

Supporting Information

A facile approach for selective detection of arsenite ion using plasmonic behaviour of silver nanoparticles

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Experimental section

Materials: AgNO₃, tri-sodium citrate, NaAsO₂, Na₃AsO₄ was obtained from Sigma-Aldrich and used as received. Double distilled water was used for all the experiments. Different metal salts [NaNO₃, KNO₃, CdSO₄, FeCl₃, CoCl₂, NiCl₂, CuCl₂, ZnCl₂, CdCl₂, HgCl₂, Pb(NO₃)₂, NH₄NO₂, NaH₂PO₄, Na₂HPO₄, Na₃PO₄, Na₂CO₃, CH₃COONa, Na₂HCO₃] used in this study were purchased from Merck, India. All the metal salt solutions (10 mM) used for the experiments were prepared by mixing the requisite amount of salt in Double distilled water.

Preparation of citrate stabilized AgNPs. We have synthesized citrate capped AgNP by following Turkevich method.^{1,2} In a 250 mL conical flask, 100 mL aqueous solution of AgNO₃ (1.0×10^{-3} M) was heated under constant stirring condition. When it was beginning to boil, 2 mL sodium citrate solution (~3%) was added at once and the solution colour slowly turned into greyish yellow within a few seconds. Heating was continued for an additional 10 min, and then the solution was cooled to room temperature for further experiments.

Sensing and selective detection of As(III). A 10 mM As(III)/As(V) solution was prepared by dissolving NaAsO₂ in double distilled water followed by heat treatment at 50-60° C for 5 min and then 1 mM solution was prepared by dilution. For the colorimetric detection of arsenite/arsenate ion, 5-15 µL of sodium bicarbonate/nitrate/carbonate/phosphate was added initially to 1 ml of AgNPs solution followed by addition of As(III)/As(V) ion with few nano molar to micro molar range. The colorimetric changes as well as UV-vis spectroscopic study were recorded with time. Interference study carried out in presence of different cations and anions maintaining the final concentration 200 µM or 100 µM. The nitrocellulose membrane strip was used for paper-based sensing where the solutions was drop casted on the nitrocellulose membrane strip to see visual change in solid state.

The real water sample analysis: The real water samples were collected from three different natural basins (Kolkata region) — Ganga River, Pond and ground water. These three water

samples were first centrifuged at 10000 rpm for 5 min to remove any solid impurities followed by filtration by Whatman filter paper. The natural water samples were spiked with sodium arsenite solution at different concentration levels, which were then analyzed using UV-visible absorption technique. The amount of arsenic present spiked water samples was also measured by Optima 2100 DV (Perkin-Elmer) inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Instrumentation: UV-vis absorption spectra of all samples were measured in Shimadzu UV-1900i UV visible spectrometer using quartz cuvettes with a 1 cm path length. For transmission electron microscopy (TEM), samples were dried by putting a drop of particle dispersion on carbon coated copper grid and imaged under FEI Tecnai G2 F20 microscope. The zeta potential and hydrodynamic diameter of the AgNPs was determined by of zeta potential analyzer (NanoZS, Malvern instrument). The dynamic light scattering, DLS -zeta potential measurement done of the sample within 1 h of arsenite addition. The electrochemical measurements were performed using CHI660D electrochemical analyzer and the AgNP with or without arsenite/arsenate were dropcasted on glassy carbon electrode followed by drying at room temperature. Then 0.5 wt% nafion solution was dropcasted on it as electrode binder followed by room temperature drying and the cyclic voltammetry study performed in 0.1 M bicarbonate medium at 50 mV/s scan rate.

