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A new way in nanosensors: Gold nanorods for sensing of Fe(III) ions in aqueous media



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ABSTRACT

A novel and systematic method for sensitive detection of Fe³⁺ ions in aqueous media using gold nanorods (Au NRs) as nanosensors is presented. One of the most rousing achievements is the detection limit which is found to be 100 ppb for Fe³⁺ ions. The whole procedure takes not more than 10 min which uses surfactant cetyltrimethylammonium bromide (CTAB) capped seed instead of a citrate to overcome the formation of spherical particles in excess amount along with rods. This work also presents a low cost and effective solution for separation of seed mediated grown Au NRs from co-produced spherical nanoparticles formed in solution. The characterization of nanomaterials and interaction of Fe³⁺ ions with sensor material was studied by UV–vis spectrophotometer to determine optical properties, while scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to determine morphology. The interaction of Fe³⁺ ions with Au NRs was investigated by surface-enhanced Raman scattering (SERS) using crystal violet (CV) molecule. The aspect ratio (length/diameter) of Au NRs was controlled by the amount of surfactant added. The method reported herein is a simple way to detect and determine Fe³⁺ ions in aqueous solution at the ppb levels and easily applicable for monitoring of Fe³⁺ ions in water sample.

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1. Introduction

Toxic heavy metals including zinc, copper, nickel, mercury, cadmium, lead and chromium cause long term significant damage to many biological systems as they disrupt biological activities at the cellular level [1,2]. As heavy metal ions can cause severe risk to human health and the environment, it is vital to develop methods for detecting them at low concentrations that are normally found in environmental samples [3–5]. Iron is the most abundant metal on earth which plays an important role in biological systems and also an essential transition metal in the human system. Iron is used in many proteins for oxygen transport, moreover as a catalyst in many reactions like oxido-reductase. Its distribution in the human system is regulated very much due to biological toxicity but deficiency of iron limits oxygen delivery to cells, poor work performance and decreased immunity [6,7]. Iron, if present in large quantities in a living cell, helps in catalyzing the formation of reactive oxygen species which damages lipids, nucleic acids and proteins [8,9]. The toxicity of iron causes serious diseases like Alzheimer's, Huntington's and Parkinson's disease [10,11]. Therefore it is essential to detect to remove excessive iron from water.

Metal nanoparticles, with particular shape, have received great attention in areas such as sensing, diagnostics, therapeutics and imaging [12,13]. Nanoparticles (NPs) at nanomolar concentration which can be observed by naked eyes, allows sensitive detection with minimum use of materials [14]. Each metal nanoparticle can be considered as an optical probe which is equivalent to millions of dye molecules [15,16]. Noble metal nanoparticles exhibit strong ultraviolet–visible (UV–vis) absorption band that is not present in the spectrum of the bulk metal. This absorption band results when the incident photon frequency is resonant with the collective oscillation of the conduction electrons and is known as the localized surface plasmon resonance (LSPR). The enhanced local electromagnetic fields near the surface of the nanoparticle are responsible for the intense signals observed in all surface-enhanced spectroscopy [12,17–21]. Therefore, NPs have been used for various applications in the traditional disciplines of analytical chemistry, including spectroscopy, electronic detection, and separations, as well as in various sensor technologies [4,5,17–21].

The gold nanoparticles (Au NPs), including spherical and rod shaped NPs, are the most common NPs used to enhance the surface plasmon resonance (SPR) signals [20]. With the possible different shapes of the nanoparticles, rod-shaped Au NPs are attractive as they have unique optical properties together with good adjustability and biocompatibility [22,23] but controlling the shape of nanoparticles is very important, since their optical, electronic, magnetic, and catalytic properties depend not only on particle size but also on its shape [24–26]. It has become possible to grow crystals of any desired shape, orientation and crystal

