Rosmarinic Acid-Capped Silver Nanoparticles for Colorimetric Detection of CN\(^{-}\) and Redox-Modulated Surface Reaction-Aided Detection of Cr(VI) in Water

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ABSTRACT: Rosmarinic acid-capped silver nanoparticles (Ro-AgNPs) were prepared and applied as a probe for selective colorimetric detection of cyanide (CN\(^{-}\)) and chromium(VI) [Cr(VI)] under different conditions in aqueous media. The carbon atom of CN\(^{-}\) interacts with the AgNPs, and the carbon atom donates electrons from the HOMO to the vacant orbitals of the coordinatively unsaturated surface atom (Ag\(^{0}\)). After donating electrons, CN\(^{-}\) attached onto the surface of the nanoparticles becomes very reactive and interacts with dissolved oxygen and generates reactive oxygen species (ROS) such as superoxide (O\(_{2}\)\(^{-}\)), singlet oxygen (\(^{1}O_{2}\)), and so forth. In this process, Ag\(^{0}\) oxidizes to Ag\(^{+}\) and combines with CN\(^{-}\) forming water-insoluble AgCN, and the ROS (O\(_{2}\)\(^{-}\)) formed reacts with Ag/Ag\(^{+}\) to form Ag\(_{2}\)O. The oxidation of Ag\(^{0}\) to Ag\(^{+}\) resulted in dissolution of AgNPs, which causes disappearance of the surface plasmon resonance band and color change from yellow to colorless. For detection of Cr(VI), ascorbic acid and CN\(^{-}\) were added first; the ascorbic acid replaced the rosmarinic acid and then reduced the added Cr(VI) to Cr(III), and, in this process, ascorbic acid was oxidized to dehydroascorbic acid, which moved away from the nanoparticles’ surface. CN\(^{-}\) then interacted with the surface Ag\(^{0}\) atom, got activated, and interacted with dissolved oxygen forming Ag\(^{+}\) and ROS, which then followed the same process as described for CN\(^{-}\) to form AgCN and Ag\(_{2}\)O with a color change. The limits of detection were found to be 0.01 and 0.03 \(\mu\)M for CN\(^{-}\) and Cr(VI), respectively. The material was also used for sensing CN\(^{-}\) and Cr(VI) in real samples, and the results obtained were satisfactory. For field application, agarose-based strips were prepared by immobilizing the nanoparticles onto the agarose film and successfully used for the detection of CN\(^{-}\) and Cr(VI) in water.

INTRODUCTION

The development of nanoparticles has made them to emerge as a wonderful material because of their fascinating properties and potential applications in various fields of sciences.\(^{1-5}\) In this context, metal nanoparticles such as gold and silver nanoparticles (AgNPs) are promising and have gained a lot of interest in recent years because of their application in sensing various analytes.\(^{6,7}\) These nanoparticles have one of the highest visible-region extinction coefficients with a red-wine color because of the surface plasmon resonance (SPR).\(^{8}\) This SPR band is very sensitive to the particle size, shape, and interparticle distances, and, in the presence of any ion, can effectively interact with the nanoparticles; a transition of state from dispersion to aggregation may take place exhibiting a distinct color change because of the coupling of plasmon absorbance.\(^{9}\) This color change along with absorption spectral change can be used as a tool to monitor the ion recognition event and that is the reason why the metal nanoparticles are emerging as important colorimetric sensors for various cations and anions.\(^{10,11}\) To use them as a probe, the nanoparticles are subjected to functionalize with a capping agent, which can covalently link with the surface of nanoparticles and can also interact with the incoming ion(s).\(^{12,13}\)

The objective of the present study is to develop a functionalized AgNP-based sensor for selective recognition of toxic ions in the environment because of their adverse effects on human health.\(^{14}\) Among various toxic ions, cyanide (CN\(^{-}\)) is one of the most health-hazardous anion, which, on exposure to human beings, deactivates oxygen transport in the human body by binding to the active sites of cytochrome c oxidase, causing deleterious effects on the central nervous system and respiratory system.\(^{15,16}\) Along with cyanide, hexavalent chromium (Cr\(_{2}O_{7}^{2-}\)) is another most prevalent toxic metal...
ion, which is known to cause hemolysis, cancer, and various genetic defects, posing serious threat to mankind. For cyanide, the maximum permissible limit in drinking water set by the world health organization (WHO) is 1.9 μM, and for chromium(VI), it is 50 μM. The extensive use of these ions in various industrial processes, such as electroplating, mining, tanning, and steel manufacturing, increases the risk of contamination in underground as well as surface water resources. It is therefore necessary to develop systems, which can selectively detect cyanide and chromium(VI) over a wide range of concentrations in aqueous media.