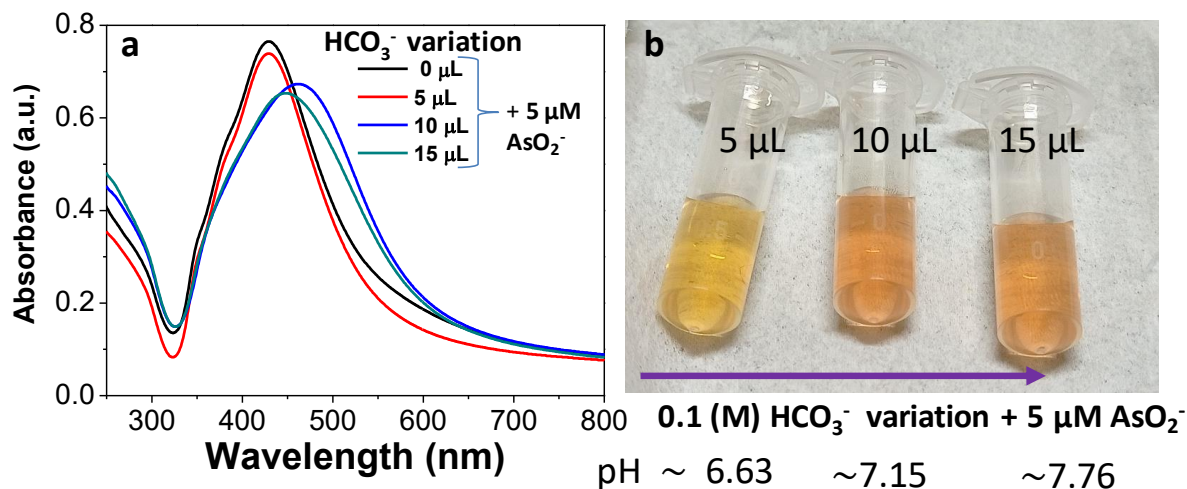


Figure S1. The UV-vis study for selection of appropriate amount of sodium bicarbonate using AgNPs towards sensing of $5 \mu\text{M}$ of arsenite ion (a) and corresponding digital images showing intense colour developed for $10 \mu\text{L}$ of 0.1 M bicarbonate ion within the time limit of 5 min.

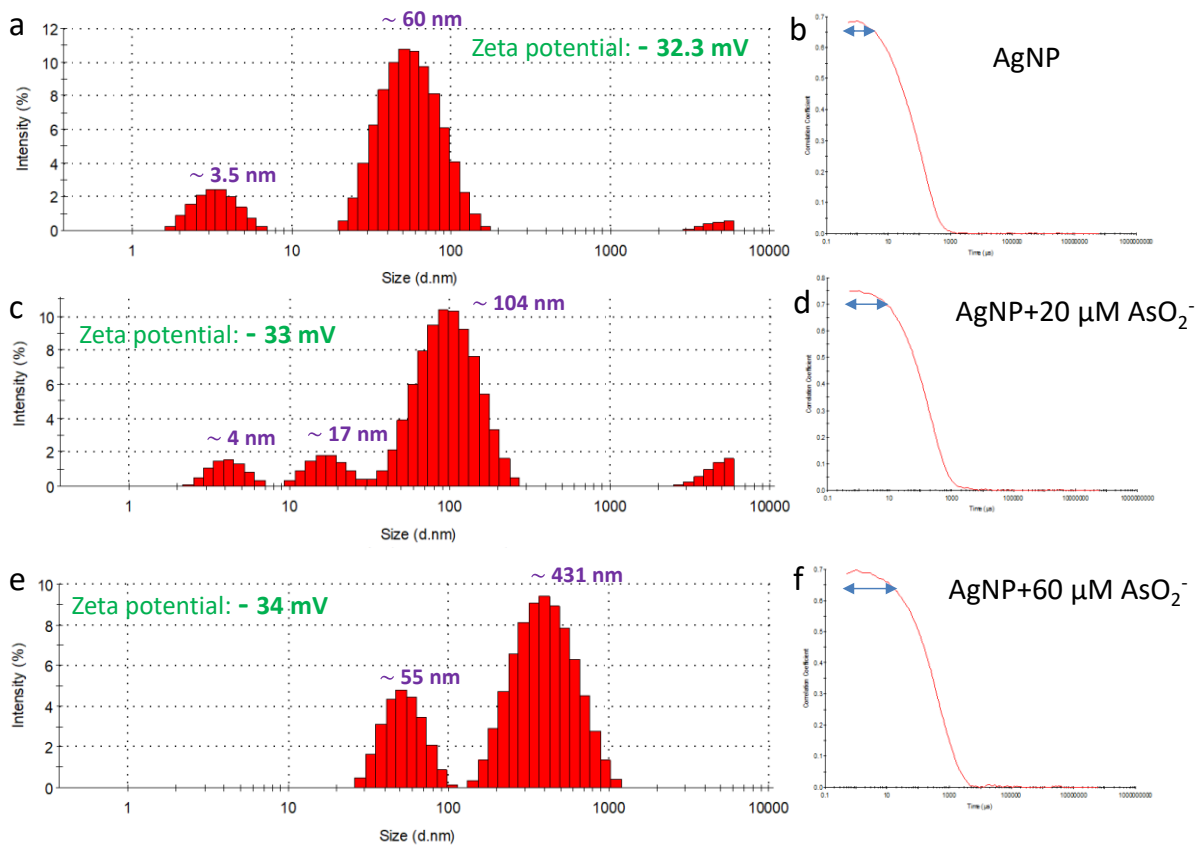


Figure S2. The intensity percentage dynamic light scattering histogram study and corresponding correlation diagram of AgNP in bicarbonate medium (a,b), after addition of $20 \mu\text{M AsO}_2^-$ (c,d) and $60 \mu\text{M AsO}_2^-$ ion (e,f). The intensity average mean diameter and zeta potential are shown on the figure and also time delay in figure (b,d,f) is shown by double headed arrow.

