



# Colorimetric and smartphone-integrated paper device for on-site determination of arsenic (III) using sucrose modified gold nanoparticles as a nanoprobe

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## Abstract

An optical colorimetric and smartphone-integrated paper device (SIPD) is demonstrated for determination of As (III) in water and soil samples using sucrose modified gold nanoparticles (AuNPs/Suc) as a nanoprobe. The mechanism for determination of As(III) is experimentally validated by performing UV-Vis, transmission electron microscope (TEM), Fourier transforms infrared spectroscopy (FTIR) and dynamic light scattering (DLS) measurements. The density function theory (DFT) calculations using B3LYP with 6-311G (2d,2p) and LANL2DZ basis sets is used to theoretically prove the mechanism for determination of As(III). In addition, the paper fabricated with AuNPs/SuC was used as a nanoprobe for quantitative determination of As(III) using smartphone and ImageJ software. Calibration plot was linear over 10–800  $\mu\text{gL}^{-1}$  for colorimetric determination of As(III) with limit of detection (LOD) of 4  $\mu\text{gL}^{-1}$  acquired when the absorbance ratio obtained at 594 nm/515 nm. The linearity range of 50–3000  $\mu\text{gL}^{-1}$  with LOD of 20  $\mu\text{gL}^{-1}$  was determined using smartphone-integrated paper device. AuNPs/Suc is successfully employed for determination of As (III) from contaminated water and soil samples in colorimetry and SIPD.

**Keywords** Arsenic (III) · Colorimetry · Smartphone-paper device · Gold nanoparticles

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## Introduction

Arsenic is a ubiquitous element with metalloid property. It is distributed in earth crust, soils, rocks and exists in nature in the form of inorganic and organic materials with oxidation state of -III, +III and + V. Arsenic is a one of the most toxic chemical substance present due to its carcinogenic in nature [1, 2]. The presence of arsenic in drinking water may relate to increased risk of diseases such as skin cancer, lungs, bladder, kidney, etc. [3, 4]. Therefore, the monitoring of arsenic present in water sample is an important issue to avoid the entry of this noxious pollutant in environmental samples. There are several techniques such as electrothermal atomic adsorption spectrometry (ET-AAS) [5], inductively coupled plasma-optical emission spectrometry (ICP-OES) [6], voltammetry [7], surface enhanced Raman scattering (SERS) [8], hydride generation-atomic absorption spectrometry (HG-AAS) [9], inductively coupled plasma mass spectrometry (ICP-MS) [10], hydride generation-atomic fluorescence spectroscopy (HG-AFS) [11], x-ray fluorescence (XRF) [12] and spectrophotometry [4] have been reported for the determination of arsenic in different types of samples. Among these, spectrophotometry

(colorimetry) is found rapid and can be applied at the sample source.

Noble metal nanoparticles (NPs) based colorimetric nanoprobe have drawn huge attention for determination of variety of inorganic and organic chemical substances due to their unique electronic, optical, chemical and properties of metal NPs. The color of gold (Au) NPs is pink and silver (Ag) NPs is yellow in color when the sizes of NPs in the range of 10–50 nm. This is due to the localized surface Plasmon resonance (LSPR) absorption band of Ag and Au NPs which arises because of their collective oscillation of free electron present in the conduction band. The color of AgNPs and AuNPs change from yellow to red and pink to blue, respectively and after addition of analyte into the NPs results the red shift of LSPR band in the visible region. The change in color intensity of Au or Ag NPs solution is found proportional to the introduction of analyte which can be observed visually [13, 14]. The addition of analyte into the NPs solution plays an important role for detection because it provided a colorimetric determination of any analyte in sample solution. Our group exploited the use of AuNPs and AgNPs as a nanoprobe for determination of metal ions [15, 16], pesticides [17, 18], vitamins [19], nucleic acid [20] and protein [21] in environmental, biological and food samples. There are other NPs-based colorimetric nanoprobe have been reported for determination of variety of chemical substances from different type of real samples [2, 3, 13, 22]. The disadvantages of these methods are use of NPs solution ( $\approx 5$  mL) for colorimetric measurements which is found to be expensive. Thus, an alternative method is needed which should require a less amount of chemical reagents for measurement of analyte in sample solution.

Currently, paper based analytical devices (PADs) is reported for quantitative determination of different chemical substances which include the simplicity, user-friendly and excludes the use of large amount of reagents. The paper devices are made from naturally occurring material which is abundant, biodegradable and inexpensive materials [23, 24]. The colorimetric paper based determination is based on the measurement of change in signal intensity of color observed on paper substrate, which is recorded using UV-Vis, camera or smartphone [25]. Apilux et al. demonstrated a paper based colorimetric method for determination of Hg (II) in real water samples by the color change of silver nanoplates after the addition of analyte on to the test zone of paper [26]. Creran et al. reported the use of inkjet-printed enzymatic test strips for detection of bacteria in contaminated water samples through the color change of paper substrate [27]. There are several other paper based devices have been illustrated for determination of metal ions, bacteria, amino acids, proteins and pesticides using nanoparticles as a nanoprobe [28, 29]. Thus, paper based device fabricated with NPs is illustrated for analysis of arsenic present in contaminated water and soil samples.

In the present work, AuNPs/Suc is synthesized by the reduction of chloroauric acid ( $\text{HAuCl}_4$ ) using sodium borohydride

( $\text{NaBH}_4$ ) as a reducing agent and sucrose as a capping agent. The colorimetric and smartphone-integrated paper device (SIPD) are demonstrated for determination of As(III) in contaminated water and soil samples. The parameter such as effect of capping agents, concentration of NPs, pH and reaction time are optimized for determination of As(III). The density functional theory (DFT) is used to optimize and determine the interaction of As(III) with sucrose molecule present on the surface of AuNPs. Finally, the proposed method is successfully applied for determination As(III) in river, pond, tube well water and soil samples.