There are analytical methods such as titrimetry, potentiometry, electrochemical analysis, chromatography, voltammetry, and so forth, which have been used for the detection of these anions. However, these methods require expensive equipment and skilled analytical personnel; in some cases, they are time consuming and the limit of detection (LOD) is also a matter of concern for a few techniques. For this reason, optical sensors, especially colorimetric sensors, are receiving increasing attention as they facilitate naked eye detection and are relatively simple and highly sensitive. Colorimetric sensors of designed discrete molecules, however, often require a complicated synthetic procedure, and sometimes it is too expensive. As an alternative, the use of metal nanoparticles, especially gold and AgNPs, has drawn much attention, as it is easy to use, detectable by the naked eye, and highly sensitive. AgNPs, however, are becoming more popular compared to gold nanoparticles because of their low cost without compromising the performance. It has been noted that, in recent times, functionalized AgNPs are being used for the selective detection of cyanide as well as chromium(VI) in aqueous media. However, there is no report on whether AgNPs are used for the selective detection of cyanide as well as chromium(VI) simultaneously.

Herein, we report the preparation of rosarinic acid-capped AgNPs (Ro-AgNPs) to use them as a probe for detection of toxic analytes. Rosarinic acid, shown in Figure S1 (Supporting Information), contains hydroxyl groups attached to adjacent carbon atoms of the benzene rings at both the ends. Rosarinic acid could be anchored onto the surface of the nanoparticles through these OH groups. Ro-AgNPs thus prepared exhibit selective detection of cyanide in aqueous media out of a large number of anions tested; it also detects chromium(VI) selectively in aqueous media when ascorbic acid was added in the presence of cyanide ahead of addition of Cr₂O₇⁻². The mechanism of detection is quite interesting, and a redox-modulated surface reaction is involved in the detection of Cr(VI): otherwise, Ro-AgNPs cannot detect Cr(VI) following the same method as used for CN⁻. In both the cases, the color of the solution changed from yellow to colorless, and the dissolved oxygen played a crucial role in this process. Agarose-based testing strips were also prepared by immobilizing the Ro-AgNPs onto the agarose film, and the portable colorimetric sensor thus developed can be used for easy on-site monitoring of cyanide and chromium(VI) in aqueous media. Practical applicability of this sensor for detection of CN⁻ and Cr(VI) in real water samples was also examined, and the results are reported herein.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization of Ro-AgNPs.** Ro-AgNPs were synthesized at room temperature using sodium borohydride as the reducing agent, as shown in Scheme 1. In order to find out the optimum concentration of rosarinic acid required for maximum capping and stabilization of Ro-AgNPs, experiments were carried out with varying molar ratios of AgNO₃/rosarinic acid (1:0.25, 1:0.5, 1:1, 1:2, 1:3, and 1:4) following the procedure described in the Materials and Methods Section. The UV−vis spectra (SPR band) for all the experiments were recorded and are shown in Figure S2 (Supporting Information). The figure shows that the intensity of the SPR band at 405 nm gradually increases with the increasing concentration of rosarinic acid and shows the maximum intensity with a AgNO₃/rosarinic acid ratio of 1:3; then, it again decreases with the increasing concentration of rosarinic acid. This observation suggests that a AgNO₃/rosarinic acid ratio of 1:3 is the optimum condition for capping experiments, and the same has been followed subsequently for the preparation of Ro-AgNPs. The capping of rosarinic acid onto the surface of the AgNPs was confirmed from IR spectra; the IR spectrum of rosarinic acid and that of Ro-AgNPs in the solid state are shown in Figure S3 (Supporting Information). The IR bands of ν(OH), ν(C=O), and ν(C−N) of rosarinic acid are also observed in the IR spectrum of Ro-AgNPs at 3443, 1633, and 1397 cm⁻¹, respectively. Some shift in the band position for Ro-AgNPs is due to the interaction of the functional groups of the rosarinic acid with nanoparticles, trapped water, and also intermolecular interaction.

The presence of different elements and functional groups was confirmed by X-ray photoelectron spectroscopy (XPS) analysis. The XPS spectra of Ro-AgNPs are shown in Figure 1, which exhibit major binding energy peaks at 285.1 and 532.1 eV, due to C and O, respectively. The moderate intensity peaks observed at 368.1 and 273.9 eV (Figure 1b) are due to Ag 3d₃/₂ and Ag 3d₅/₂, respectively. The high-resolution expanded spectrum of O 1s (Figure 1c) exhibits a peak at 531.8 eV and a small peak at 535.8 eV, which are attributed to C=O and C−O−C/C=OOH, respectively. The expanded peak of C 1s (Figure 1d) exhibits a strong peak at 284.7 and a weak peak at 288.3 eV, which are assigned to C=O and C=O, respectively. XPS analysis, therefore, confirmed the presence of Ag and various functional groups containing carbon and oxygen.