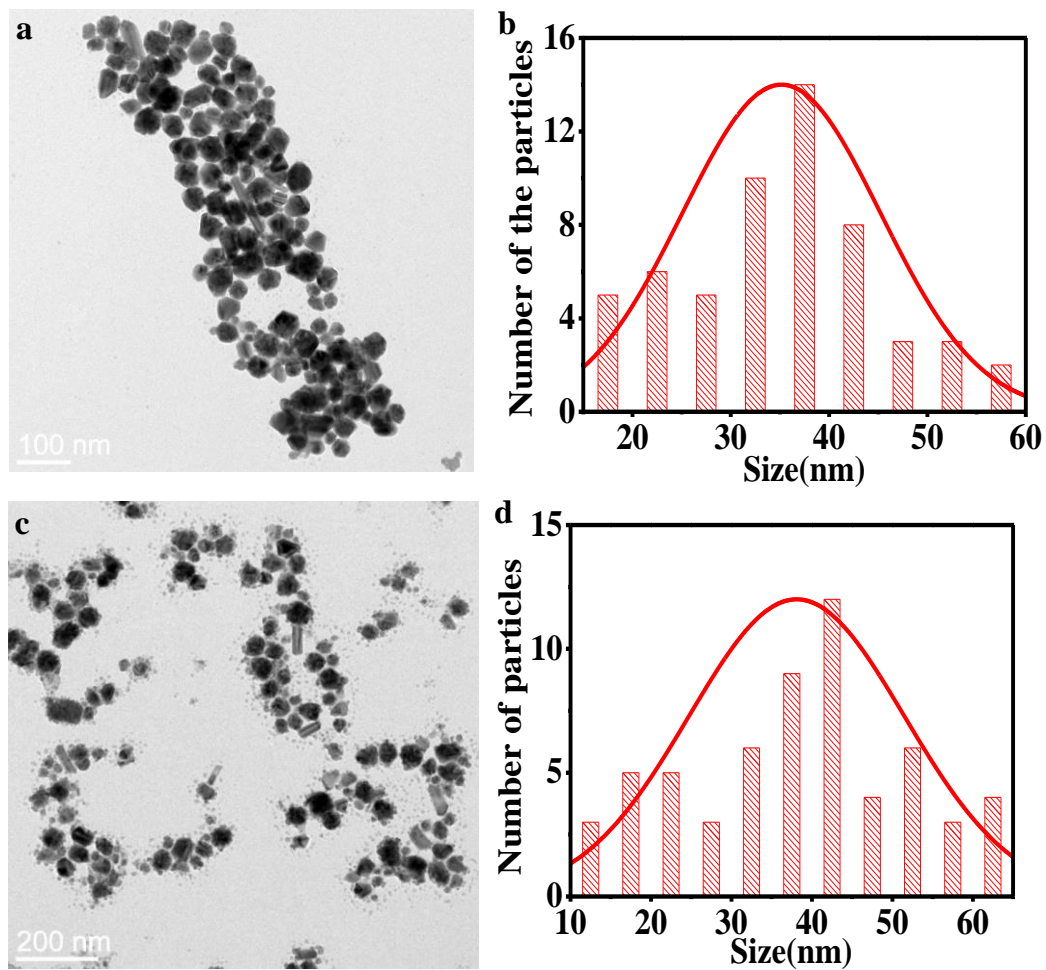


Figure S3. The TEM histogram study of AgNPs in bicarbonate medium without AsO_2^- addition and after addition of $20 \mu M$ of AsO_2^- ion.

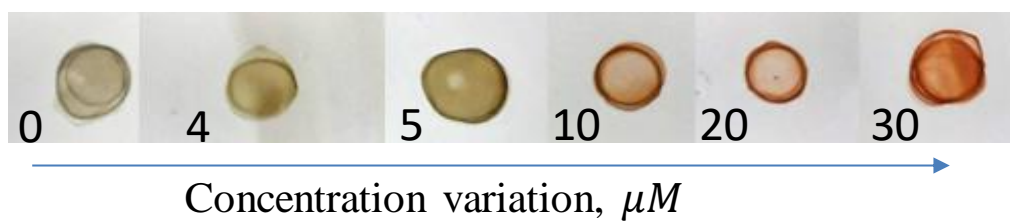


Figure S4. The paper based naked eye detection of AsO_2^- ion in the concentration range 0 to 30 μM .