## Experimental section

### Chemical reagents and materials

All chemicals used were of analytical grade reagents. Chloroauric acid ( $\text{HAuCl}_4$ ), sodium borohydride ( $\text{NaBH}_4$ ), sucrose, sodium hydroxide ( $\text{NaOH}$ ), hydrochloric acid ( $\text{HCl}$ ), salts of all metal ions were obtained from HiMedia (<http://www.himedialabs.com/>, India). Paper based nanoprobe was prepared from glass microfiber Whatman filters paper (GF/A) (<https://www.sigmaaldrich.com/>, USA). The standard solution ( $100 \mu\text{g mL}^{-1}$ ) of As(III) was prepared by dissolving an appropriate amount of  $\text{NaAsO}_2$  in dilute  $\text{HCl}$  and total volume was made-up with deionized water (DW). The working standard solution of As(III) was prepared from the stock standard solution by appropriate dilution.

### Apparatus

UV-visible spectrophotometer evolution-300 (Thermo scientific, USA) matched with 1 cm quartz cell was used for determination of As(III). Fourier transforms-infra red spectrometer (FTIR) of type-nicolet-10 (Thermo Scientific, USA) was used for recording the IR spectra of pure sucrose and AuNPs/sucrose and solution mixture of AuNPs/Suc with As (III). The transmission electron microscope (TEM), Jeol, JEM-2100 (MA, USA) was applied for measurement of size and shape of AuNPs/Suc. Dynamic light scattering (DLS), Anton paar, kallioppe version 2.2.0 of type Litesizer 500 confirmed the zeta potential of NPs in aqueous solution before and after the addition of As(III). Gaussian 09 (C.01) program was used to perform the density functional theory (DFT) calculations with B3LYP using 6-311G (2d,2p) basis sets and LANL2DZ basis set.

### Synthesis of sucrose modified AuNPs

AuNPs modified with sucrose was synthesized by reduction of salt of  $\text{HAuCl}_4$  with  $\text{NaBH}_4$  prescribed in the literature [19]. The glassware's were cleaned with aqua-regia followed by

washing with DW prior to synthesis of AuNPs/Suc. Briefly, 10 mL of  $1.0 \times 10^{-3}$  M HAuCl<sub>4</sub> solution was taken into a 50-mL conical flask and mixed with 1 mL 0.03 M sucrose solution. The solution mixture was stirred with magnetic stirrer for 20 min. After, 1 mL 0.02 M NaBH<sub>4</sub> solution was added drop wise till the color of the solution change from yellow to pink. The color of the solution mixture changed from yellow to pink indicated the formation of AuNPs/Suc.

### Collection of water and soil samples for determination of As(III)

Real water samples such as river, pond and tube well were collected from Ambargarh Chowki, Chhattisgarh, India in the month of March-2019. The samples were brought to the laboratory in polyethylene bottle for analysis of As(III). These water samples were collected and filtered with Whatman filter paper No. 42 and stored in refrigerator at 5 °C until the analysis. The soil samples were collected in polyethylene bags and dried in oven at 60 °C. The dried soil sample was cooled down and then crushed in to a fine powder using mortar and pestle. The microwave was used for the digestion of soil samples. A 0.1 g of fine powder was taken into a Teflon vessel containing 5 mL of HNO<sub>3</sub> and 2 mL HF and total volume was diluted to 10 mL with DW. The sample solution was placed into a microwave digester for 30 min at 180 °C. The obtained solution was filtered with Whatman filter paper No. 42 and diluted accordingly to the level of arsenic present in sample [1].

### Colorimetric and smartphone-integrated paper device (SIPD) for determination of As(III) using AuNPs/Suc as a nanoprobe

For colorimetric determination, 1 mL of AuNPs was taken in 5-mL glass vial followed by the addition of different concentration of standard solution of As(III) and total volume of the solution was made up to 3 mL with DW. The solution mixture was kept for prescribed reaction time at room temperature while maintaining the pH of the solution with 0.1 M NaOH and 0.1 M HCl. The color of solution mixture was changed from pink to blue depending upon the concentration of analyte. The color intensity of solution mixture was measured using UV-Vis spectrophotometry in the wavelength range of 200–800 nm. The standard calibration plot was estimated between different concentration of As(III) and absorbance ratio at 594 nm/515 nm. Similarly, the concentration of As(III) in water sample was determined by adding a 1.5 mL of filtered sample into 5-mL of glass bottle containing 1 mL of AuNPs/Suc. The pH of the solution mixture was maintained to 7 and total volume was made up to 3 mL of DW. The sample solution was kept at room temperature for 1 min of reaction time. The absorbance ratio at 594 nm/515 nm was calculated and the amount of As(III) in water sample was determined using

standard calibration plot. The schematic diagram for determination of As(III) in sample using AuNPs/Suc as a nanoprobe is shown in Fig. 1a.

Smartphone-paper-based device for determination of As(III) was processed using filter paper of circle diameter (0.5 cm) which mounted on the hydrophobic surface of the paper. Then, 50 µL AuNPs/Suc was placed on paper substrate followed by the addition of different concentration of As(III) while the pH of solution to 7. The color intensity of AuNPs with As(III) was measured using ImageJ software and the calibration plot was drawn between the different concentration of As(III) and their respective color intensity. Similarly, 50 µL of filtered water samples were deposited on test zones of paper substrate containing AuNPs/Suc. The color intensity of paper was estimated using ImageJ software and concentration of analyte was determined using calibration plot. The schematic diagram for determination of As(III) using smartphone-integrated paper based device is shown in Fig. 1b.

