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ARTICLE

Simple cyanide sensing probe based on Ag/Fe₃O₄ nanoparticles

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Here, the development of a highly sensitive and selective surface plasmon-enhanced light scattering technique for ultra-trace cyanide sensing using silver magnetic nanoparticles probe is reported. The assay relies upon the nanoparticles plasmonic enhanced effects and rapid interaction of cyanide with Ag nanoparticles in the Ag/Fe₃O₄ nanostructures. A decrease in Rayleigh intensity in the presence of cyanide was observed and the decrease in Rayleigh scattering intensity (ΔI_R) is directly proportional to the concentration of CN⁻ in a certain range.

Introduction

Cyanide (CN⁻) is known to be extremely toxic to humans. Monitoring of cyanide, because of its deleterious effects on the environment and human health, has been considered by different researchers^{1, 2}. Cyanide optical sensors have been studied energetically over the past ten years²⁻¹¹. Many of these systems, however, are relatively costly and complicated, use indirect or difficult procedures, and are impractical for routine monitoring. Thus, it would be of great interest to develop a simplistic method that has improved characteristics, such as lower costs, greater speeds, higher sensitivity, and selectivity.

Cyanide is a powerful nucleophile and a strong ligand; cyanometallates are generally prepared by the direct reaction of cyanide salts with simple metals. By far the largest affinity of cyanide is in the formation of Au and Ag complexes¹². Cyanidation is the most common method used in the leaching of gold from low grade ores by the production of [Au(CN)₂]⁻ complexes^{11,13,14}. Different studies have suggested the ability of cyanide to etch silver selectively^{10, 15-17}. The use of Ag-CN interactions is therefore attractive for a label-free approach in CN⁻ detection.

Noble metals (especially Ag and Au) in nanometer sizes are specifically interesting because of their unusual optical properties which are related to their ability in supporting surface plasmons. The coherent oscillation of the metal conduction band free electrons at the surface of metal nanoparticles, in resonance with an electromagnetic field of incoming light is called surface plasmon resonance (SPR)^{18, 19}. SPR was theoretically explained by Mie in 1908, including extinction and scattering of small spherical metal particles²⁰. The excitation of the SPR results in the enhancement of any spectroscopic signals from the molecules at the material surface, that is surface enhanced spectroscopy, such as strong plasmon absorption^{18, 21-23}, surface enhanced luminescence^{18, 22}, surface enhanced Raman scattering^{18, 19, 22-24}, and surface enhanced Rayleigh scattering^{19, 23, 25}. For the past few decades, many research

studies have utilized the new techniques based on these surface enhanced phenomena for a wide range of applications in catalysis, optics, measurement of chemical and biological quantities and medical therapeutics¹⁸⁻²⁶.

The Rayleigh theory for elastic light scattering by small particles (i.e., much smaller than the wavelength of light) is well known^{20, 27}. In recent years, Rayleigh scattering, a highly sensitive, simple and quick analytical technique, has shown its broad application in pharmaceutical analysis (the study of proteins, nucleic acids, heparin and cellular imaging)²⁸⁻³⁰, metal ions and nonmetal ions monitoring³¹ and also nanoparticles sensing (the study of the size, shape, composition, concentration and the local environment of single plasmonic nanoparticles)³².

Recently, the use of silver nanoparticles (AgNPs) as analytical and bioanalytical sensors has been receiving significant attention³³. Silver exhibits many advantages such as high absorptivity, sharp absorption bands, high ratio of scattering to absorbance, extremely high field enhancements, and as they have the same scale with biological macromolecules, proteins and nucleic acids, they are particularly suitable for biological sensing^{23, 33}. It has been employed in the development of sensors based on surface enhanced spectroscopies³⁴. As compared to gold nanoparticles, silver nanoparticles of the same size, possess much higher extinction coefficients that cause sensitive detection with minimal material consumption^{17b}.