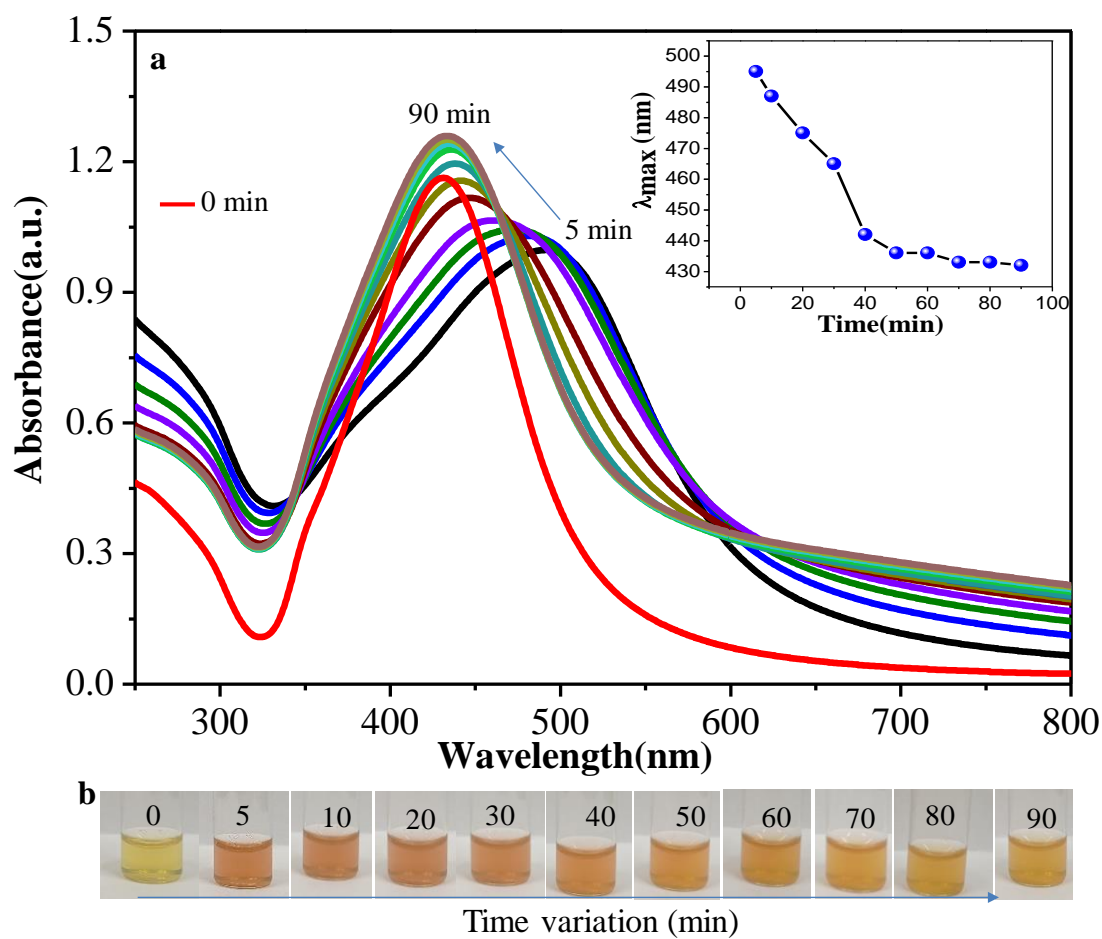


Figure S5. The UV-visible spectroscopic observation at different time interval after addition of 60 μM arsenite ion with inset picture showing the shifting in λ_{max} (a) and corresponding solution based colorimetric assay (b).