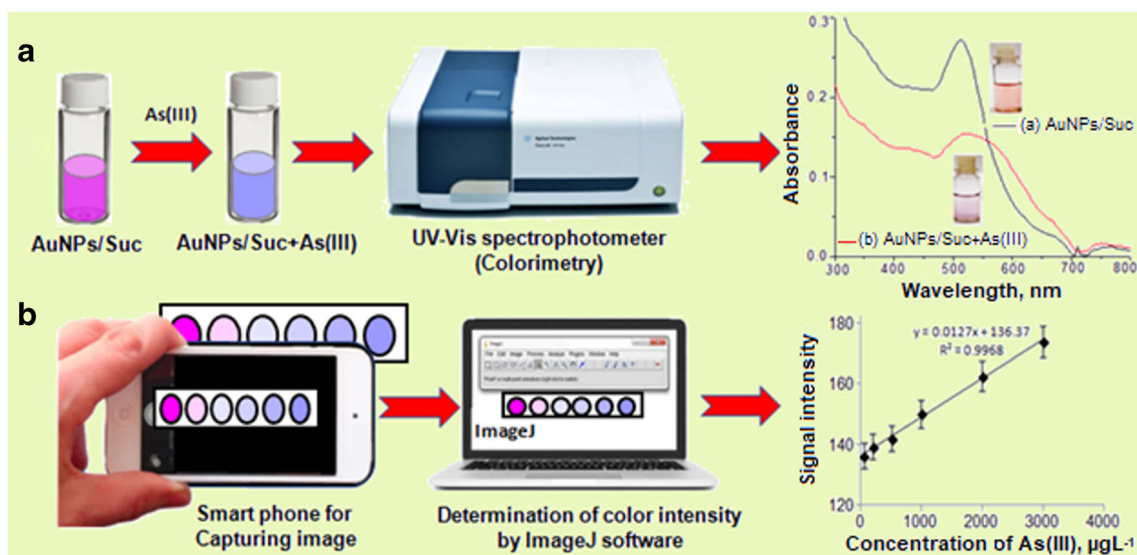
## Result and discussion

### Choice of AuNPs/Suc for determination of As(III)

AuNPs, AgNPs and CuNPs metal NPs are exploited for optical colorimetric determination of different type of chemical substances based on the color change of these NPs after the addition of specific analyte. Here, AuNPs used as a nanoprobe for determination of target analyte from sample solution because of the better chemical stability, extinction coefficient and LSPR properties compared to AgNPs and CuNPs. In addition, AgNPs and CuNPs are susceptible to oxidation when exposed to open air and light. Further, the surface modification of AuNPs is very important for selective binding of particular analyte for determination of chemical substances in real sample solutions [13, 19]. For this, AuNPs was functionalized with different capping agents such sucrose, calixarene, citrate as well as with bare NPs (without any modification). The AuNPs capped with sucrose exhibited the transition of color from pink to blue and appearance of extra LSPR band at 594 nm in the spectrum after the introduction of As(III), shown in Fig. S1 (Electronic supplementary material, ESM). Thus, sucrose capped AuNPs was used as a nanoprobe for selective determination of As(III) from sample solution.

### Screening of different metal ions using colorimetric and smartphone-integrated paper device using AuNPs/Suc as a nanoprobe

AuNPs/Suc was used as a colorimetric nanoprobe for selective detection of particular metal ions. For this, different metal ions such as Ba (II), Pb (II), Tb (III), Zn (II), Fe (III), Cd (II), As(III), Y (III), Cu (II), La (III), Hg (II), Gd (III), Na(I), Ni (II),



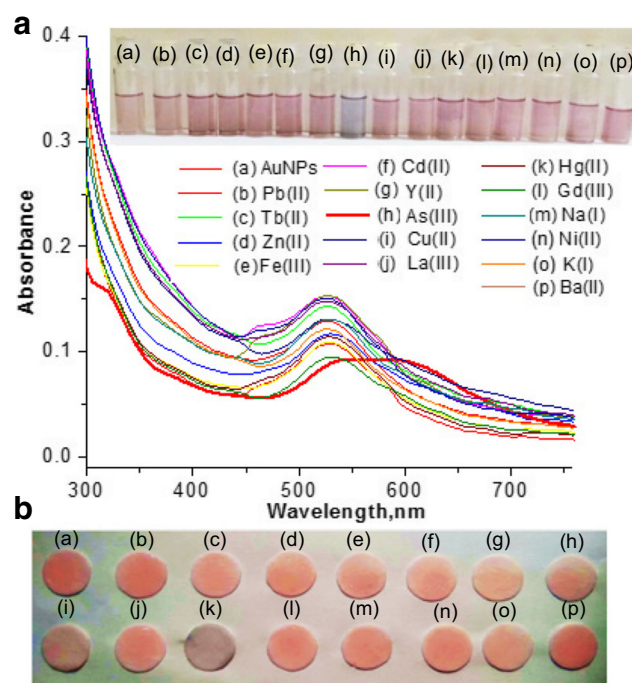
**Fig. 1** (A) Procedure for colorimetric (UV-Vis spectrophotometric) detection of arsenic using AuNPs as a nanoprobe and (B) Procedure for detection of arsenic using smartphone-integrated paper device fabricated with AuNPs/Suc

K(I), Ca (II) and Co (III) were separately taken in a 5-mL glass vial followed by the addition of 1 mL of AuNPs/Suc and total volume of the solution was made up to 3 mL of DW. The results are shown in Fig. 2A. AuNPs/Suc with As(III) showed the color change from pink to blue which can be differentiated visually (Fig. 2h). The solution mixture with metal ions other than As(III) did not show any color change and remained the same as a pink color, shown in Fig. 2a–g and i–p. Further, UV-Vis was used to determine the spectra of each solution mixture to verify the optical change of AuNPs/Suc with analyte. The broad red shift of LSPR absorption band was found in the range of 515–615 nm with As(III) and not with other metal ions. The reason for red shift of LSPR absorption band is due to the aggregation of particles after the addition of analyte into the NPs solution. In addition, paper strip fabricated with AuNPs/Suc was also used as a nanoprobe for determination of As(III) by depositing 50  $\mu\text{L}$  of NPs on test zones of paper substrate followed by the addition of different metal ions, shown in Fig. 2B. The paper strip containing As(III) exhibited the blue color (Fig. 2K–k) and other spots did not show any color change, shown in Fig. 2a–j and l–p. This demonstrated the usefulness of SIPD as a nanoprobe for determination of As(III) from sample solution.