The UV−visible spectrum of Ro-AgNPs exhibits a SPR band at 405 nm (Figure 2a), which is the characteristic absorption band for the AgNPs. The transmission electron microscopy (TEM) image of the Ro-AgNPs (Figure 2a) exhibits well-dispersed particles of almost spherical shape with an average size of 2−5 nm. High magnification of one of the particles showed highly ordered lattice fringes with a lattice spacing of 0.236 nm (Figure 2b), which corresponds to the (111) plane of silver. The powder X-ray diffraction pattern of Ro-AgNPs (Figure 3) obtained after drying the sample shows four distinct peaks with 2θ values of 38.0, 44.2, 64.5, and 77.4°, which correspond to the (111), (200), (220), and (311) planes of the cerium oxide.
face-centered cubic (fcc) silver, which is in well agreement with the reference unit cell (JCPDS no. 870718). The stability of Ro-AgNPs in the pH range 2–12 was examined; the bar diagram depicting the plot of the absorbance of the SPR band at 405 nm as a function of pH (Figure S4, Supporting Information) shows that there is no significant change in absorbance in the studied pH range 4–12. The observation, therefore, suggests that rosmarinic acid served as an excellent capping agent imparting stability to the AgNPs.

**Anion Sensing Property of Ro-AgNPs.** For the detection of anions, initially, the pH and the incubation time of the reaction for the best result were examined. Detection of anions was monitored with the aid of UV–visible spectral changes as a function of pH in the range 2–12. The experiment was carried out with variation in pH taking CN$^-$ as an example; the bar diagram showing the plot of absorbance at 405 nm against pH (Figure S5, Supporting Information) shows that the variation in absorbance at different pHs is not significant; therefore, experiments were conducted at the natural pH of water (7.0). To determine the incubation time, the absorbance of Ro-AgNPs at different concentrations of CN$^-$ (5, 20, 60, 120, and 240 μM) was recorded as a function of time from 0 to 30 min, and the absorbance at 405 nm for each concentration of CN$^-$ was plotted against time, as shown in Figure S6 (Supporting Information). It may be noted in the figure that the maximum change in absorbance is observed within 6 min, which is therefore considered as the incubation time, and all the experiments were carried out at the natural pH of water and an incubation time of 6 min.

After determination of the optimum experimental conditions, the anion-sensing property of Ro-AgNPs was investigated following the method described in the Materials and Methods section with the anions OH$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, CH$_3$COO$^-$, HPO$_4^{2-}$, H$_2$PO$_4^-$, NO$_3^-$, HSO$_4^-$, and CN$^-$ in

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**Figure 1.** (a) XPS survey spectrum of Ro-AgNPs and (b–d) high-resolution expanded spectra of (b) Ag 3d, (c) O 1s, and (d) C 1s showing the assignment of peaks.

**Figure 2.** TEM image of Ro-AgNPs and their UV–visible absorption spectra (inset image). (b) Typical HRTEM image of a single Ro-AgNP particle.

**Figure 3.** Powder XRD diffractogram of the synthesized Ro-AgNPs.
aqueous media. The UV−vis spectra of the resulting solution upon addition of anions were recorded after incubation of 6 min, and the spectral changes are shown in Figure 4. It may be noted in the figure that for CN⁻, the SPR band of Ro-AgNPs almost disappeared, and the color of the solution changed from yellow to colorless, as shown in the inset of Figure 4. However, for other anions, no appreciable change in the SPR band is observed, except iodide, which exhibited a significant decrease in intensity with a slight red shift without any change in color, suggesting that I⁻ also interacts considerably with Ro-AgNPs. The interaction of Cr₂O₇²⁻ with Ro-AgNPs has not been conducted with the series of anions mentioned above because Cr₂O₇²⁻ has a strong absorption band close to the SPR band of Ro-AgNPs, and the solution of Cr₂O₇²⁻ is also highly colored, so no color change due to their interaction is expected to be visible. However, a separate experiment was conducted with Cr₂O₇²⁻ under similar experimental conditions, and the spectra, shown in Figure S7 (Supporting Information), show a well resolved shoulder around 405 nm and the position of the SPR band, with the absorption intensity close to that of the SPR band, indicating no or very weak interaction of it with the Ro-AgNPs.

**Interference Study with Competing Anions.** The interference study with all the competing anions was also carried out following the procedure described in the Materials and Methods Section, and the bar diagram plotting the change in absorbance (ΔA₄₀₅ nm), corresponding to all the competing anions studied, is shown in Figure 5. It exhibits no significant variation in absorbance, which suggests that no considerable interference from any competing anions has taken place. In the case of I⁻, the intensity of the SPR band decreased considerably when 2 mM solution was used (Figure 4); however, at lower concentrations (in μM), no significant change was noted (Figure 5). The concentration of I⁻ in natural water samples is very low, so it may not affect the detection of CN⁻ seriously. The results, therefore, suggests that Ro-AgNPs can be used for the selective detection of CN⁻ in aqueous media.