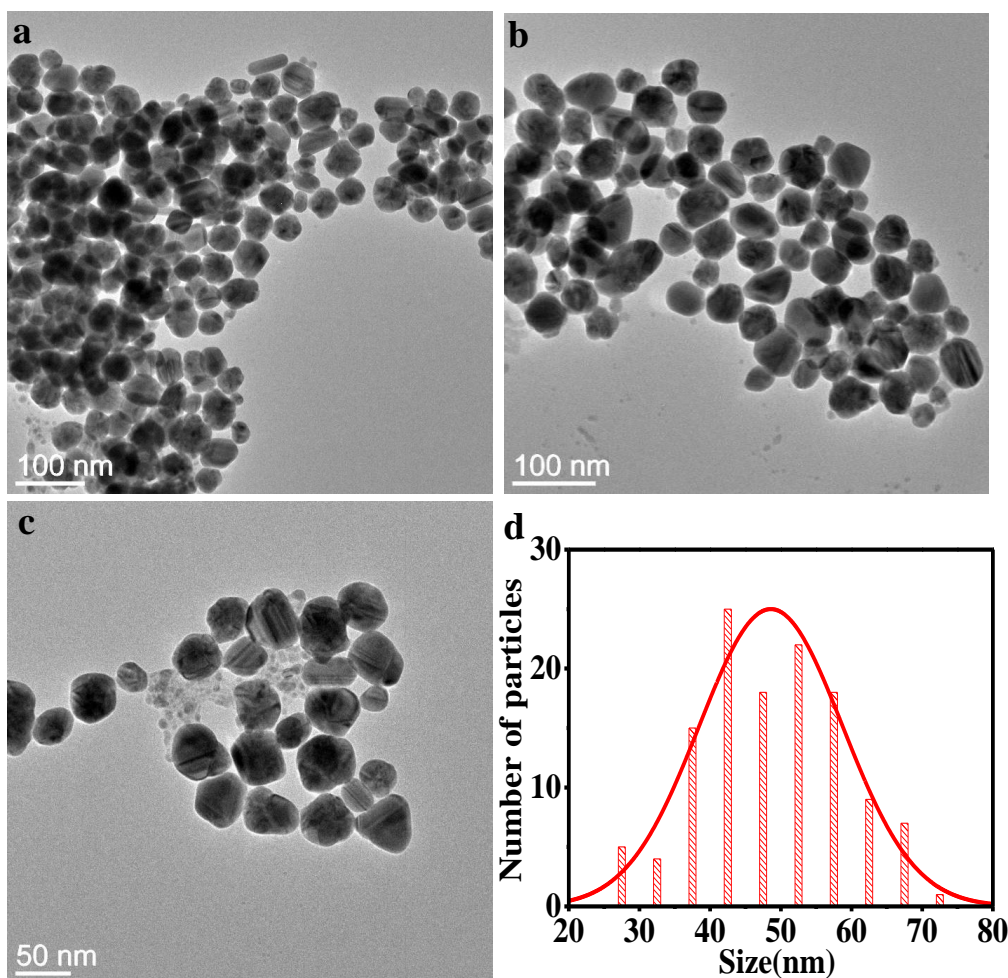


Figure S6. The TEM images of AgNPs in presence of $60 \mu\text{M}$ AsO_2^- ion at different magnifications (a,b,c) and corresponding size distribution histogram study (d). The sample dropcasted on carbon coated copper grid after almost after 1h of arsenite addition.

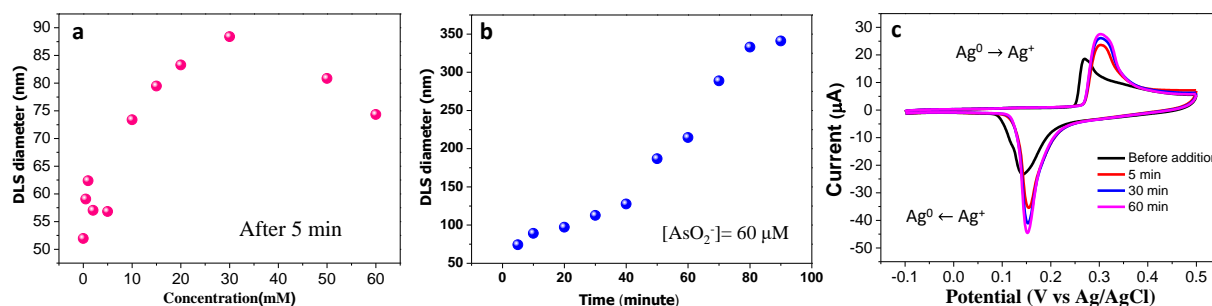


Figure S7. The hydrodynamic diameter of Ag NPs (based on intensity percentage) vs arsenite ion concentration keeping time constant (after 5 min) (a); size vs time keeping concentration fixed at $60 \mu\text{M}$ AsO_2^- (b) and corresponding cyclic voltammetry plot (c).

