Highly Selective Detection of Iodide in Biological, Food, and Environmental Samples Using Polymer-Capped Silver Nanoparticles: Preparation of a Paper-Based Testing Kit for On-Site Monitoring

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Supporting Information

ABSTRACT: This work describes a facile synthesis of polymer-capped silver nanoparticles at room temperature. Chitosan oligosaccharide lactate-capped silver nanoparticles (COL-AgNPs) show the surface plasma resonance (SPR) band at 400 nm. The color of the COL-AgNPs was observed to be brownish yellow. The synthesized COL-AgNPs are stable for 5 months. The COL-AgNPs were characterized by UV–vis, X-ray diffraction, high-resolution transmission electron microscopy (HR-TEM), mass, and Fourier transform infrared spectral techniques. The obtained COL-AgNPs are monodispersed, and the range of the particle diameter was calculated to be 16.37 ± 0.15 nm by HR-TEM. We have utilized the COL-AgNPs as a probe to sense iodide (I−). The SPR band of COL-AgNPs decreased after the addition of iodide, and the color of the solution changed to colorless. Based on the decreases in SPR band absorbance, the concentration of iodide was calculated. The detection limit was found to be 108.5 × 10−9 M (S/N = 3). Other interferences (825- and 405-fold) did not interfere with the detection of 1.48 × 10−6 M iodide. The sensing mechanism was also discussed. Finally, we have successfully applied our sensing system for the detection of iodide in tap water, river water, pond water, blood serum, urine, and food samples. Good recoveries are obtained with spiked iodide in the real samples. Importantly, we have developed a paper-based kit using wax-printed paper for the on-site monitoring of iodide. The developed paper-based kit absorbance was validated with the microplate reader. To the best of our knowledge, this is the first report that used six different real samples for the detection of iodide and development of the paper-based kit for on-site monitoring.

1. INTRODUCTION

Iodide plays a vital role in metabolism and neurological activities. It is involved in the development of bones, muscles, and thyroid functions. Thyroid cells absorb iodide from food and then combine with amino acid to prepare T3 and T4 thyroid hormones.1,2 These thyroid hormones, which will be released into the blood and circulated throughout the body, are involved in several metabolic reactions. Therefore, the presence of iodide in food and water is very important for the normal function of the thyroid gland. Millions of people are affected by iodide deficiency globally, which is known as hypothyroidism.2,3 On the other hand, an excess of iodine present in our body is called hyperthyroidism. Hypo- and hyperthyroidism can cause goiter, anxiety, nervous agitation in dementia, confusion, circulatory system disorders, agitation, and weight loss.5–7 These deficiencies also can cause mental defects, spontaneous abortion, and an increased number of infant deaths.8–10 Iodide deficiency can be prevented by ensuring optimal iodide intake from food and medicine.11 The World Health Organization (WHO) has recommended that the daily intake of iodide is 150 μg/day.12,13 Therefore, the detection of iodide using a simple protocol with high sensitivity and selectivity is very important for both physiological and environmental impact.14,15

Recently, there have been many reports available for the detection of iodide, such as voltammetry,16 fluorescence,17 flame atomic absorption spectrometry,18 gas chromatography–mass spectrometry,19 ion chromatography,20 etc. Nevertheless, these methods have some demerits, which include a long measuring time, lengthy procedure, high-cost instrument, etc. On the other hand, a spectrophotometric detection method has gained momentum due to its simple experimental setup, high sensitivity, and less time-consumption.21 Recently, metal nanoparticles have been extensively used for sensor applications. For example, silver nanoparticles have received much attention because of their simple synthesis, unique optical properties, ultrasmall size and SPR band, etc.22,23