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structure. The lattice of gold is composed of single element displaying a simple face centered cubic (fcc) structure. When small Au NP seeds grow selectively in certain directions, anisotropic Au NRs are formed [27]. Thus, Au NRs with short aspect ratio are the best candidate for sensing and imaging applications as they exhibit the transverse as well as longitudinal plasmon bands in the visible region of the spectrum [28]. Therefore, Au NRs have been recognized as sensitive sensing material [29–33]. Sensitive approaches towards the detection of metal ions in environmental samples are extremely important with respect to concerns over toxic exposure to metal ions. Metallic NRs are favored over spherical NPs as they have greater molar extinction coefficients and lead to lower detection of various chemical species [34]. More attention has been focused on the development of sensitive nanosensors generally for toxic metal ions [35–54] to medicines [13,55] but scarcely for iron detection [21,56]. Thus due to the lack of suitable iron indicators, the development of practical sensors for Fe^{3+} is still desirable and remains a challenge for analytical chemists. Therefore, the present paper reports the synthesis of Au NRs using CTAB as representative material to develop nanosensor for the detection of Fe^{3+} ions with limit of detection 100 ppb. Significant absorption changes were observed for various concentrations of Fe^{3+} at the ppb levels. The detection was also assessed using UV–vis absorption spectroscopy and surface-enhanced Raman scattering (SERS).

2. Materials and methods

2.1. Materials

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$, 99.9%), trisodium citrate (99.9%), L-ascorbic acid (99%), hexadecyltrimethylammonium bromide, i.e. cetyltrimethylammonium bromide (CTAB, 99%), sodium borohydride (NaBH_4 , 99%), silver nitrate (AgNO_3), ammonium hydroxide (NH_4OH), ferric nitrate were purchased from Sigma Aldrich and used as received. Crystal violet molecules were also procured from Sigma Aldrich. Ultrapure water purified with Milli-Q Plus 185 Water System (Millipore) was used in all aqueous solutions and rinsing. All the glassware was cleaned by freshly prepared aqua-regia and finally rinsed with deionized distilled water prior to their experimental use.

2.2. Synthesis of gold nanorods

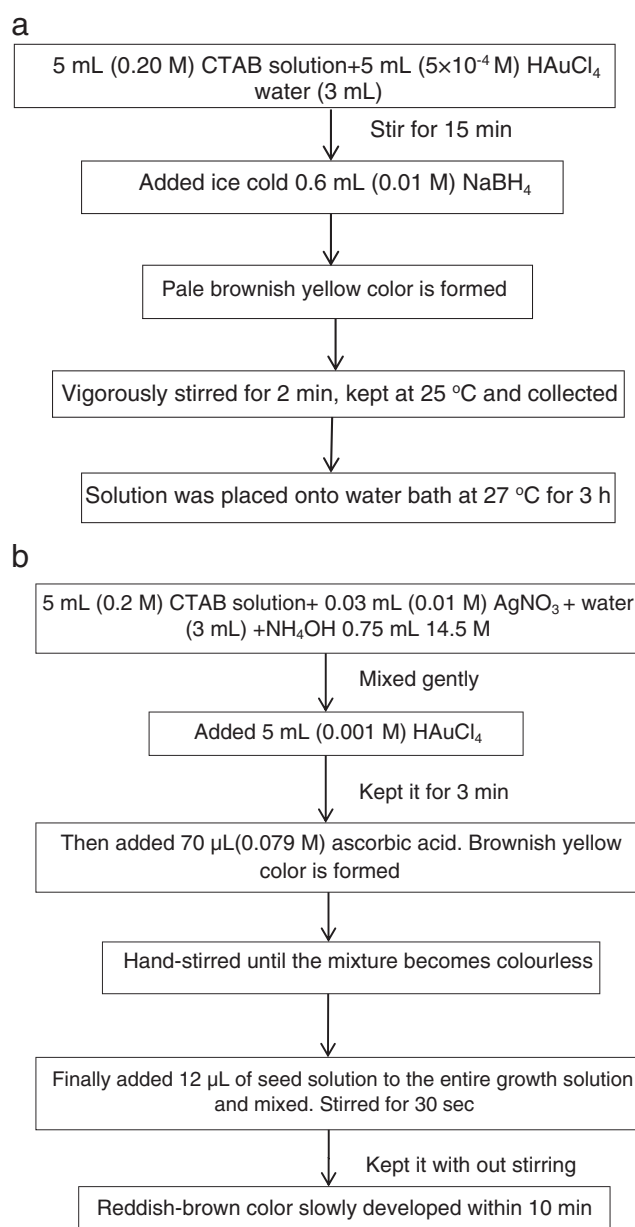
Gold nanorods were synthesized in aqueous solutions using a well-documented seed-mediated approach shown in Scheme 1(a, b) [57,58]. This synthesis explains the reduction of metal salt by use of strong reducing agent in the presence of synthesized metallic seed particles. The particle sizes in Au NRs and core-shell particles along with the morphological investigations have been carried out using scanning electron microscope (SEM) and transmission electron microscope (TEM) as per the requirements.