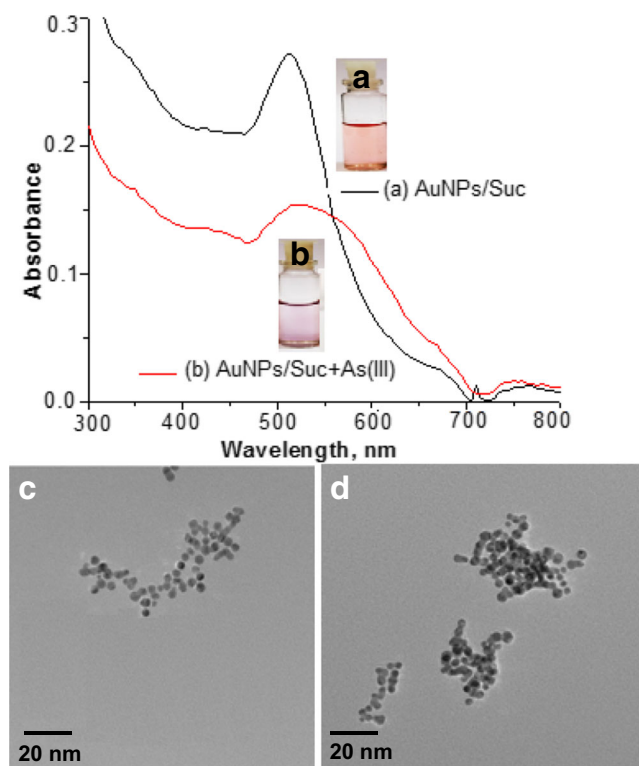
### Mechanism for determination of As(III) using colorimetric and smartphone-integrated paper based device using AuNPs/Suc as a nanoprobe

The change of color from pink to blue with addition of As(III) is due to aggregation of AuNPs/Suc which caused the broad red shift of LSPR absorption band in the visible region after the addition of analyte. The results are shown in Fig. 3a and b. The red shift of LSPR band from 515 to 615 nm is because of

the aggregation of NPs confirmed by TEM measurements. The TEM image (Fig. 3c) shows the size of NPs ( $11.2 \pm 1.4$ ) without the addition of As(III) representing the dispersed particle in aqueous medium. Figure 3d shows the TEM image of aggregated NPs with As(III) where average size of NPs ( $50.4 \pm 2.4$ ) was found to be many folds higher



**Fig. 2** (A): (a) to (p) showing the screening of different metal ions for colorimetric detection of arsenic using 0.3 mM AuNPs/Suc as a nanoprobe for 1 min of reaction time at room temperature along with their respective UV-Vis spectra; and (B): (a) to (p) showing SIPD approach for detection of arsenic where the paper containing 50  $\mu\text{L}$  of 0.3 mM AuNPs/Suc with different metal ions and NPs where As(III) showed the color change from pink to blue



**Fig. 3** (a) Glass vial containing AuNPs/Suc, (b) AuNPs/Suc with As(III) along with their UV-Vis spectra using 0.3 mM AuNPs/Suc as a nanoprobe for 1 min reaction time; (c) TEM image of AuNPs/Suc and (d) TEM image of AuNPs/Suc after the addition of As(III)

than the dispersed NPs. DLS measurement was also carried out for determination of mean zeta potential of AuNPs before and after the addition of analyte. The mean zeta potential of sucrose capped AuNPs was  $-27.6$  mV and decrease in the zeta potential  $-9.5$  mV after the addition of metal ions As(III) confirmed the binding of AuNPs/Suc with As(III). Hence, the dispersed AuNPs exhibited a pink color in the absence of analyte and blue color and red shift of NPs in the presence of analyte. This phenomenon of color transition of AuNPs/Suc from pink to blue was examined for selective determination of As(III) from sample solution using colorimetric and SIPD.

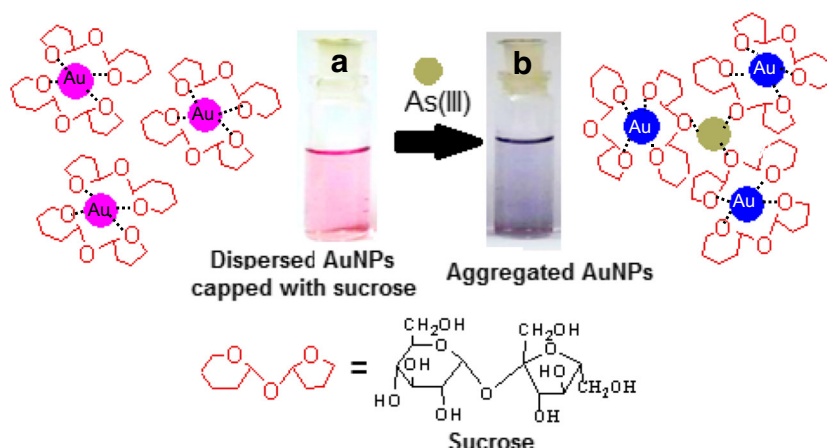
The capping of sucrose on the surface of AuNPs and further interaction with As(III) was confirmed by taking the FTIR spectra of pure sucrose compound, AuNPs/Suc and AuNPs/Suc + As(III). The results are shown in Fig. S2. The FTIR spectra of pure sucrose (Fig. Sa) showed an intense peak at  $3510\text{ cm}^{-1}$  due to OH stretching of sucrose molecule. The absorption peak observed at  $1080\text{ cm}^{-1}$ ,  $1120\text{ cm}^{-1}$  and  $1160\text{ cm}^{-1}$  attributed to C-O and C-O-C stretching [30]. Fig. S2(b) represents the FTIR spectrum of AuNPs functionalized with sucrose in which the absorption peak observed at  $1080\text{ cm}^{-1}$  and  $1120\text{ cm}^{-1}$  for AuNPs/Suc was found to decrease compared to pure sucrose verifying the binding of C-O on the surface of AuNPs. Fig. S2(c) shows the FTIR spectrum

of AuNPs/Suc with As(III). The absorption peak of C-O shifted from  $1020\text{ cm}^{-1}$ ,  $1058\text{ cm}^{-1}$  to  $1194\text{ cm}^{-1}$ ,  $1199\text{ cm}^{-1}$  showing the binding of As(III) with C-O. The peaks observed at  $712$  and  $818\text{ cm}^{-1}$  were related to As-O stretching frequency confirmed the binding of As(III) to the surface of AuNPs/Suc. Thus, the color change from pink to blue and red shift of LSPR band was achieved with As(III) and not with other metal ions verifying the selective determination of As(III) using AuNPs/Suc as colorimetric and SIPD.