**Titration and LOD Determination for CN⁻.** To determine the LOD for CN⁻, the titration experiments were carried out upon incremental addition of cyanide with the concentration ranging from 0 to 400 μM. As shown in Figure 6, incremental addition of CN⁻ leads to a concomitant decrease in the absorbance intensity at 405 nm and finally it disappeared. The inset (a) of Figure 6 shows the change in absorbance (A₀ − A) at 405 nm as a function of concentration of cyanide, while the inset (b) shows the color change of Ro-AgNPs upon incremental addition of cyanide. The LOD value of 0.01 μM. The LOD found is lower than the concentration of CN⁻ permissible in drinking water, set by the USEPA and WHO. The LOD obtained in the present study is compared to some of the recently reported LOD values of similar systems (Table 1), and it is noted that the LOD of the present system is comparable to or even better than many other reported values.

**Detection of Cr₂O₇²⁻/Cr(VI) Using Ro-AgNPs.** In order to explore the applicability of the system further, the redox-modulated surface chemistry concept was utilized to make the Ro-AgNPs eligible for detection of Cr(VI). For this purpose, ascorbic acid was added in the presence of CN⁻, followed by the addition of Cr₂O₇²⁻, which resulted in a color change from yellow to colorless. After addition of ascorbic acid, the SPR band shifted slightly to 412 nm; the UV−vis spectrum, color of

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**Figure 4.** UV−visible spectral change of RO-AgNPs (at 405 nm) in the presence of 11 different anions (2 mM, 1 mL) and the corresponding color change shown as the inset.

**Figure 5.** Change in the absorbance of Ro-AgNPs (ΔA₄₀₅ nm) upon addition of cyanide (100 μM, 2 mM) in the presence of 10 equiv of other anions (1 mL, 2 mM).

**Figure 6.** Change in the UV−visible spectra upon incremental addition of cyanide (0−400 μM). The inset (a) shows the plot of change in absorbance (A₀ − A) at 405 nm as a function of concentration of cyanide, while the inset (b) shows the color change of Ro-AgNPs upon incremental addition of cyanide.
some of the recent reports using silver nanoparticles for sensing of CN⁻

| probe               | method          | LOD (µM) | linear range (µM) | reference |
|---------------------|-----------------|----------|-------------------|-----------|
| PFS-AgNPs           | fluorescence    | 0.25     | 0.5—600           | 48        |
| SDS-AgNPs           | colorimetric    | 1.8      | 16.7—133.3        | 49        |
| Au@Ag core shell NPs| colorimetric    | 0.4      | 0.4—100           | 50        |
| AgNPs               | electrochemical | 0.068    | 14—40             | 63        |
| Cds@AgNPs           | fluorescence    | 5.17     | 12.3—61.9         | 64        |
| QDs@AgNPs           | fluorescence    | 0.004    | 0.01—2.5          | 65        |
| Ag/Fe₃O₄ NPs        | Rayleigh scattering | 0.0015 | 0.13—60          | 66        |
| Au@AgNC₃@ew         | fluorescence    | 0.138    | 0.2—10            | 67        |
| Ag@Au core shell Ir complex | fluorescence | 0.036  | 0.05—80           | 68        |
| Ro-AgNPs            | colorimetric    | 0.01     | 0.01—90          | this work |

For conducting the sensing experiment with anions, initially, the optimum conditions with respect to the concentrations of ascorbic acid and incubation time were checked following the procedure described above for CN⁻. Experiments with ascorbic acid of concentrations 5, 10, 20, 40, 60, 80, and 100 mM revealed the optimum concentration of 20 mM for best results (Figure S9, Supporting Information). For the determination of incubation time, the UV—visible absorption spectrum showing absorption maxima at 412 nm (inset image).

![Figure 7. TEM image of Ro-AgNPs + ascorbic acid and its UV—visible absorption spectrum showing absorption maxima at 412 nm (inset image).](image)

Figure 7. TEM image of Ro-AgNPs + ascorbic acid and its UV—visible absorption spectrum showing absorption maxima at 412 nm (inset image).

The ion sensing property of the ascorbic acid-aided surface-modified Ro-AgNPs was examined with anions such as OH⁻, F⁻, Cl⁻, Br⁻, I⁻, CH₂COO⁻, HPO₄²⁻, H₂PO₄⁻, NO₃⁻, HSO₄⁻, and Cr₂O₇²⁻ following the procedure described in the Materials and Methods Section, and the spectral changes are shown in Figure 8. It may be noted in the figure that the absorption intensity of the SPR band at 412 nm is reduced substantially in the case of Cr₂O₇²⁻; it is also reduced considerably in the presence of I⁻, but for other anions, no significant change in absorption intensity is noted. The observation suggests that the surface-modified Ro-AgNPs interact strongly with Cr₂O₇²⁻/Cr(VI) with a sharp color change from yellow to colorless, as shown in the inset of Figure 8. For I⁻ and for other anions, however, no color change was noted (inset, Figure 8), suggesting that surface-modified Ro-AgNPs are suitable for the colorimetric detection of Cr₂O₇²⁻ selectively. An interference study with the competing anions was also carried out, and the bar diagram, shown in Figure S11 (Supporting Information), reveals that no significant interference is evident from any of the competing anions. This indicates that the ascorbic acid-modified Ro-AgNPs system served as a selective probe for Cr(VI) detection.