2.2.1. Seed solution

For the synthesis of seed solution, CTAB protected gold seeds were prepared by the reduction of 5 mL, 5×10^{-4} M HAuCl_4 solution by ice-cold 0.6 mL, 0.01 M NaBH_4 in presence of 5 mL, 0.2 M CTAB in a test-tube. The solutions were gently mixed till the solution appeared pale brown-yellow color. This was followed by rapid stirring for 2 min while allowing the escape of the evolved gas during mixing. Then the test tube containing solution was kept in a water bath maintained at 25 °C for 3 h. This synthesized seed solution was used after its preparation for growth solution.

2.2.2. Growth solution

Growth solution was prepared by addition of 12 μL seed solution to a solution containing (5 mL, 0.2 M) CTAB, (0.03 mL, 0.01 M) AgNO_3 , (0.75 mL, 14.5 M) NH_4OH , (5 mL, 1.0 mM) HAuCl_4 and (70 μL , 0.079 M) ascorbic acid; all taken in sequence. A reddish-brown color was slowly developed within 10 min. The resultant solution was kept



Scheme 1. (a) Synthesis of seed solution for the synthesis of gold nanorods. (b) Synthesis of growth solution with the addition of seed solution leading to the synthesis of gold nanorods.

undisturbed for 10–12 h. The Au NRs were purified by three cycles of centrifugation at 9000 rpm for 10 min followed by suspension in deionized water [30].

2.3. Treatment of Fe^{3+} ions with Au NRs

The source of Fe^{3+} ions was 0.01 M ferric nitrate solution. The Au NRs were treated with Fe^{3+} at various concentrations of 100, 1000, 2000, 5000 and 10,000 ppb. The quantity of Au NRs was maintained constant as 5 mL in all the reactions while adding to 5 mL of Fe^{3+} solution of required concentration, i.e. total volume of 10 mL. For studying the SERS activity throughout the experiment, the crystal violet dye with concentration of 1.5×10^{-5} M and concentrated the Au NR solution was used in such a way that dye to NR ratios were maintained as 10:1 by mixing 500 μL of dye and 50 μL of Au NRs. 100 μL of this solution was dropped on a well cleaned indium tin oxide (ITO) slide and was dried at 25 °C for 12 h which was further used for SERS study.

2.4. Equipment and analytical methods

Optical absorption spectra were recorded on Shimadzu UV-2401 spectrophotometer in 1 cm quartz cell. A Hitachi 2010 TEM was used to investigate the particle morphology. Samples for TEM were prepared by depositing on copper grids. SEM images were obtained using XL30 SEM with 30 kV operating voltage equipped with energy dispersive X-rays (EDX) analyser. Raman spectra were recorded with a Renishaw 2000 equipped with Ar⁺ ion laser (wavelengths = 532 nm) and a charge-coupled device (CCD) as the detector (Renishaw Co., U.K.). Samples for Raman spectra were prepared on ITO (vide supra). The 200 μ L gold nanorods were mixed with 0.01 M Fe³⁺ solution and concentrations of samples were made 100, 1000, 2000, 5000 and 10,000 ppb. 500 μ L of CV molecules of 10^{−4} M and 50 μ L of Au NR solution were mixed and deposited on ITO slide while the films were allowed to dry at 25 °C for about 12 h for SERS study. pH of the media was measured by Hanna Instruments pH meter model S358236, using BDH buffer for standardization.