At the same time, there has been a focus on the usage of magnetic nanoparticles (MNPs) because of their unprecedented advantages³⁵. MNPs integration with analytical methods has opened a new path for sensing, purification, and quantitative analysis³⁵. The plasmonic field application of MNPs is still limited, but it is mentionable that the high refractive index and molecular weight of the magnetic nanoparticle, in spite of their small size, make them a powerful enhancer for plasmonic responses³⁶. Therefore the use of MNPs as SPR amplification factor has gained the interest of many³⁶.

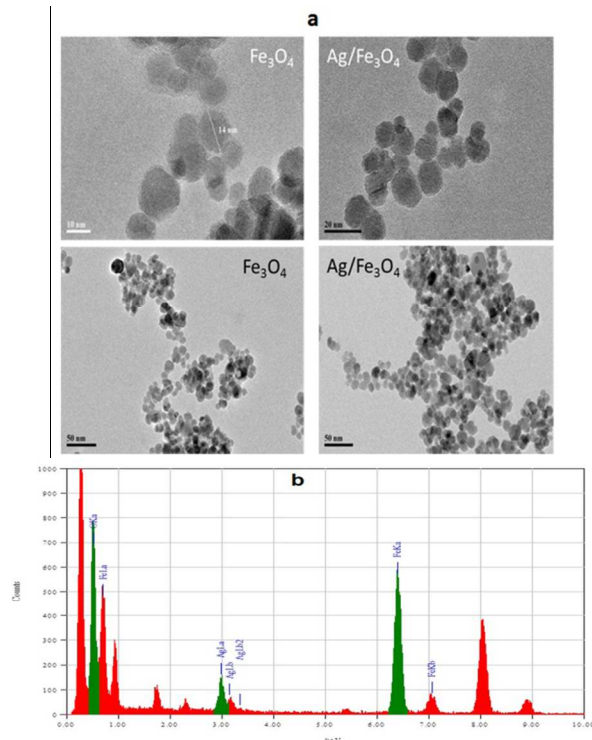


Fig. 1 (a) TEM images and (b) EDX plot of synthesized nanoparticles.

Nanoparticle-based sensing strategies

Here in the study on the new analytical Rayleigh scattering technique for CN^- monitoring, we had synthesized and utilized $\text{Ag}/\text{Fe}_3\text{O}_4$ hybrid nanostructures. The sensitivity improvement was importantly ascribed to the surface plasmon enhancing of Ag and MNPs that exhibited high Rayleigh scattering in the solution, and strong specific interaction of Ag with CN^- ions.

Studies indicated that the Rayleigh scattering intensity decreased rapidly by addition of a trace amount of cyanide. Under the selected conditions, decreasing in Rayleigh scattering peak at 313 nm, (ΔI_R), was linearity proportional to the cyanide concentration due to the nano silver – cyanide complex formation. Finally the recyclable magnetic nanoparticles were collected simply for further usage. To the best of our knowledge, this is the first direct approach used in the determination of an ultra-trace amount of cyanide as all the other earlier procedures reported had to use an intermediate to indirectly determine the cyanide concentration. Therefore, a new method for the determination of toxic cyanide is developed in this contribution, which is rapid, simple, sensitive, selective and accurate.

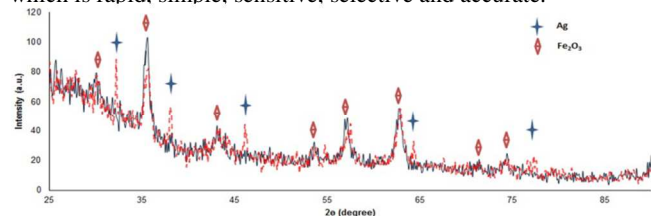


Fig. 2 XRD patterns of the Fe_3O_4 nanoparticles and $\text{Ag}/\text{Fe}_3\text{O}_4$ magnetic nanoparticles.