A schematic diagram (Fig. 4) on the basis of experimental and theoretical investigation for selective determination As(III) using AuNPs/Suc as a nanoprobe. The diagram represents the AuNPs stabilized with sucrose in aqueous solution which makes them stable for a long period of time, shown in Fig. 4a. After introducing the As (III) into AuNPs causes the color change from pink to blue because of As(III) get interacted with oxygen atom of sucrose molecules which is already coordinated to AuNPs, shown in Fig. 4b. Thus, As(III) is selectively sensed by the complex formed with AuNPs. The change in color intensity and shift of LSPR is found proportional to the amount of analyte added in to the NPs solution which is exploited in colorimetry for determination of As(III) from different sample solution. Similar mechanism for determination of As(III) from water sample is illustrated using cysteine capped AuNPs where the oxygen moieties of capping agent coordinate with analyte. This causes the agglomeration of particles and then color change of AuNPs which is measured in DLS for quantitative determination of As (III) from contaminated water samples [31]. In addition, several other literatures also demonstrated the binding of As (III) with humic acid [32], polyethylene glycol [33] and glutathione [34] through As-O linkage for quantitative determination of different type of samples.

Further, the theoretical study was also demonstrated to illustrate the sensing mechanism for determination of As(III) performed by density functional theory (DFT) using Gaussian 09 (C.01) program with B3LYP and 6-311G (2d,2p) and LANL2DZ basis sets [35, 36]. The cartesian coordinates, bond parameters and energy values, charge distributions acquired DFT calculation is given in Table S1 and Table S2 (ESM) and interaction of gold with sucrose is shown in Fig. S3. The bond parameters calculated also helpful in favor of the present study, where average bond length of Au-O ( $2.4895\text{ \AA}$ ), bond angle of O-Au-O ( $90.0567^\circ$ ) and dihedral angle of O-Au-O-C ( $-50.4471^\circ$  and  $154.4918^\circ$ ) were observed. The total energy was  $-2741.6864$  a.u. (Table S1). The optimized structure of the sucrose and its interaction with gold and As(III) is shown in Fig. (S3a and S3b). The energy gap between HOMO and LUMO is found to be  $1.7\text{ eV}$  (Fig. S3c). The electrostatic potential (ESP) is one of the parameters to measure for any molecule's interaction characteristics, especially non-covalent interactions. Here, the positive (yellow color) and negative is oval (orange) of the molecules which

**Fig. 4** Schematic diagram to show the mechanism for detection of As(III) using sucrose capped AuNPs as nanoprobe



varies the SCF total charge density from  $-2.276 \times 10^1$  to  $+2.276 \times 10^1$  is shown in Fig. 6d.

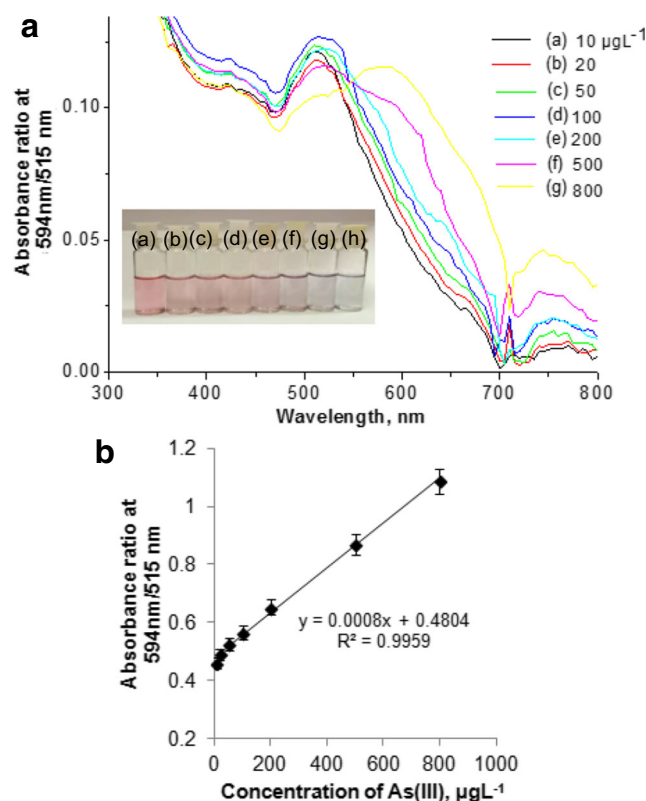
### Optimization of AuNPs/Suc as a nanoprobe for determination of As(III)

Different parameter such as capping agent, pH of sample, concentration of NPs and reaction time were optimized to get the better performance of AuNPs/Suc as a nanoprobe for determination of As(III) using colorimetric and SIPD. The results are given in Fig. S4(a) to S4(c), ESM. The optimum determination of As(III) was achieved when 0.3 mM AuNPs/Suc used as a nanoprobe for 1 min of reaction time at pH 7.