3. Result and discussion

There has been detailed report on the synthesis, characterization and sensing application of Au NRs [32,33]. Hence in present discussion, only the essential aspects are provided. The detection of Fe³⁺ has been reported in literature using nanoparticles [59,60]. However the present paper discusses a very simple and efficient solution used as nanosensors for the detection of Fe³⁺. According to reports in the literature, the nanoparticles show two absorption bands corresponding to the transversal and longitudinal modes of surface SPR [61,62]. The transversal mode band belongs to the SPR along the short axis of the nanorod and appears at a shorter absorption maximum than the longitudinal mode band [61,62]. The maximum absorption wavelength of the longitudinal modes which corresponds to the SPR along the long axis of the rods presents a linear correlation with the aspect ratio (length/diameter) of the nanorods. As the aspect ratio of the nanorods increases, the longitudinal mode band shifts to longer wavelengths [63]. The similar behavior has been observed as the dielectric constant of the medium increases [64,65]. The nanorod with an average aspect ratio of 4.5 was used in present study.

3.1. Characterization of Au NRs

The SPR spectra for Au NRs and Au NPs in liquid form are depicted in Fig. 1. As shown in Fig. 1(a), the SPR of Au NPs is sharper as compared to Au NRs depicted in Fig. 1(b). The λ_{max} due to Au NPs in Fig. 1(a) is at ~522 nm and that due to Au NRs in Fig. 1(b) at 513 nm are transverse peaks while λ_{max} 745 nm shown in Fig. 1(b) corresponds to longitudinal

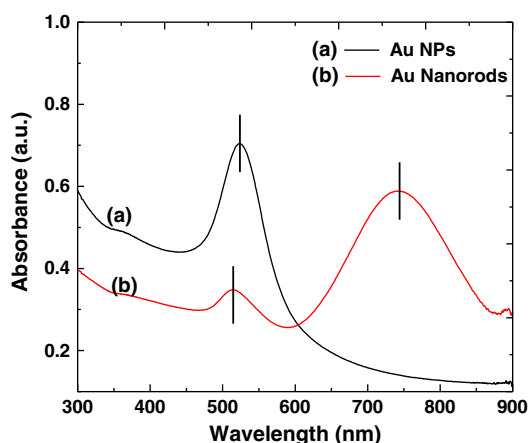


Fig. 1. Surface plasmon resonance spectra of (a) gold nanoparticles and (b) gold nanorods.

peak. The sharpness of the longitudinal peak shows the monodispersity of the Au NR sample whereas low intensity of the transverse peak indicates that the amounts of spherical particles present in sample are minimal.

Fig. 2 shows the SERS spectra of Au NRs at different laser power using CV as a molecule which shows increased Raman intensity with increasing laser power. The formation of nanorods was confirmed from electron microscopy. Fig. 3(a) and (b) shows the TEM images of Au NRs which act as nanosensors. The distribution of the size of particles with Au NRs formed is presented in form of a histogram and shown in Fig. 3(c). The aspect ratio of prepared Au NRs sample was estimated to be 4.5 by measuring its length as well as diameter [Fig. 3c]. It is clear from Fig. 3(a, b) that these Au NRs appear as separate rods with nanogaps between them which results in large number of adsorption sites for detection of foreign ions, i.e. Fe³⁺ in present study. Therefore, presently synthesized Au NRs have been helpful in detection of Fe³⁺ in water.

3.2. Application in Fe³⁺ ion sensing

The interaction of Fe³⁺ ions with the Au NRs was investigated using several spectroscopic and microscopic tools and a discussion of the data have been presented below in the following sections.

3.2.1. UV-visible spectroscopy

The SPR spectra of Au NRs in the presence of Fe³⁺ ions at different concentration have been depicted in Fig. 4. Fig. 4 clearly shows that upon addition of Fe³⁺ ions into the Au NR solution there is a change in the characteristics of the Au NRs which depends on the [Fe³⁺]. The 513 nm transverse peak that was seen in Fig. 1 nearly disappeared upon addition of 100 ppb solution of Fe³⁺ ions. This change in SPR spectrum is due to change in the optical properties of the medium in which Fe³⁺ ions are dispersed. This is attributed to the fact any concentration of the analyte Fe³⁺ results in agglomeration, and thus was not possible to obtain a unique optical signal for varying amounts of the analyte. The addition of aliquots of Fe³⁺ into the Au NR colloid shows distinguishable changes in the longitudinal peak position (800 nm) as well as shape. The change in the concentration of Fe³⁺ ions, clearly changes the absorption peak position towards lower wavelength and thus blue shift was absorbed (Fig. 4). Therefore, the width of the surface plasmon resonance peak progressively increased with the increase in concentration of Fe³⁺ ions in the aqueous media.