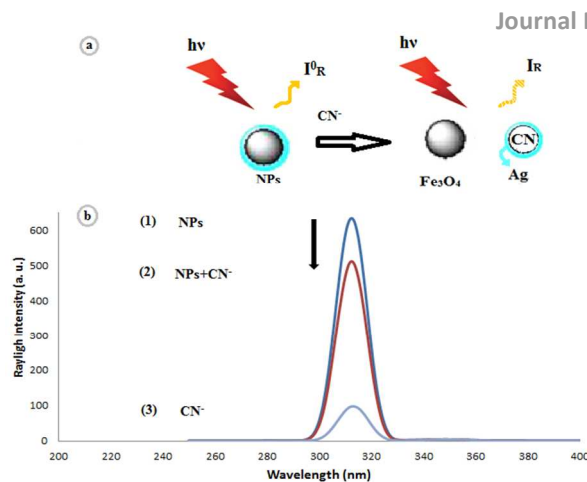


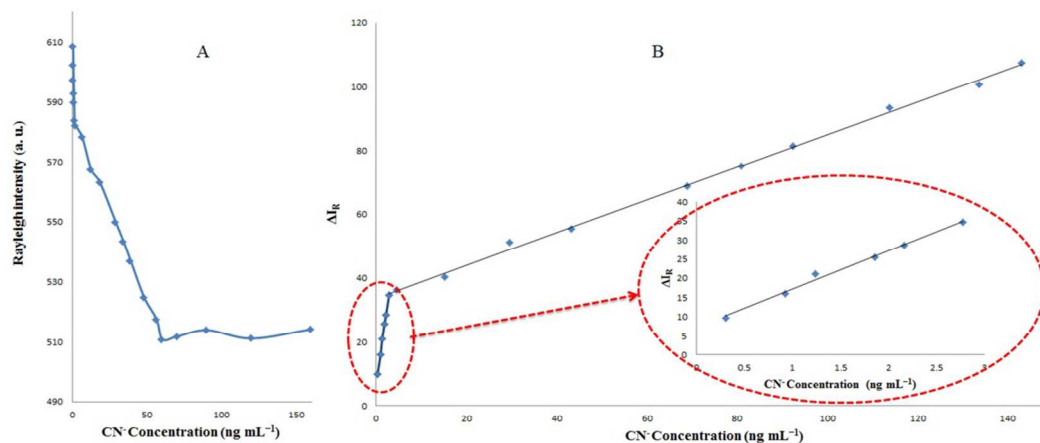
Fig. 3 (a) Schematic representation of CN^- sensing based on the Rayleigh scattering decreasing of $\text{Ag}/\text{Fe}_3\text{O}_4$ NPs resulting from etching of Ag by the CN^- . (b) Rayleigh scattering spectra ($\lambda_{\text{ex}} = 300$ nm) for $\text{Ag}/\text{Fe}_3\text{O}_4$ NPs (25 ng mL^{-1}) in the (1) absence and (2) presence of CN^- ions (65 ng mL^{-1}) and (3) for the solution of CN^- ions lonely (65 ng mL^{-1}).

Magnetic (Fe_3O_4) NPs were synthesized according to our previous works by alkaline precipitation of ferric and ferrous iron salts from their acidic aqueous solutions³⁷. The prepared particles possess an average diameter below 20 nm through TEM images (Fig. 1) and crystallite size of 15 nm from Scherrer equation calculations similar to our earlier works³⁸ (ESI Fig. S1). $\text{Ag}/\text{Fe}_3\text{O}_4$ NPs have been synthesized simply by reducing silver nitrate on the as-synthesized Fe_3O_4 NPs (ESI Fig. S2) and upon Scherrer equation the crystallite size of Ag nanoparticles was obtained around 24 nm³⁹. XRD pattern for $\text{Ag}/\text{Fe}_3\text{O}_4$ nanostructures, as compared to bare Fe_3O_4 nanoparticles, is given in Fig. 2. As XRD pattern clearly shows, the presence of metallic Ag was detected in the prepared nanostructure. Curves in the pattern obviously show two sets of strong diffraction peaks, indicating that the as-synthesized products are composite materials having good crystallinity and high purity. It was found that no shift in the positions of the reflection peak of Fe_3O_4 particles was occurred, and compared with the peaks of bare Fe_3O_4 sample, the decrease and broadening of the Fe_3O_4 peaks are attributed to the reduction of the crystalline size of the nanoparticles. We also calculated the crystallite size of Fe_3O_4 nanoparticles after coating by silver NPs around 10 nm (Fig. 2).