### Determination of LOD for Cr(VI).
To determine the LOD for Cr(VI), the titration study of the surface-modified Ro-AgNPs was performed by incremental addition of Cr(VI) in the concentration range of 0—55 µM following the method described above for CN⁻. The UV—visible spectral change with incremental addition of Cr₂O₇²⁻ is shown in Figure 9, and the plot of change in absorbance (Aₐ — A) at 412 nm as a function of the concentration of Cr(VI) is shown as inset (a) of Figure 9.

![Figure 8. UV—visible spectral change of (RO-AgNPs + AA + CN⁻) in the presence of 11 different anions (2 mM, 1 mL) and the corresponding color change shown in the inset; AA = ascorbic acid.](image)

Figure 8. UV—visible spectral change of (RO-AgNPs + AA + CN⁻) in the presence of 11 different anions (2 mM, 1 mL) and the corresponding color change shown in the inset; AA = ascorbic acid.

![Figure 9. Change in the UV—visible spectra upon incremental addition of Cr(VI) (0—30 µM). The inset (a) shows the plot of change in absorbance (Aₐ — A) at 412 nm as a function of concentration of Cr(VI), while the inset (b) shows the color change of Ro-AgNPs + AA+CN⁻ upon incremental addition of Cr(VI); AA = ascorbic acid.](image)

Figure 9. Change in the UV—visible spectra upon incremental addition of Cr(VI) (0—30 µM). The inset (a) shows the plot of change in absorbance (Aₐ — A) at 412 nm as a function of concentration of Cr(VI), while the inset (b) shows the color change of Ro-AgNPs + AA+CN⁻ upon incremental addition of Cr(VI); AA = ascorbic acid.
9 (R² = 0.994), and the corresponding color change from yellow to colorless is also shown as inset (b). The plot of the change in absorbance against the concentration of Cr(VI) is shown with magnification in Figure S12 (Supporting Information), which shows the minimum detectable concentration of 0.04 μM. The LOD obtained is compared with the values of a number of recently reported nanoparticle-based Cr(VI) sensors (Table 2), and it is noted that the LOD of the present study is lower than or comparable with those of many other reported systems. It is also lower than the permissible limit of Cr(VI) in drinking water, stated in the USEPA guidelines.69

Mechanistic Aspect of CN⁻ and Cr(VI) Detection. It is well documented in the literature that CN⁻ is capable of dissolving Au/Ag NPs in water in the presence of oxygen.77−80 In general, the nanoparticles were used to stabilize by functionalizing their surfaces with various functional groups/molecules; in this case, it is rosmarinic acid. Even after functionalization, there are plenty of atoms on the surface of the AgNPs, which are coordinatively unsaturated having unoccupied orbitals and can accept electrons from a nucleophilic agent such as CN⁻.41,81 The MO diagram of CN⁻ shows that the electrons in the HOMO are from the Ag⁺; it is evident from the fact that the intensity of the SPR band/shoulder appeared, which eliminated the possibility of coordination of Cr(VI), and ascorbic acid was oxidized to dehydroascorbic acid, which creates the loss of interaction with the surface of the AgNPs. Then, the CN⁻ interacted with the silver atoms on the surface of the AgNPs and was activated after donation of electrons to the coordinatively unsaturated surface atom, and it reacted with dissolved oxygen to form ROS. The rest of the process is same as described above for CN⁻, and the color of the solution changed from yellow to colorless. It may be noted that for both the CN⁻ and Cr(VI), the changes in UV−vis spectra are similar, which indicated that the reactions involved in the detection of both the ions are similar. Moreover, the SPR band slowly disappeared with progress of the reaction and no new band/shoulder appeared, which eliminated the possibility of aggregation and suggested only the dissolution of the AgNPs.86 The gradual disappearance of the SPR band and color change from yellow to colorless are due to oxidation of Ag⁺ of AgNPs to Ag²⁺; it is evident from the fact that the intensity of the SPR band decreases with the progress of the reaction, and λmax exhibited a slight red-shift due to oxidation of silver, which supports the proposed mechanism. The TEM images of Ro-AgNPs recorded at different concentrations of cyanide (20, 60, and 120 μM) and Cr(VI) (40, 80 μM) are shown in Figures 11 and S13 (Supporting Information), respectively, which are in good accordance with the proposed mechanism.