3.2.2. The effect of pH

The effect of pH on the addition of different concentration of Fe³⁺ ions to Au NRs solution was also studied. As shown in Fig. 5, a sharp change in pH at 100 ppb Fe³⁺ ions in water was observed. It was observed that the final pH was lower than that of the initial pH which

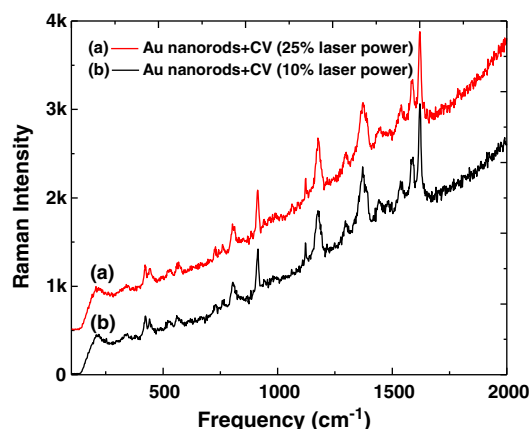


Fig. 2. SERS spectra of gold nanorods with CV molecule using different laser power.

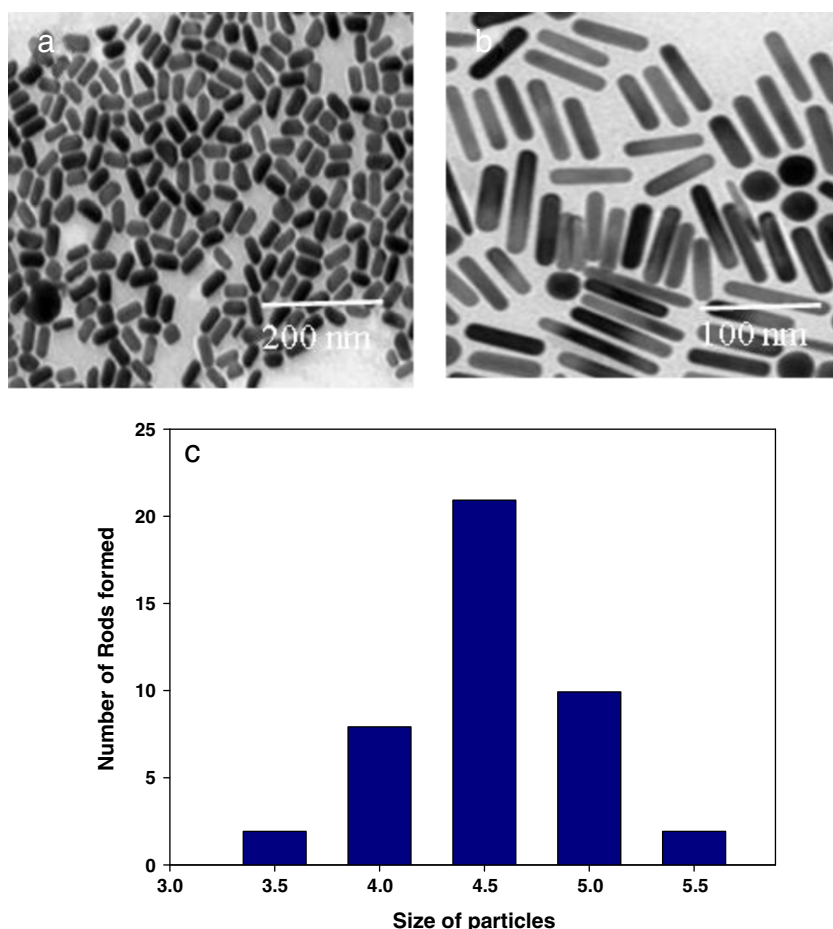


Fig. 3. (a) and (b). TEM images of gold nanorods synthesized. (c). The distribution of size of particles with number of Au nanorods formed with average aspect ratio of 4.5.

may be due to adsorption of Fe^{3+} ions over Au NRs where oxidation of Au NRs takes place leading to decrease of aspect ratio of Au NRs. However, the increasing concentration of Fe^{3+} ions in the solution leads to formation of the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ which has acidic character and caused decrease in pH. This approach is motivated by the 'slow growth principle,' which is effective protocol to prepare high aspect-ratio nanostructures [63].

