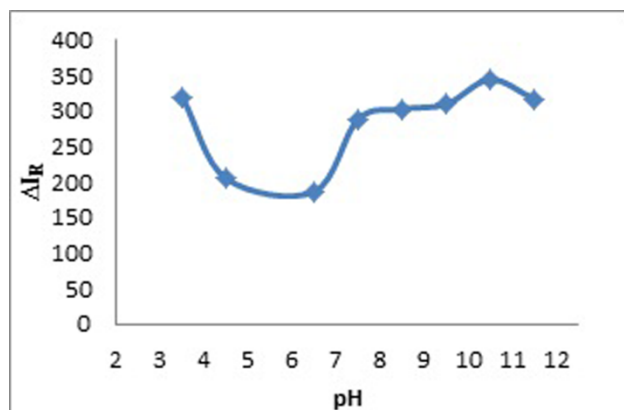


Fig. S6. Effect of pH on ΔI_R , $C_{\text{nanoparticles}} = 33 \text{ ng mL}^{-1}$, $[\text{CN}^-] = 0.5 \text{ ng mL}^{-1}$.

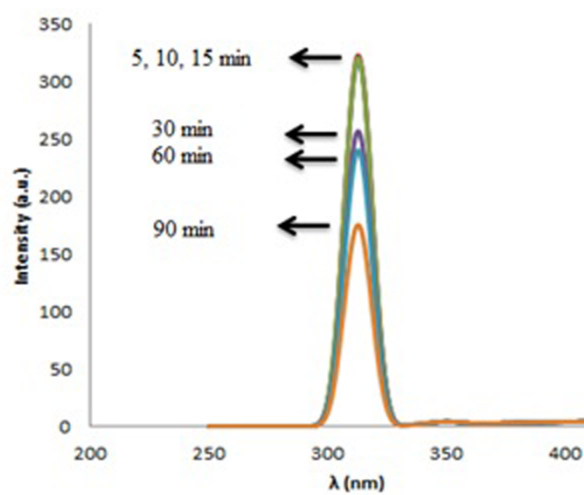


Fig. S7. Time-dependent Rayleigh spectra of 80 ng mL^{-1} of $\text{Ag/Fe}_3\text{O}_4$ after addition of 3 ng mL^{-1} cyanide nanoparticles, immediately up to 90 min, pH 8.0.

Table S1 Comparison of the analytical characteristics of the proposed method with those of previously reported similar methods

Method	LDR^a (ng mL⁻¹)	LOD^b (ng mL⁻¹)	Ref.
Silver nanoparticles-colorimetric assay	434-3458	47	17b
Surface-enhanced Raman spectroscopy	1-300	0.5-1.0	17c
Silver nanoparticles-fluorescent detection	13-15600	6.5	17d
Gold nanoparticles-colorimetric assay	52-260	13	17e
electrochemical cyanide sensor based on Ag nanoparticles	39-5460	0.4	17f
Surface plasmon-enhanced Rayleigh scattering based on silver magnetic nanoparticles probe	0.13-60	0.04 ^b	Proposed work

^a Liner dynamic range, ^b Limit of detection

Table S2 Results for cyanide determination (ng mL⁻¹) in real water samples obtained using 25 ng mL⁻¹ of Ag/Fe₃O₄ NPs (N=3).

Sample	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	RSD (%)	Recovery (%)
Tap water 1	-	-	-	-
	0.65	0.62	3.8	95.2
	3.9	3.8	1.5	97.8
Tap water 2	-	-	-	-
	0.65	0.62	1.3	95.3
	3.9	4.1	3.0	105.6