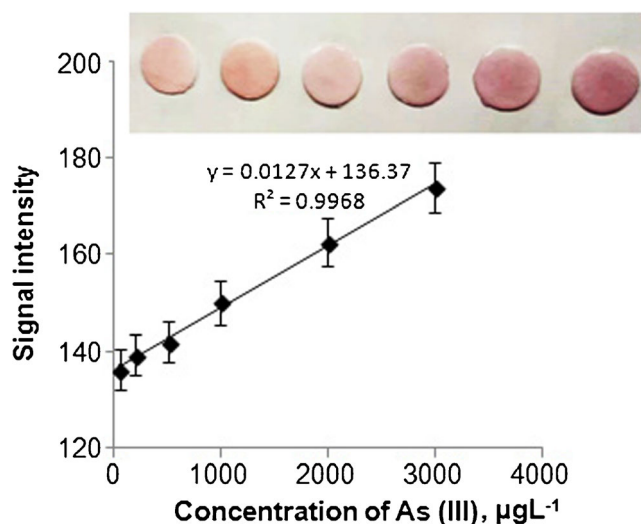
### Analytical evaluation for determination of As(III) from water sample using colorimetric and SIPD AuNPs/Suc as a nanoprobe

The analytical evaluation for determination of As(III) in water sample is performed by evaluating the calibration plot, limit of detection (LOD), accuracy and precision. Figure 5 shows the calibration plot estimated by spiking different concentration of analyte into the AuNPs. The calibration plot was drawn by taking the absorbance ratio of solution mixture at 594 nm and 515 nm against addition of different concentration of analyte, Fig. 5A. A good linear line was acquired in the range of 10–800  $\mu\text{gL}^{-1}$  for determination of As(III) with correlation coefficient ( $r^2$ ) of 0.993, respectively, Fig. 5B. LOD value was determined at three time of the standard deviation by spiking a lowest concentration of analyte into NPs solution. The LOD for determination of As(III) was 4  $\mu\text{gL}^{-1}$  using AuNPs as a nanoprobe in colorimetry. The precision of the method was estimated by determination of relative standard deviation (RSD). For this, 300  $\mu\text{g L}^{-1}$  of As(III) was spiked into a 1 mL of AuNPs/Suc and analyzed ( $n=6$ ) at the optimized conditions of the method. The better reproducibility value of RSD (3.0%) showed that the assay can used as a colorimetric nanoprobe for determination of As(III). The accuracy of the

method was validated by calculating the recovery percentage (%) in real water samples. For this, 50 and 100  $\mu\text{gL}^{-1}$  of As(III) was spiked into tube well, river and pond water samples containing 1 mL of AuNPs. Good recovery percentage of 90.6 to 97.3% (Table S3) in tube well, river and pond water showing the better selectivity of the method for determination of target analyte in complex sample matrixes. The accuracy of



**Fig. 5** (A) Glass vial containing AuNPs with different standard solutions (10, 20, 50, 100, 200, 500 and 800  $\mu\text{gL}^{-1}$ ) of As(III) using 0.3 mM AuNPs/Suc as a nanoprobe for 1 min of reaction time at pH 7 along with their respective UV-Vis spectra and (B) standard calibration plot for determination concentration of arsenic ((10, 20, 50, 100, 200, 500 and 800  $\mu\text{gL}^{-1}$ ) using AuNPs/Suc as a nanoprobe for 1 min of reaction time at pH 7.0



**Fig. 6** Test zones of filter paper deposited with AuNPs/Suc and different concentrations of As(III) from 50 to 3000  $\mu\text{gL}^{-1}$  along with calibration plot for determination of As(III) using SIPD using AuNPs as a nanoprobe for 1 min of reaction time at pH 7

the method was also tested by analyzing the reference standard material (SRM 2710a) of soil containing arsenic of  $52.5 \pm 1.6 \text{ mgKg}^{-1}$ . The amount of arsenic in soil sample was  $51.4 \pm 3.1 \text{ mgKg}^{-1}$  using present method was found close to the reference standard material. Therefore, the analysis of reference standard samples verified the validity of the NPs-based colorimetric method for determination of arsenic using AuNPs/Suc as a nanoprobe.

Similarly, the calibration plot was drawn for SIPD by depositing the different concentration of As(III) on test zones of filter paper fabricated with AuNPs/Suc. The image recorded with smart phone was used to calculate the color intensity for standard solution of As(III). The calibration plot was prepared between standard solution of As(III) and their respective mean color intensity shown in Fig. 6. Good linear range (50–3000  $\mu\text{gL}^{-1}$ ) was obtained for determination of As(III) using AuNPs as a nanoprobe in SIPD. The linear least square equation ( $y = 0.013x + 136.37$ ) with  $r^2$  of 0.997 was used to estimate the As(III) in real samples. The LOD obtained for determination of As(III) was  $20 \mu\text{gL}^{-1}$ . Thus, SIPD was applied for

determination of As(III) in sample solution using AuNPs/Suc as a nanoprobe.

### Application for colorimetric determination of As(III) in real water and soil samples in colorimetric and SIPD using AuNPs/Suc as a nanoprobe

The validity of present method was tested by analyzing the real water sample such as tube well, pond, river water and soil samples from Ambagarh chowki, Chhattisgarh, India. The water, soil and sediments samples of this region are highly contaminated with arsenic [19]. Here, the AuNPs/Suc was employed as a nanoprobe for determination of As(III) in water and soil samples. The level of analyte in sample solution was determined using calibration plot ( $y = 0.0008x + 0.4904$ ). The results are given in Table 1. Similarly, SIPD was used for determination of As(III) in same samples using the calibration plot acquired using paper based device validated the results of colorimetric determination. Further, the results of colorimetric and SIPD were validated with the results of ICP-AES analysis, given in Table 1. Thus, the colorimetric and SIPD approaches were successfully employed for determination of As(III) in river, tube well, pond water and soil samples.

### Effect of interferences for determination of As(III) using AuNPs/Suc as a nanoprobe

Metal ions such as Na(I), K(I), Ca (II), Ba (II), Mg (II), Mn (II), Pb (II), Tb (II), Zn (II), Fe (III), Cd (II), Y (III), Cu (II), La (III), Hg (II), Gd (III), Sb (III), Bi (III), Mo (VI) and Ni (II) and anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  that exists in water and soil samples were investigated using AuNPs/Suc as a nanoprobe. For this, different concentrations of these substances were spiked into AuNPs/Suc and the tolerance limit of metal ions and anions were determined. The results are given in Table S4. The tolerance limit for determination of metal ions and anions was found to be many folds more than their actual level in the sample matrixes. Therefore, the results generated showing that these diverse substances did not interfere for determination of As(III) using AuNPs/Suc as a nanoprobe.