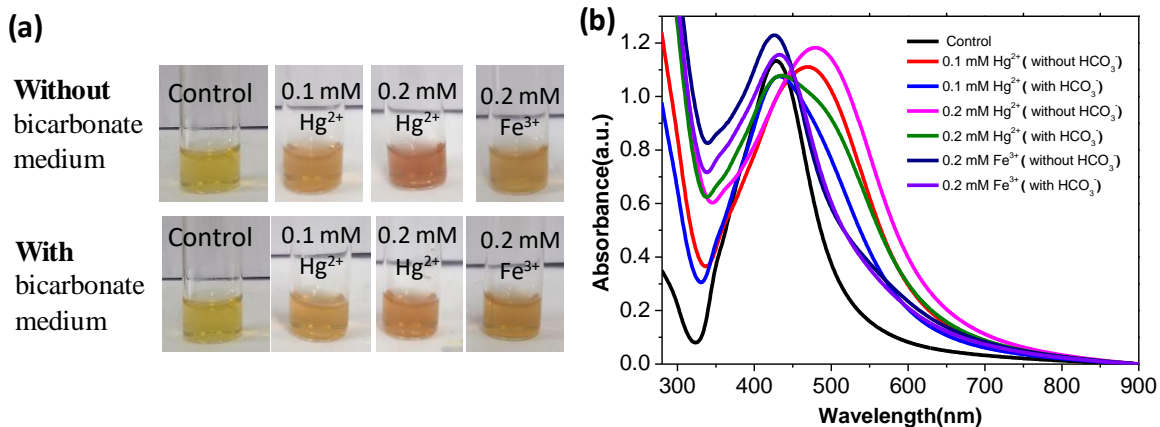


Figure S8. The digital images of interference study by Hg²⁺ ions and Fe³⁺ ions in the absence and presence of bicarbonate medium (a). Corresponding UV-visible spectra (b).

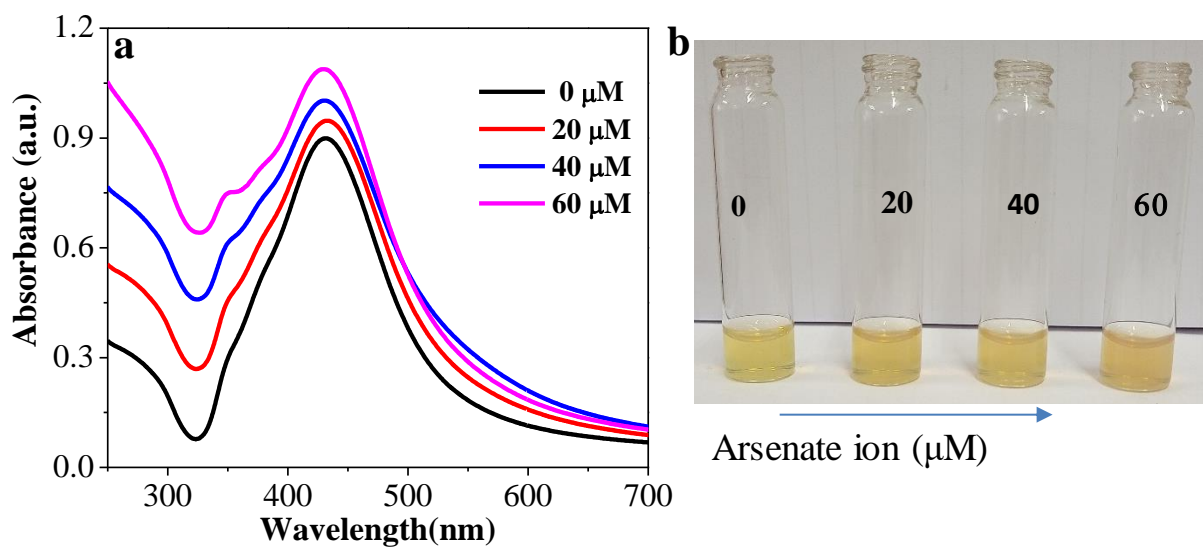


Figure S9. The UV-visible spectra of AgNPs in bicarbonate medium in presence of different concentration (20 to 60 μM) of AsO_4^{3-} ion.

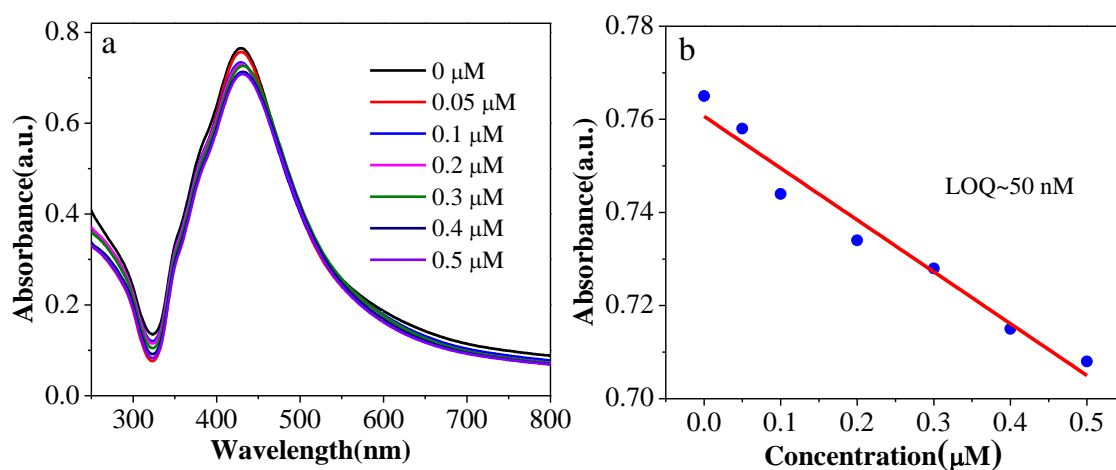


Figure S10. The nanomolar level sensing of arsenite ion by UV-vis spectroscopic study (a) and corresponding linear plot (b) with lower limit of quantification 50 nM (5.3 ppb) using diluted AgNP in bicarbonate medium.