It is mentionable that all EDX (a typical part EDX result shows in Fig. 1b), XRD and optical results confirmed the presence of silver in the nanostructure⁴⁰ (Fig. 2 and Fig. S3).

Experiment and theory yield that the Rayleigh bands, particularly in the hybrid nanostructure, are stronger than those observed with the bare magnetic nanoparticles resulted in a sensitivity and selectivity improvement of the probe³⁷ (ESI Fig. S4).

Upon adding CN^- ions to the aqueous $\text{Ag}/\text{Fe}_3\text{O}_4$ NPs solution, the Rayleigh scattering of $\text{Ag}/\text{Fe}_3\text{O}_4$ nanoparticles decreased within few seconds (Fig. 3). (Warning: care should be taken during contact with any solutions containing cyanide¹⁶). The Rayleigh scattering decreasing for $\text{Ag}/\text{Fe}_3\text{O}_4$ NPs is due to the etching of Ag NPs by the CN^- ions¹⁵⁻¹⁷. Silver can be etched by cyanide, liberated from the nanostructure, form a stable complex by cyanide and decreasing in Rayleigh scattering spectra is occurred. Meanwhile silver has a high selectivity to cyanide and is inert to most other substances, which



can be used as a powerful cyanide detector^{10, 15-17}.

It is mentionable that we carried out the tests for the experiments containing silver nanoparticles, and though limited scattering was shown, there was a plasmon fluorescence peak. But, an increasing amount of cyanide showed no significant changes in the fluorescence peak and the fluorescence intensity values were approximately constant. (ESI Fig. S5).

The decrements of NPs enhanced Rayleigh scattering was represented as $\Delta I_R = I_R^0 - I_R$, where I_R^0 and I_R are Rayleigh intensities of the NPs in the absence and in the presence of cyanide ion, respectively. ΔI_R at 313 nm, was linearly proportional to the cyanide concentration (Fig. 4). To evaluate the assessment of the method, different concentrations of CN⁻ (0.13–60.0 ng mL⁻¹) were added to a series of solutions containing 25 ng mL⁻¹ of Ag/Fe₃O₄ NPs. As shown in Fig. 4A, the Rayleigh scattering of the NPs reduced by increasing CN⁻ concentration, and then became constant. The decrease in the Rayleigh scattering intensity for NPs was linearly dependent on CN⁻ concentration in given ranges as in Fig. 4B. Also Table 1 shows the linear detection ranges for different CN⁻ concentrations. The limit of detection (LOD) for CN⁻, at a signal-to-noise ratio of 3, was estimated to be 0.04 ng mL⁻¹, which is extremely small compared to the acceptable concentration of CN⁻ in drinking water (49.4 ng mL⁻¹ or 1.9 μM) according to the World Health Organization¹⁵. Also as a competition study, the results showed not only the performance of our method in ultra-trace cyanide determinations (ESI Table S1), but also it presents a direct approach compared to all previous similar analytical techniques.

To investigate the applicability of the method for real samples, some water samples were used instead of pure water. Proposed method was applied to the quantitative determination of cyanide in these spiked real samples (ESI Table S2). Mentionable that the addition of the water samples spiked with cyanide led to almost the same changes of the Rayleigh intensity in this system as standard solutions in pure water. That shows the matrix has no egregious effect on the decreasing of the Rayleigh intensities and this probe is largely free from the matrix effect in testing real water samples.