**Table 1** Application for determination of arsenic in water ( $\mu\text{gL}^{-1}$ ) and soil ( $\text{mgKg}^{-1}$ ) samples using colorimetry and SIPD and ICP-AES

Samples/ Sources	Colorimetry	RSD, % (n = 3)	SIPD	RSD, % (n = 3)	ICP-AES	RSD, % (n = 3)
Pond	644	3.5	632	4.2	642	4.5
River	210	2.7	216	3.1	208	3.8
Tube well-1	417	4.0	411	2.9	415	4.1
Tube well-2	685	2.9	691	3.5	680	3.0
Soil-1	207	3.5	212	2.8	210	3.1
Soil-2	113	4.3	109	2.7	114	4.0

**Table 2** The comparison of colorimetric and paper based sensor for determination of arsenic with other reported colorimetric methods

Methods	Linear range, $\mu\text{gL}^{-1}$	LOD, $\mu\text{gL}^{-1}$	Samples	Ref.
AuNPs/Aptamer	1.26–200	1.26	Water	2
AuNPs/GSH-DTT-CYs-PDCA	2–20	2.5	Water	3
AuNPs/SDS	5–500	2	Water	14
KI + octylacetamide	20–1200	10	Water	4
Rhodamine-B	40–400	–	Soil, water and food	37
Methylene blue+SDS	0–8630	1300	Water	38
Variamine blue	200–1400	22	Environmental and biological	39
AuNPs/Suc-Colorimetry	10–800	4	Water and soil	Present method
SIPD	50–3000	20	Water and soil	

Colorimetric and Smartphone-integrated paper device used for selective detection of arsenic from contaminated water samples using sucrose modified gold nanoparticles (AuNPs/Suc) as a sensing probe

### Comparison of colorimetric and SIPD nanoprobe for determination of As(III) with other reported methods

The present work is compared with other colorimetric methods such as AuNPs/Aptamer-colorimetry [2], AuNPs modified with glutathione (GSH), DL-dithiothreitol (DTT)-cysteine (CYs)- 2,6-pyridinedicarboxylic acid (PDCA) [3], AuNPs/Sodium dodesylsulfate (SDS) [14], potassium iodide (KI) + octylacetamide [4], rhodamine-B [37], methylene blue+SDS [38] and variamine blue [39] for determination of arsenic in water sample, given in Table 2. The better sensitivity is achieved when AuNPs/Aptamer [2], AuNPs/GSH-DTT-CYs-PDCA [3] and AuNPs/SDS [14] are used for determination of arsenic though the synthesis of gold NPs with these methods are found to be tedious and multi steps process. The better LOD value is obtained with present work compared to KI + octylacetamide [4] rhodamine-B [12], methylene blue+SDS [13] and variamine blue methods [14]. In addition, the large volume of chromophoric reagents are employed in these conventional colorimetric methods for determination of As(III) which is sometimes not found selective. AuNPs/Suc-based colorimetry and SIPD is free from the chromophoric reagent and avoiding the use of large amount of NPs solution compared to conventional colorimetric methods [2, 3, 14]. Thus, the present method is rapid and economic for determination of arsenic from water and soil samples.

### Conclusions

The colorimetric and smartphone-integrated paper based device was successfully demonstrated for quantitative determination of As(III) from water and soil samples from this region. The present assay is free from the use of large amount of chromophoric reagents and solvents for the complexation of target analyte from sample solution. The smartphone-paper

based nanoprobe minimizes the volume of NPs solution to 50  $\mu\text{L}$  where the nanoparticles-based colorimetric methods utilize a 3 mL of AuNPs for determination of arsenic from sample solution. Further, smartphone-integrated paper based device is rapid and portable for monitoring of arsenic at the sample source. For future prospect, the use of such portable device will useful for analysis of variety of analytes in biological, environmental and food samples.

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### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

### References

- Patel KS, Shrivastava K, Brandt R, Jakubowski N, Corns W, Hoffmann P (2005) Arsenic contamination in water, soil, sediment and rice of central India. *Environ Geochem Health* 27:131–145
- Zhan S, Yu M, Lv J, Wang L, Zhou P (2014) Colorimetric detection of trace arsenic (III) in aqueous solution using arsenic aptamer and gold nanoparticles. *Aust J Chem* 67:813–818
- Gonzalez RD, Varela LG, Barrera PB (2014) Functionalized gold nanoparticles for the detection of arsenic in water. *Talanta* 118:262–269
- Shrivastava K, Patel KS (2004) On-site determination of arsenic in contaminated water. *Anal Lett* 37:333–344
- Kildahl BT, Lund W (1996) Determination of arsenic and antimony in wine by electrothermal atomic absorption spectrometry. *Fresenius J Anal Chem* 354:93–96
- Paula JFR, Froes-Silva RES, Ciminelli VST (2012) Arsenic determination in complex mining residues by ICP – OES after ultrasonic extraction. *Microchem J* 104:12–16
- Mays DE, Hussam A (2009) Voltammetric methods for determination and speciation of inorganic arsenic in the environment—a review. *Analytica Chimica Acta* 646:6–16