3.2.3. Electron microscopy (SEM and TEM) study

Detailed structural and chemical analyses for the reaction between Fe^{3+} ions and Au NRs were further carried out with TEM and SEM studies. The Fe^{3+} ions could strongly be bonded on the Au NR surface to form aggregated mass (Fig. 6) which could be accounted for the blue shift of the surface plasmon absorption band of Au NRs (vide supra). In other words, the aggregation of particles was seen in the SEM study of Au NRs in the presence of 100 ppb Fe^{3+} (Fig. 6) which attributes to the blue shift of SPR band of Au NRs as shown in Fig. 4. The aggregation of the nanorods indicates that 100 ppb of Fe^{3+} ions destroy the separate nanorods having nanogaps in them, which was further confirmed by SERS spectral data as shown in Fig. 7.

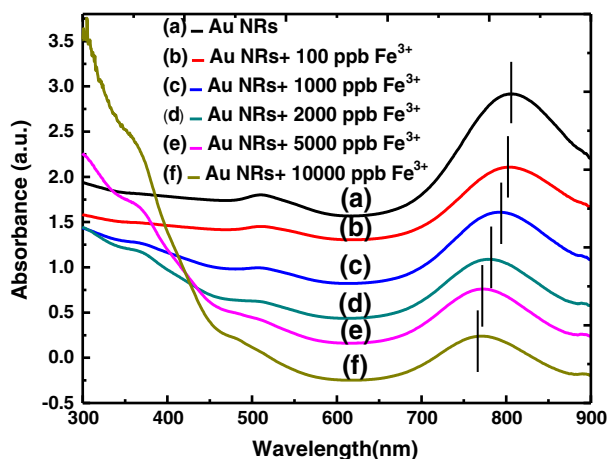


Fig. 4. Changes in surface plasmon resonance peaks due to addition of Fe^{3+} ions at different ppb levels in gold nanorods solution.

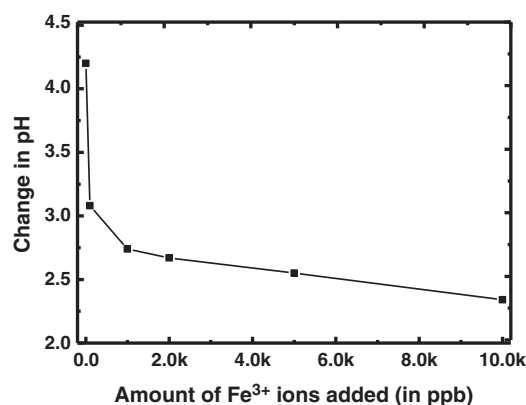


Fig. 5. Effect of pH on the addition of different concentration (100, 1000, 2000, 5000 and 10,000 ppb) of Fe^{3+} ions to gold nanorods solution.

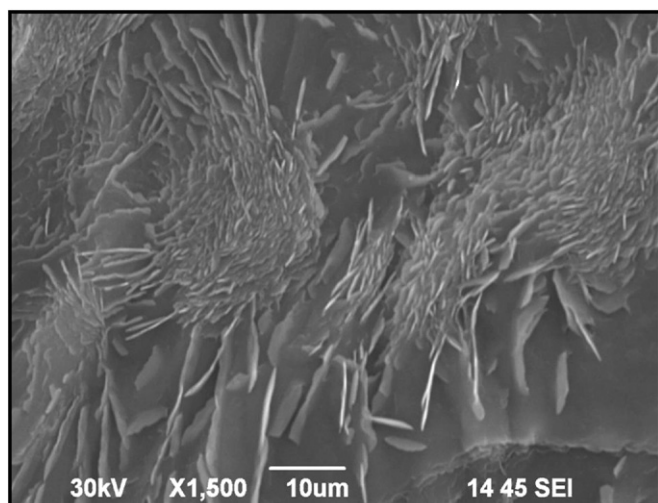


Fig. 6. SEM image after the addition of 100 ppb Fe^{3+} ions to gold nanorods solution.