Fig. 4 Rayleigh decreasing ($\lambda_{\text{ex}} = 300$ nm) of Ag/Fe₃O₄ NPs (25 ng mL⁻¹) in the presence of different CN⁻ concentrations (A). The decrease in the Rayleigh intensity (ΔI_R) for Ag/Fe₃O₄ NPs as a function of CN⁻ concentration (B).

The recovery results showed the accuracy and reliability of the present method for cyanide determination in practical applications. The relative standard deviation for three repeated measurements illustrated that the response of NPs toward cyanide was highly reproducible (ESI Table S2).

Lastly, the removal of iron oxide nanoparticles using an external magnetic force helps to decrease their pollution effects. At the same time, the iron oxide cores recovered could be reused in forming nanostructures with silver. (Note: iron oxide were highly magnetic, even after they formed a nanostructure with silver³⁶)

For Rayleigh scattering less proportionality to the pH is recommended. The effect of pH in the range 3.5–11.5 on the intensity of Rayleigh spectra was investigated (ESI Fig. S6). pH below 3.5 was not studied because Fe₃O₄ and Ag NPs are soluble in too acidic media. As seen from the results, the Rayleigh intensity values in the pH range of 7.5–11.5 are relatively constant, that indicate the robustness of the method. Also time-dependent Rayleigh spectra were monitored in the presence of 3 ng mL⁻¹ of cyanide and 80 ng mL⁻¹ of Ag/Fe₃O₄ nanoparticles (ESI Fig. S7). The results revealed that the interaction can be completed immediately after the addition of NPs (repeated at least 3 times and the relative standard deviation of Rayleigh changes was in the order of ±1%). The highly selective Ag⁺–CN⁻ interactions, to form cyanide soluble complexes^{10, 15-17}, provided the excellent selectivity of this method towards cyanide over other environmentally relevant ions. The ionic selectivity towards the cyanide response was investigated (Fig. 5).

Table 1. The analytical characteristics of the proposed method for the determination of CN⁻.

Regression equation ^a	Range of concentration (ng mL ⁻¹)	Regression coefficient (R ²)
$\Delta I_R = 23.731C + 7.2054$	0.13–1.2	0.9929
$\Delta I_R = 1.2242C + 33.675$	1.2–60.0	0.9982

^a Concentration of CN⁻ in ng mL⁻¹.

As shown in Fig. 5, the decrease in Rayleigh intensity by cyanide was considered as a base, and the change in Rayleigh intensity by the other ions were shown relative to cyanide. The sensitive Ag/Fe₃O₄ NPs were highly robust towards various ions, making this method suitable for examining samples from various environments.

In conclusion, a new, simple and label-free method was developed for direct detection of CN⁻ ions using highly selective and sensitive probe, based on Ag/Fe₃O₄ nanostructures, consist of plasmonic nanoparticles, that shows largely enhanced Rayleigh scattering. The sensing mechanism was based on the selective etching of Ag by the CN⁻ ions, which effectively decreased the Rayleigh intensity of Ag/Fe₃O₄ NPs. The Ag NPs showed a remarkably high selectivity for CN⁻ over other foreign ions. Detection of CN⁻ at concentrations as low as 0.04 ng mL⁻¹ became possible which in compared with previously reported methods, was improved by several orders of magnitude. Also the main performance of this work is that cyanide concentration can be obtained directly despite the previous reported works. Under the conditions proposed, the reaction is simple and rapid without the use of any toxic and expensive reagents by use of simply synthesised nanostructures. The method is applicable for showing the existence of silver nanoparticles in real systems as well.