8. Mulvihill M, Tao A, Benjauthrit K, Arnold J, Yang P (2008) Surface-enhanced raman spectroscopy for trace arsenic detection in contaminated water. *Angew Chem* 120:6556
9. Becker EM, Dessuy MB, Boschetti W, Vale MGR, Ferreira SLC, Welz B (2012) Development of an analytical method for the determination of arsenic in gasoline samples by hydride generation-graphite furnace atomic absorption spectrometry. *Spectrochim Acta B* 71:102–106
10. Entwisle J, Hearn R (2006) Development of an accurate procedure for the determination of arsenic in fish tissues of marine origin by inductively coupled plasma mass spectrometry. *Spectrochim Acta B* 61:438–443
11. Montesinos PC, Cervera ML, Pastor A, Guardia MDL (2003) Determination of arsenic and antimony in milk by hydride generation atomic fluorescence spectrometry. *Talanta* 60:787–799
12. Barros H, Parra LMM, Bennum L, Greaves ED (2010) Determination of arsenic in water samples by total reflection X-ray fluorescence using preconcentration with alumina. *Spectrochim. Acta B* 65:489–492
13. Motl NE, Smith AF, De Santisa CJ, Skrabalak SE (2014) Engineering plasmonic metal colloids through composition and structural design. *Chem Soc Rev* 43:3823–3834
14. Shrivastava K, Shankar R, Dewangan K (2015) Gold nanoparticle as a localized surface plasmon resonance based chemical sensor for on-site colorimetric detection of arsenic in water samples. *Sens Actuators B* 220:1376–1383
15. Shrivastava K, Sahu S, Patra GK, Jaiswal NK, Shankar R (2016) Localized surface Plasmon resonance of silver nanoparticles for sensitive colorimetric detection of chromium in surface water, industrial waste water and vegetable samples. *Anal Methods* 8:2086–2096
16. Shrivastava K, Sahu B, Deb MK, Thakur SS, Sahu S, Kurey R, Kant T, Patle TK, Jangde R (2019) Colorimetric and paper-based detection of lead using PVA capped silver nanoparticles: Experimental and theoretical approach. *Microchem J* 150:104156
17. Shrivastava K, Nirmalkar N, Thakur SS, Kurey R, Sinha D, Shankar R (2018) Experimental and theoretical approaches for the selective detection of thymine in real samples using gold nanoparticles as a biochemical sensor. *RSC Adv* 8:24328–24337
18. Shrivastava K, Nirmalkar N, Ghosale A, Thakur SS (2016) Application of silver nanoparticles for a highly selective colorimetric assay of endrin in water and food samples based on stereoselective endorecognition. *RSC Adv* 6:29855–29862
19. Shrivastava K, Nirmalkar N, Thakur SS, Deb MK, Shinde SS, Shankar R (2018) Sucrose capped gold nanoparticles as a plasmonic chemical sensor based on non-covalent interactions: Application for selective detection of vitamins B1 and B6 in brown and white rice food samples. *Food Chem* 2:5014–5021
20. Shrivastava K, Nirmalkar N, Thakur SS, Kurey R, Sinha D, Shankar R (2018) Experimental and theoretical approaches for the selective detection of thymine in real samples using gold nanoparticles as a biochemical sensor. *RSC Adv* 8:24328–24337
21. Shrivastava K, Nirmalkar N, Deb MK, Dewangan K, Nirmalkar J, Kumar S (2019) Application of functionalized silver nanoparticles as a biochemical sensor for selective detection of lysozyme protein in milk sample. *Spectrochim Acta Part A* 213:127–133
22. Lin Y, Chen C, Wang C, Pu F, Ren J, Qua X (2011) Silver nanoprobe for sensitive and selective colorimetric detection of dopamine via robust Ag - catechol interaction. *Chem Commun* 47:1181–1183
23. Tang RH, Liu LN, Zhang SF, He XC, Li XJ, Xu F, Ni YH (2019) A review on advances in methods for modification of paper supports for use in point-of-care testing. *Microchim Acta* 186:521
24. Ghosale A, Shrivastava K, Shankar R, Ganesan V (2017) Low cost paper electrode fabricated by direct writing with silver nanoparticles based ink for detection of hydrogen peroxide in waste water. *Anal Chem* 89:776–782
25. Zhou M, Yang M, Zhou F (2014) Paper based colorimetric biosensing platform utilizing cross-linked siloxane as probe. *Biosens Bioelectron* 55:39–43
26. Apilux A, Siangproh W, Praphairaksit N, Chailapakul O (2012) Simple and rapid colorimetric detection of Hg(II) by a paper-based device using silver nanoplates. *Talanta* 97:388–394
27. Creran B, Li X, Duncan B, Kim CS, Moyano DF, Rotello VM (2014) Detection of bacteria using inkjet-printed enzymatic test strips. *ACS Appl Mater Interfaces* 6:19525–19530
28. Nery EW, Kubota LT (2013) Sensing approaches on paper-based devices: a review. *Anal Bioanal Chem* 405:7573–7595
29. Zhou G, Pu H, Chang J, Sui X, Mao S, Chen J (2018) Real-time electronic sensor based on black phosphorus/Au NPs/DTT hybrid structure: Application in arsenic detection. *Sens Actuators B* 257:214–219
30. Max JJ, Chapdos C (2001) Sucrose hydrates in aqueous solution by IR spectroscopy. *J Phys Chem A* 105:10681–10688
31. Kalluri JR, Arbneshi T, Khan SA, Neely A, Candice P, Varisli B, Washington M, McAfee S, Robinson B, Banerjee S, Singh AK, Senapati D, Chandra Ray P (2009) Use of gold nanoparticles in a simple colorimetric and ultrasensitive dynamic light scattering assay: selective detection of arsenic in groundwater. *Angew Chem Int Ed* 48:9668–9671
32. Buschmann J, Kappeler A, Lindauer U, Kistler D, Berg M, Sigg L (2006) Arsenite and arsenate binding to dissolved humic acids: influence of pH, type of humic acid and aluminum. *Environ Sci Technol* 40:6015–6020
33. Boruah BS, Daimari NK, Biswas R (2019) Functionalized silver nanoparticles as an effective medium towards trace determination of arsenic (III) in aqueous solution. *Results Phys* 12:2061–2065
34. Li J, Chen L, Lou T, Wang Y (2011) Highly sensitive SERS detection of As<sup>3+</sup> ions in aqueous media using glutathione functionalized silver nanoparticles. *ACS Appl Mater Interfaces* 3:3936–3941
35. Becke AD (1993) A new mixing of Hartree–Fock and local density-functional theories. *J Chem Phys* 98:1372–1377
36. Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789
37. Pillai A, Sunita G, Gupta VK (2000) A new system for the spectrophotometric determination of arsenic in environmental and biological samples. *Anal Chim Acta* 408:111–115
38. Kundus S, Ghosh SK, Mandal M, Pal T, Pal A (2002) Spectrophotometric determination of arsenic via arsine generation and in-situ color bleaching of methylene blue (MB) in micellar medium. *Talanta* 58:935–942
39. Narayana B, Cherian T, Mathew M, Pasha C (2006) Spectrophotometric determination of arsenic in environmental and biological samples. *Ind J Chem Toxicol* 13:36–40

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