3.2.4. Surface-enhanced Raman scattering

Single-molecule detection by Raman spectroscopy is possible owing to the enormous enhancement in order of 10^{14} – 10^{15} folds of the Raman response of specific molecules on a colloidal medium which is known as SERS for non-resonant conditions without the resonant factor [66,67]. Such enhancement in the intensity of Raman signals is comparable to that of fluorescence. Interaction of Fe^{3+} ions with Au NRs was investigated using Raman spectroscopy which was used to investigate the interactions at molecular level. The SERS spectra of Au NRs using CV molecule are shown in Fig. 7. Firstly, no signal of Au NRs on ITO surfaces was observed. Therefore, Au NRs were mixed with CV and then coated over ITO substrate (slide). When CV molecules alone were spread on ITO substrates they gave SERS signals only at $\sim 500\text{ cm}^{-1}$. Large enhancement of signals of CV molecule was observed and a number of peaks appeared in SERS spectra when the CV molecule interacted with Au NRs (Fig. 7). When Fe^{3+} ions in varied amounts were added in the Au NR solution and coated on ITO slides, it was noticed that the peaks appeared at 1620 cm^{-1} (sh), 1585 cm^{-1} (s), 1532 cm^{-1} (s), 1473 cm^{-1} (m), 1443 cm^{-1} (s), 1375 cm^{-1} (s), 1302 cm^{-1} (w), 1214 cm^{-1} (sh), 1175 cm^{-1} (s), 986 cm^{-1} (vw), 916 cm^{-1} (s), 813 cm^{-1} (w), 764 cm^{-1} (w) and 525 cm^{-1} (w) where s, strong; m, medium; w, weak; vw, very weak, sh, shoulder (Fig. 7). Increase in intensity but with signals got suppressed when 100 ppb Fe^{3+} ions were present. It means when CV molecules are dispersed in Au nanosensor

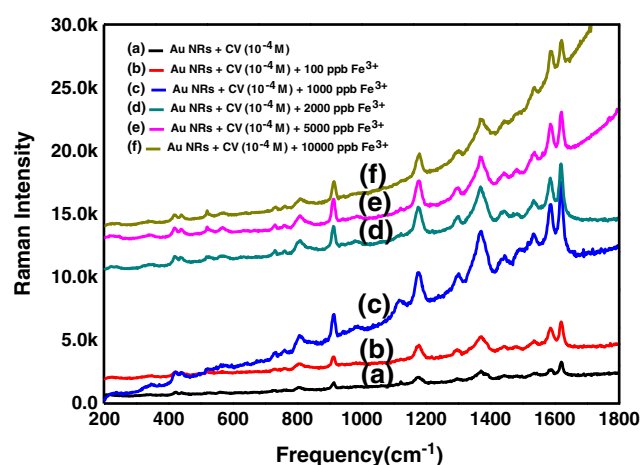


Fig. 7. SERS spectra using CV (10^{-4} M) as a molecule. (a) CV + Au NRs (b) CV + Au NRs + 100 ppb Fe^{3+} (c) CV + Au NRs + 1000 ppb Fe^{3+} (d) CV + Au NRs + 2000 ppb Fe^{3+} (e) CV + Au NRs + 5000 ppb Fe^{3+} (f) CV + Au NRs + 10,000 ppb Fe^{3+} .

solution, various vibration modes appear with large intensity. Therefore, with addition of Fe^{3+} ions, the signal of CV molecules started getting suppressed. Thus, it has been shown with conformity that Au NRs are behaving as sensitive nanosensors for detection of Fe^{3+} ions in water as low as 100 ppb level.

4. Conclusions

An approach with tremendous potential for the detection/determination of Fe^{3+} ions in water samples has been demonstrated using Au NRs with aspect ratio 4.5. It has been observed that Au NRs are highly sensitive towards Fe^{3+} ions at a level of 100 ppb and the same has been confirmed by SPR, UV–vis, SEM and SERS studies. Thus, Au NRs behave as nanosensors for detection of Fe^{3+} ions as low as 100 ppb level.

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