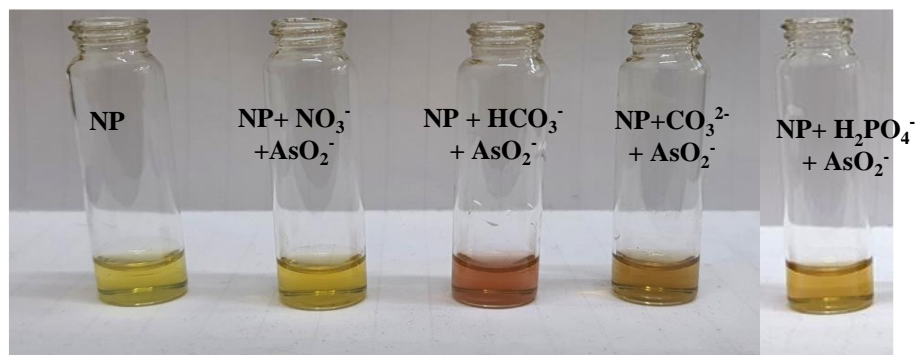


Figure S11. The selectivity of arsenite ion in bicarbonate medium compared to other medium (1 mM medium concentration and 20 μM arsenite ion used for every case)

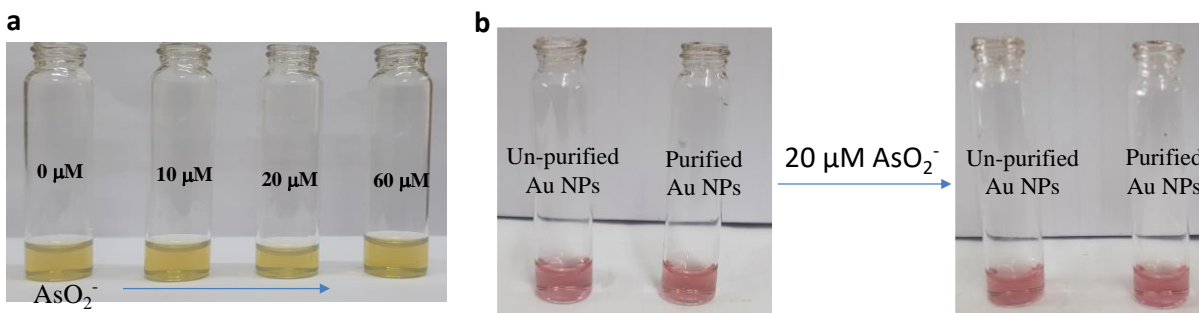


Figure S12. The colorimetric test for arsenite ion sensing using purified Ag NPs (a) and using Au NPs in bicarbonate medium (b). The purification done by high-speed centrifugation at 10000 rpm for 7 min.