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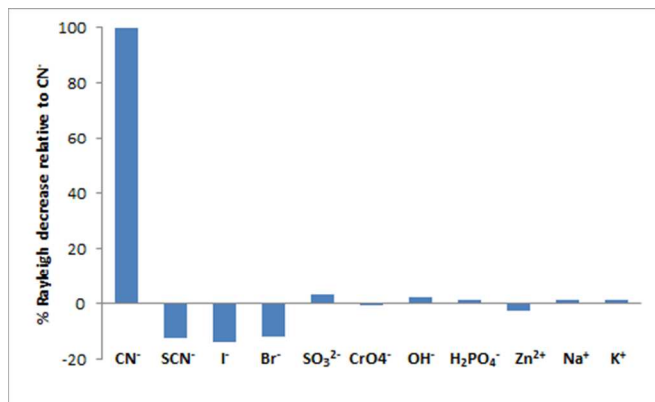


Fig. 5 The Rayleigh response of the mixture solution containing Ag/Fe₃O₄ NPs (10 ng mL⁻¹) and CN⁻ (60 ng mL⁻¹) at $\lambda_{\text{ex}} = 300$ nm in the presence of 300 ng mL⁻¹ various ions.

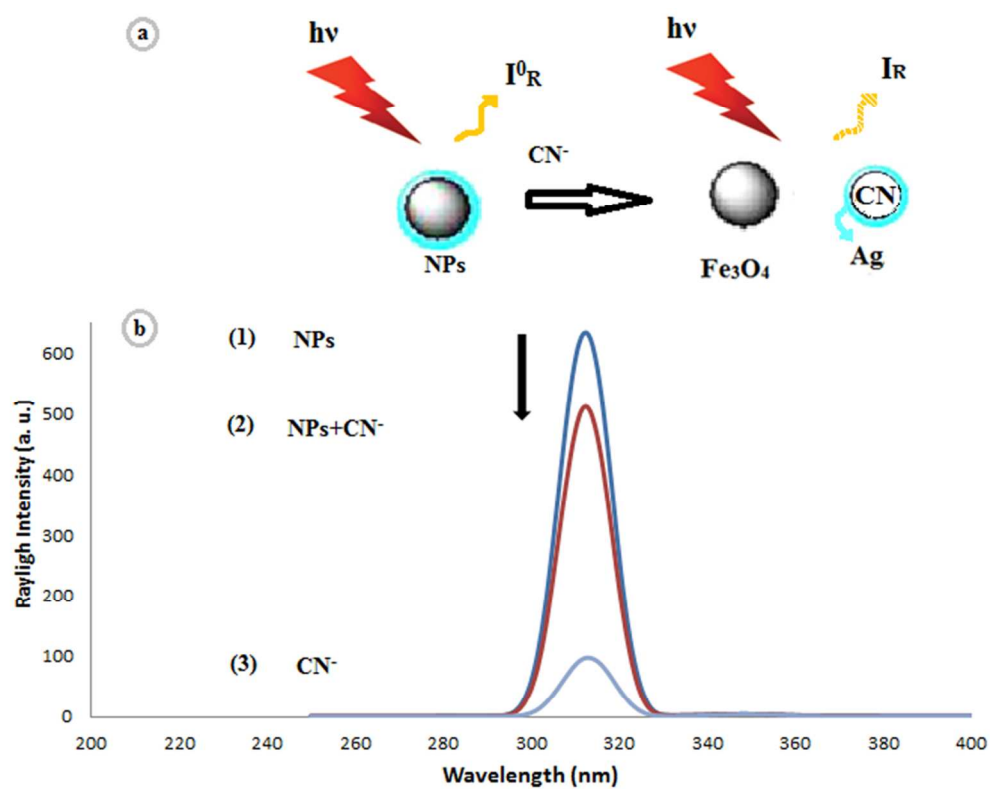
Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental and Reagents; Experimental details of the synthesis of NPs and their characterization (FESEM, TEM, EDX and XRD); Optical properties of NPs; Consideration of pH and time effects; Table of comparison and real determination results]. See DOI: 10.1039/b000000x/

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Novelty of the work:

The first direct approach in ultra-trace cyanide determination through a simple, selective and rapid reaction by simply-synthesized recyclable Ag/Fe₃O₄ nanostructures.