Table 2. Comparison of LOD Obtained for Cr(VI) with That of Some Other Recently Reported Values Using Silver Nanoparticles for Cr(VI) Sensing

| probe          | method       | LOD (μM) | linear range (μM) | reference |
|----------------|--------------|----------|-------------------|-----------|
| PVP-AgNPs     | colorimetric | 0.034    | 0.1−2.4           | 51        |
| AA-AgNPs      | colorimetric | 0.05     | 0.07−1.84         | 52        |
| PEI-AgNCs     | colorimetric | 1.1      | 5−100             | 70        |
| AgNPs         | colorimetric | 1.0      | 1.0−1.0×10⁵       | 71        |
| AgNPs-BPQ     | voltammetric | 2.0×10⁻⁶ | 0.01−1.0          | 72        |
| SA-AgNPs      | SERS         | 0.001    | 0.0017−0.171      | 73        |
| AgNPs         | colorimetric | 0.001    | 0.03−5×10⁴        | 74        |
| PEI-AgNCs     | fluorescence | 0.00004  | 0.0001−3.0        | 75        |
| PANI-AgNPs    | fluorescence | 6.5      | 10−7.5×10⁷        | 76        |
| Ro-AgNPs      | colorimetric | 0.04     | 0.04−30           | this work |

412 nm (Figures 2 and 7). When Cr(VI) was added, the ascorbic acid, being a strong reducing agent, reduced Cr(VI) to Cr(III), and ascorbic acid was oxidized to dehydroascorbic acid and moved away from the surface of the AgNPs due to the oxidation of the −OH group to =O, the proton, which causes the loss of interaction with the surface of the AgNPs. Then, the CN⁻ interacted with the silver atoms on the surface of the AgNPs and was activated after donation of electrons to the coordinatively unsaturated surface atom, and it reacted with dissolved oxygen to form ROS. The rest of the process is same as described above for CN⁻, and the color of the solution changed from yellow to colorless. It may be noted that for both the CN⁻ and Cr(VI), the changes in UV−vis spectra are similar, which indicated that the reactions involved in the detection of both the ions are similar. Moreover, the SPR band slowly disappeared with progress of the reaction and no new band/shoulder appeared, which eliminated the possibility of aggregation and suggested only the dissolution of the AgNPs.86 The gradual disappearance of the SPR band and color change from yellow to colorless are due to oxidation of Ag⁺ of AgNPs to Ag²⁺; it is evident from the fact that the intensity of the SPR band decreases with the progress of the reaction, and λmax exhibited a slight red-shift due to oxidation of silver, which supports the proposed mechanism. The TEM images of Ro-AgNPs recorded at different concentrations of cyanide (20, 60, and 120 μM) and Cr(VI) (40, 80 μM) are shown in Figures 11 and S13 (Supporting Information), respectively, which are in good accordance with the proposed mechanism.

Figure 10. Schematic diagram showing the mechanism of sensing of CN⁻ and Cr(VI).

Figure 11. TEM images of RO-AgNPs at different concentrations of cyanide (A) 20, (B) 60, and (C) 120 μM.
APPLICATION

Determination of CN$^-$ and Cr(VI) in Real Samples. In order to examine the practical applicability of Ro-AgNPs, analysis of CN$^-$ and Cr(VI) was carried out with tap and drinking water samples, collected from the institute. The analysis of the collected samples by inductively coupled plasma-mass spectrometry (ICP-MS) revealed that there is no detectable amount of CN$^-$ and Cr(VI) in these samples; therefore, known amounts of CN$^-$ and Cr(VI) were added into the drinking and tap water, and it was treated as unknown samples. The amounts of CN$^-$ and Cr(VI) in these samples were then determined experimentally following the method described in the Materials and Methods section, and the standard graphs used for calculation of the amount are shown in Figure 12. The amount of CN$^-$ and Cr(VI) salt used for spiking and the corresponding amount obtained experimentally are shown in Table 3, and the data show that the % recovery is satisfactory. The results therefore suggest that the new material (Ro-AgNPs) developed has potential for application to detect and determine the concentrations of CN$^-$ and Cr(VI) in environmental samples.

Ro-AgNP-Embedded Agarose Test Strips as a Portable Sensor. With the aim to develop a portable sensor for easy application and detection of CN$^-$ and Cr(VI) in the field for environmental samples, agarose-based test strips were prepared following the procedure described in the Materials and Methods section. As test samples, a set of aqueous solutions of different concentrations (1, 10, 20, and 60 μM) of CN$^-$ and Cr(VI) were prepared using drinking water.