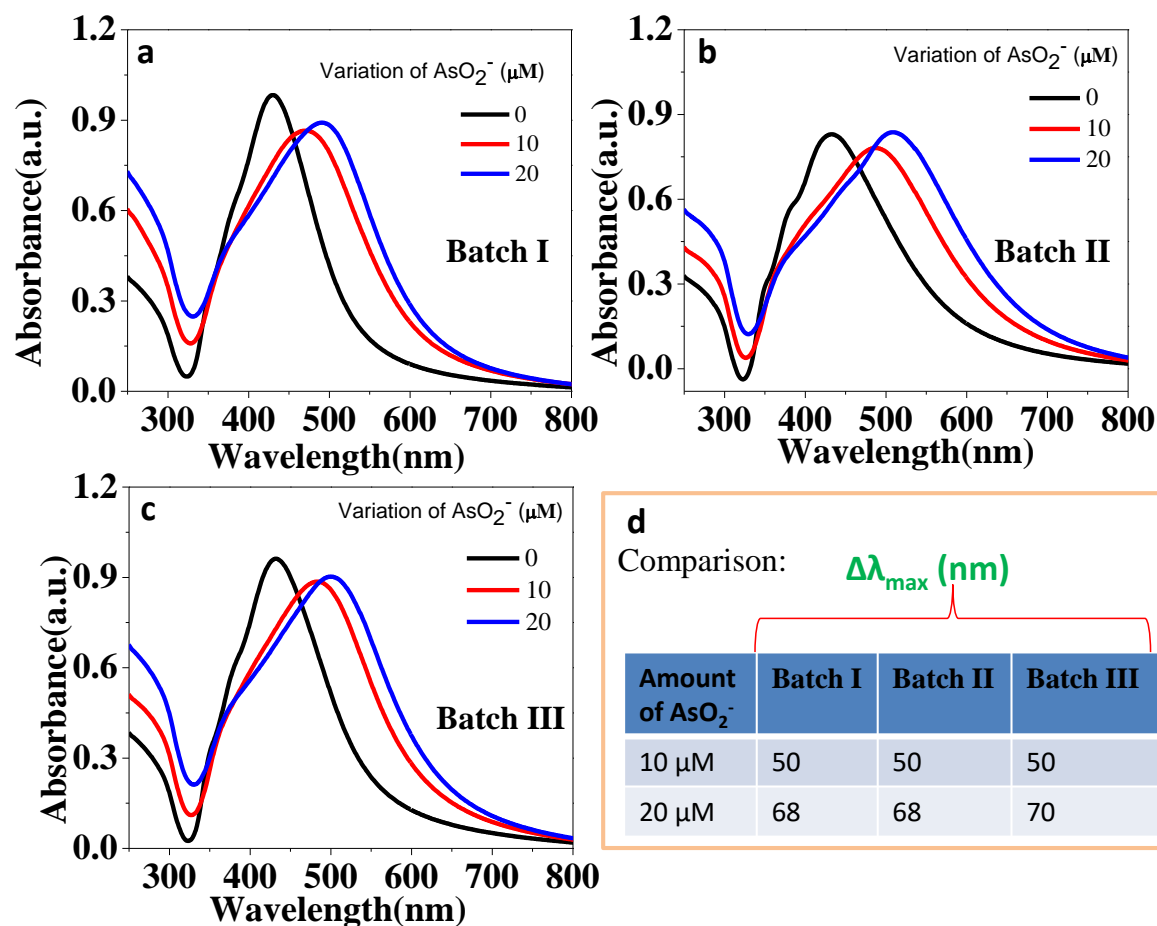


Figure S13. The UV-visible spectra of arsenite ion assay using three batch of Ag NPs which were prepared under similar condition (a,b,c) and a comparative table of change in λ_{max} with level of arsenite ion in various batch (d).

Table S1. A comparative table of different arsenic detection methods used in literature with this work.

Material	Detection Technique	Dynamic Range	Limit of Detection / Quantification	Reference
Aptamer based Au nanoparticle	colorimetric	1.0 – 100 ppb	16.9 ppb	3
Citrate stabilized Au nanoparticle	Enzymatic, colorimetric	10–11670 ppb	<0.01 mg/L	4
Gold nanorod	colorimetric	10–500 ppb	10 ppb	5
PlasmonicAgNPs	colorimetric	0.5-1000 ppb	0.005 ppm	6
PVP based silver nanoprisms(AgNPrs)	colorimetric SERS	0-1000 ppb	75 ppb	7
Multi-Ligands Modified Silver Nanoparticles	colorimetric	0.4-20 ppb	0.36 ppb	8
Aptamer based Au nanoparticle	colorimetric	75-750 ppb	161 ppb	9
Glucose Functionalised AuNP	colorimetric	20–500 ppb	5.6 ppb	10
AgNP	colorimetric	5.3-50 ppb 100 -2000 ppb	5.3 ppb	This work

Table S2: Analysis of AsO_2^- ion in real water samples.

Sample	COLORIMETRIC METHOD				ICP MEASUREMENT			
	Spiked As(III) [μ M]	Observed As(III) [μ M]	RSD(%)	Recovery(%)	Spiked As(III) [μ M]	Observed As(iii) [μ M]	RSD(%)	Recovery(%)
Tap Water	5	4.89	1.57	97.87	~	~		
	10	9.8	1.42	98	10	10.34	2.36	103.4
	15	14.9	0.47	99	15	15.63	2.9	104.2
River Water	5	4.86	2	97.2	~	~		
	10	9.75	1.79	97.5	10	10.72	4.9	107.2
	15	14.7	1.42	98	15	16.1	5	107.3
Pond Water	5	4.87	1.876	97.4	~	~		
	10	9.77	1.64	97.7	10	10.26	1.8	102.6
	15	14.96	0.188	99.7	15	15.41	1.9	102.7

$$[\text{Recovery (\%)}] = [(C_{\text{Found}} - C_{\text{Blank}})/C_{\text{Added}}] \times 100$$

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