Further, AgNPs show good conductivity, catalytic activity, chemical stability, and are extensively used in sensor, food storage, and textile industries.22,24 The size- and distance-
dependent SPR properties of AgNPs can help the researchers use it as a probe for sensor applications.\textsuperscript{5,26} Chitosan oligosaccharide lactate (COL) is a degradable biopolymer. It is used in several fields, including water treatment, thin film and food industries, etc., due to their biocompatibility, nontoxicity, and good aqueous solubility.\textsuperscript{27,28} Keeping these objectives in our minds, we have synthesized COL-capped silver nanoparticles (COL-AgNPs) at room temperature. Then, the COL-AgNPs were used as a probe for the selective detection of iodide. Further, we have applied them to a developed system for the detection of iodide in several real samples, including blood serum, urine, food, and water samples. Importantly, the paper-based kit also was developed for on-site monitoring of iodide.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Chitosan oligosaccharide lactate, sodium borohydride, and silver nitrate were purchased from Aldrich and were used as received. Potassium iodide, sodium chloride, sodium fluoride, potassium bromide, potassium chloride, aluminum oxide, sodium nitrate, potassium cyanide, sodium nitrite, hydrochloric acid, sodium hydroxide, sodium sulfate, sodium thiosulfate, sodium acetate, sodium carbonate, potassium thiocyanate, monosodium phosphate, and disodium phosphate were purchased from Aldrich and used as received without further purification. Magnesium acetate, iron(III) chloride, iron(II) chloride, zinc sulfate, nickel sulfate, magnesium sulfate, and copper nitrate were purchased from Fisher and used as received without further purification. Dialysis tubes with a 29.3 mm diameter and 3.5 kDa molecular weight cutoff (MWCO) were obtained from Fisher Scientific. A phosphate buffer solution (pH 3.0 to pH 13) was prepared with monosodium phosphate and disodium phosphate (0.2 M), further adjusted with sodium hydroxide and hydrochloric acid. All glassware was thoroughly washed with (3:1 ratio of HCl/HNO₃) aqua regia and was then rinsed with ultrapure water prior to use. Ultrapure water was used in all of the experiments.

2.2. Synthesis of AgNPs. The COL-AgNPs was synthesized by a wet-chemical method. Briefly, a 2 mL solution of 0.01 M AgNO₃ and 25 mL of water were added into a 50 mL beaker. The solution was allowed to be stirred vigorously for 5 min. Then, 3 mL of 1% chitosan oligosaccharide lactate was added and allowed to be stirred for 5 min. Then, 0.3 mL of 0.25% NaBH₄ was added into the above mixture. The solution immediately turns brownish yellow. After 5 min of stirring the COL-AgNPs, the solution was centrifuged three times with 1000 rpm and washed with water. Finally, the purified COL-AgNPs were stored at 4 °C.

2.3. Characterization of COL-AgNPs. Absorption spectral studies are performed in a Shimadzu UV-2550 UV–vis spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded using a PerkinElmer Spectra 100 FT-IR spectrometer. Transmission electron microscopy (TEM) images and the EDX (energy dispersive X-ray) spectrum were collected with a JEOL-2100 transmission electron microscope that was operated at 200 kV. The X-ray diffraction (XRD) pattern was obtained from a Rigaku X-ray diffraction unit using Ni-filtered Cu K (λ = 1.5406) radiation. A voltammetry experiment was carried out in an HCHI instrument (U.S.A.), and glassy carbon, a Ag/AgCl electrode, and platinum wire were used as working, reference, and counter electrodes, respectively. Mass spectra were recorded, and GC–MS spectra were measured on GC/MS systems (5977 series of Agilent Technology). An electrospray ionization quiet time of the light mass spectrometry measurement was performed by a Xevo G2-S-Q-TOF (U.S.A.) instrument via a direct infusion method. Microplate absorbance was recorded with an EnSpire multilabel plate reader with Alpha Tech (PerkinElmer, U.S.A., 2013).

2.4. Iodide Sensing Procedure. In a 3 mL cuvette, 0.5 mL of COL-AgNPs and 1.5 mL (pH 7.2) of 0.2 M phosphate buffer were taken (blank). In this mixture, a different concentration of I⁻ was added. After 10 min of reaction time, the UV–vis spectrum was recorded, and the UV–vis spectral scale was kept from 200 to 750 nm.

2.5. Real Sample Analysis. Tap water was collected from our institute. River and pond water were collected from nearby places. The dust and small particles are removed by filtration using Whatman filter paper. Similarly, the urine sample also was filtered by Whatman filter paper. The blood serum sample was collected from a nearby medical center and used without further purification. The food sample of kelp (Laminaria japonica Aresch) was purchased from a local supermarket. Dried kelp (0.25 g) was burned to ash in which the existing iodine is converted into iodide. Then, the burned ash was dissolved into boiling water. Then, the solution was filtered by 0.2 μm filter paper. Finally, we have spiked a known volume of the real sample into the COL-AgNPs and recorded the UV–vis spectrum.