The agarose-based test strips prepared were then immersed in the solutions of the test samples of CN$^-$ and Cr(VI) and kept for 10 min, and the visual change in the color of the films was noted after air drying the strips for 5 min. The strips before (as blank) and after treatment with solutions of different concentrations of CN$^-$ and Cr(VI) are shown in Figure 13a, b, which exhibits a clear visual color change from yellow to colorless, detectable at a concentration of 1.0 μM for both CN$^-$ and Cr(VI) and almost colorless at a concentration of 60 μM. The agarose-based test strips developed, therefore, can be used in the laboratory as well as in the field for detection of CN$^-$ and Cr(VI) in water.

CONCLUSIONS

Ro-AgNPs were prepared and applied as a colorimetric probe for the detection of CN$^-$ and Cr(VI) in aqueous media. It detects CN$^-$ directly with color change from yellow to colorless; however, Cr(VI) cannot be detected using the same method. For detection of Cr(VI), ascorbic acid was added in the presence of CN$^-$, followed by the addition of Cr$_2$O$_7^{2-}$, which resulted in a similar color change as noted for CN$^-$.

A mechanistic study revealed that a CN$^-$-mediated redox reaction occurred on the surface of the nanoparticles, which reduced dissolved oxygen into ROS (O$_2$ to O$_2^*$ etc.) and oxidized silver (Ag$^+$) to Ag$^*$. The Ag$^*$ thus formed combined with CN$^-$ to form AgCN and also with O$_2^*$ forming AgO$_3$, and this destruction of nanoparticles (Ag$^*$) caused a color change from yellow to colorless with disappearance of the SPR band. In the case of Cr(VI), the added ascorbic acid was anchored on the surface of the AgNPs replacing the rosmarinic acid at least partially, and when Cr(VI) was added, ascorbic acid reduced Cr(VI) to Cr(III) oxidizing itself to dehydroascorbic acid and moved away from the surface of the nanoparticles, as the protons which cause the interaction with the nanoparticles is lost. Then, CN$^-$ interacted with the surface atoms of AgNPs forming Ag$^*$ and ROS and then followed the same mechanism as described for CN$^-$. The analysis of the titration data revealed that the linear detection ranges are 0.01–90 and 0.04–50 μM for CN$^-$ and Cr(VI), respectively, and the LOD was found to be 0.01 and 0.04 μM for CN$^-$ and Cr(VI), respectively. Applicability of the material for sensing of CN$^-$
and Cr(VI) in water samples was also tested, and the results obtained are satisfactory. For field application, agarose-based strips were prepared by immobilizing the surface-modified nanoparticles onto the agarose film and successfully used for the detection of CN\(^-\) and Cr(VI) in water. The probe developed therefore is selective for CN\(^-\) under a particular condition and selective for Cr(VI) under a different condition.

### MATERIALS AND METHODS

**Materials.** Rosmarinic acid, sodium borohydride, ascorbic acid, HEPES buffer, sodium phosphate monobasic, and agarose (low melting point) were purchased from Sigma-Aldrich. AgNO\(_3\) was purchased from S. D. Fine Chemicals. Tetrabutylammonium (TBA\(^+\)) salts of fluoride, bromide, chloride, iodide, periodate, cyanide, dihydrogen phosphate, acetate, nitrate, and bisulfate were purchased from Sigma Aldrich. Potassium dichromate was purchased from Merck Ltd. Solutions of all the chemicals were prepared in Milli-Q water. Aldrich. Potassium dichromate was purchased from Merck Ltd. acetate, nitrate, and bisulfate were purchased from Sigma-

**Methods.** UV–vis absorption spectra were recorded using a Varian CARY-500 spectrophotometer. The particle size and morphology were studied by drop casting the samples onto the copper grids and imaging on a JEOL model JEM 2100 transmission electron microscope (200 kV). The mass spectra were recorded using a Q-TOF micro liquid chromatograph coupled with a mass spectrometer. The zeta potential measurements were carried out using a Malvern instrument (Zetasizer, Nano series, Nano-ZS90). Powder XRD patterns were recorded using a PanAnalytical EMPYREAN (Cu-K\(_\alpha\) radiation).

**Preparation of Ro-AgNPs.** Ro-AgNPs were prepared by chemical reduction of silver nitrate (AgNO\(_3\)) with the aid of sodium borohydride (NaBH\(_4\)) in the presence of rosmarinic acid. To optimize the concentration of rosmarinic acid for maximum yield without aggregation, six different experiments were carried out with different concentrations of rosmarinic acid. For this purpose, AgNO\(_3\) (17.0 g, 0.1 M) and rosmarinic acid (0.025, 0.05, 0.1, 0.2, 0.3, and 0.4 mM) were added to deionized water (100 mL), and the mixture was allowed to stir for 10 min at RT to obtain a clear solution. To this solution, NaBH\(_4\) (8.8 mg in 2 mL water) was added under vigorous stirring and was allowed to stir for 10 min. The color of the solution changed from colorless to yellow, confirming the formation of Ro-AgNPs. The concentration ratio at which maximum absorbance was recorded was considered as the optimum concentration of rosmarinic acid required for the optimum yield, and the same has been used for the synthesis of Ro-AgNPs.

**Study on the Ion Recognition Property of Ro-AgNPs.**

For this study, 1 mL of the as-prepared Ro-AgNPs was mixed with 1 mL each of 2 mM stock solutions of the TBA\(^+\) salts of the anions OH\(^-\), F\(^-\), Cl\(^-\), Br\(^-\), CH\(_3\)COO\(^-\), HPO\(_4\)\(^{2-}\), H\(_2\)PO\(_4\)\(^-\), CN\(^-\), NO\(_3\)\(^-\), HSO\(_4\)\(^-\), and I\(^-\), and the mixture was diluted using Milli-Q water to a final volume of 3 mL in a cuvette. After incubation of each reaction mixture for 6 min, the UV–visible spectra of the solutions were recorded, and the changes in the spectra were noted. It has been noted that Ro-AgNPs selectively detect CN\(^-\); therefore, UV–visible titration study for CN\(^-\) was carried out by adding different amounts of stock solution of cyanide to 1 mL of Ro-AgNPs, so that the concentration of the anion is in the range of 0 μM–400 mM after adjustment of the final volume to 3 mL, and the spectra of the solutions were recorded after the incubation time. In order to study the effect of competing anions over cyanide, 1 mL of Ro-AgNPs was mixed with 1 mL (2 mM) of solution of various anions, followed by the addition of 100 μL (2 mM) of CN\(^-\); the UV–visible spectra of the solutions were recorded after an incubation of 6 min.

For detection of chromium(VI), 1 mL of RO-AgNPs, 100 μL (20 mM) of ascorbic acid solution, and 500 μL (2 mM) of CN\(^-\) solution were added into the cuvette, followed by the addition of 1 mL (2 mM) solution of respective anions, and the UV–vis spectra were recorded. The UV–visible titration study for Cr(VI) was carried out following the same procedure as described above; except that in place of different anions, different aliquots of Cr(VI) were added to make the concentration of anions in the range of 0–55 μM after adjustment of the final volume to 3 mL, and the spectra were recorded after incubation. To study the effect of competing anions over chromium(VI), 400 μL of RO-AgNPs, 100 μL of 20 mM ascorbic acid solution, and 500 μL of 2 mM CN\(^-\) were added into the cuvette. To this mixture, 1 mL (2 mM) solution of the competing anions was added and after the addition of 100 μL of Cr(VI), the UV–visible spectra were recorded after an incubation time of 10 min.

**Detection of Cyanide in Water as Real Samples.** For real sample analysis, the tap water and drinking water samples were collected locally from the institute and were used without any pretreatment. As the water samples were free from cyanide and chromium(VI), as determined by ICP-MS analysis, they were spiked with various concentrations of cyanide and chromium(VI) in the concentration range of 0.05–1.2 mM. Then, 100 μL of each of the spiked solution was added to 1 mL of RO-AgNPs, and the mixture was diluted to a final volume of 3.0 mL with Milli-Q water. The absorbance spectra after addition of each spiked sample were recorded after incubating for 6 min.

**Preparation of Agarose Gel-Based Test Strips for Detection of CN\(^-\) and Cr(VI).** In order to prepare agarose-based test strips for monitoring CN\(^-\) levels in environmental samples, agar powder (0.1 gm) was added to 15 mL of Milli-Q water, and the solution was heated in a microwave oven for 30 s for complete dissolution of agar powder. The solution was allowed to cool to about 45 °C, to which 5 mL of Ro-AgNPs was added, and the mixture was allowed to stir for 5 min. A similar protocol was followed to prepare agarose-based test strips for Cr(VI) monitoring, except that along with 5 mL of Ro-AgNPs, 0.5 mL of 20 mM ascorbic acid and 5 mL of 2 mM cyanide solution were added, thereby making the final volume to 20 mL. Film casting for both the solutions was carried out upon pouring the solutions into Petri dishes, which turned to a nice thin film upon drying at room temperature. The dried films were cut uniformly into a rectangular shape as ready-to-use sensor strips.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05946.

UV–vis spectra of Ro-AgNPs prepared with varying amounts of rosmarinic acid (Ro), IR spectra of Ro and Ro-AgNPs, absorbance of Ro-AgNPs and Ro-AgNPs + CN\(^-\) at 405 nm with pH variation, absorbance of Ro-AgNPs + CN\(^-\) at 405 nm as a function of time, UV–vis spectral change in the presence of Cr\(_2\)O\(_7^{2-}\), plot for determination of LOD for CN\(^-\) and Cr(VI), bar diagram
showing absorbance with variation in the amount of ascorbic acid, absorbance at 412 nm as a function of time after addition of CrO7\(^{2-}\), and bar diagram showing changes in absorbance at 412 nm in the presence of competitive ions (PDF)

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**Notes**
The authors declare no competing financial interest.

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