2.6. Paper-Based Iodide Sensor. An Advantech chromatography paper sheet (grade no.1, A4 sheet) was taken and fitted into the solid ink printer (Xerox Color Qube 8570 wax printer). The ink printer created the hydrophobic wax barriers on the paper. The wax-printed paper was placed in a hot plate at 140 °C for 3 min, which melted the wax and formed a hydrophobic barrier. After cooling the wax-printed paper, 100 μL of COL-AgNPs was added into each well and allowed to dry at room temperature for 20 min.\textsuperscript{29} Then, the I⁻-spiked river water sample was added into a well of COL-AgNP-coated wax-printed paper. Finally, the absorbance of each well area was measured using a Synergy HT microplate reader (BioTek) at 405 nm.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of COL-AgNPs. The COL-AgNPs were synthesized by an eco-friendly and environmentally friendly method at room temperature. The synthesized COL-AgNPs were purified by centrifugation and dialysis methods. Then, the purified COL-AgNPs were characterized by the following techniques.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (A) UV–vis spectrum of COL-AgNPs. Inset of (A): Photograph of COL-AgNPs. (B) UV–vis spectra of (a) freshly prepared and (b) 5 month aged COL-AgNPs. Inset of (B): (a, b) photographs of corresponding (a) and (b) curves.
3.1.1. Absorption Spectrum and Stability of COL-AgNPs. The synthesis of COL-AgNPs was monitored by a UV–vis spectrophotometer. The UV–vis spectrum of AgNO₃ shows the absorbance peak at 262 nm (Figure S1, curve a), and COL exhibited the absorbance band at 280 nm (Figure S1, curve b). After mixing AgNO₃ and COL, the absorbance band shifted to 254 nm (Figure S1, curve c). Then the addition of NaBH₄ led to changing the solution color from colorless to brownish yellow, and the SPR band was observed at 400 nm, which successfully confirmed the formation of COL-AgNPs (Figure S1, curve d). We have used COL as a stabilizer to get the high stability of AgNPs.

Further, we have monitored the stability of COL-AgNPs by a UV–vis spectrophotometer. Interestingly, the 5 month aged COL-AgNPs had unaltered absorbance and wavelength compared with freshly prepared COL-AgNPs (Figure 1B, curve a). The color of the solution also was unaltered (Figure 1B, inset a) with freshly prepared and 5 month aged COL-AgNPs.

3.1.2. FT-IR Spectra of COL and COL-AgNPs. The existing chemical functional groups of COL and COL-capped AgNPs...
were characterized by the FT-IR spectral technique. FT-IR spectra of COL and COL-AgNPs are shown in Figure 2A(a and b), respectively. The FT-IR spectrum of COL shows the characteristic peaks at 3325 and 2901 cm$^{-1}$, which are corresponding stretching frequencies ($\nu$) of OH and NH, and symmetrical stretching frequencies ($\nu_s$) of CH were observed at 2901 cm$^{-1}$. The stretching frequency peaks of NH were merged together with the OH peak.30 The stretching frequencies of C−O and C−O−C were observed at 1606 and 1046 cm$^{-1}$, respectively.31 The stretching frequency ($\nu$) of CH was observed at 1386 cm$^{-1}$.28,32 Further, we have characterized the COL-capped AgNPs by the FT-IR spectral technique. The FT-IR spectrum of COL-AgNPs shows the similar FT-IR characteristic peaks of COL (Figure 2A(b)). It is expected that the $-\text{NH}_2$ group of COL was adsorbed on the surface of AgNPs. As we expected, the resolved NH peak intensity was decreased.28 These results confirmed the presence of COL on the surface of AgNPs.

### 3.1.3. HR-TEM Images and XRD Pattern of COL-AgNPs.

The size, dispersity, and morphology were examined by high-resolution transmission electron microscopy (HR-TEM) images. Figure 3A shows the HR-TEM images with different magnifications. The synthesized COL-AgNPs were observed as spherical in nature and monodispersed by the HR-TEM image (Figure 3B). The average particle diameter was calculated to be 16.37 ± 0.15 nm, which was calculated using Image J software. The obtained HR-TEM image particle size has good agreement with the particle size calculated by the XRD pattern Scherer equation (Figure 2B). Further, we have observed a crystal lattice of COL-AgNPs by the HR-TEM image. The crystal lattice distance was estimated to be 0.24 nm in size (Figure 3A, inset). The obtained lattice distance confirmed the d-spacing of the silver lattice of the (111) plane35 (JCPDS file no. 04−0783). These results confirmed that the COL-AgNPs are crystalline in nature and highly pure.

The XRD pattern of COL-AgNPs is shown in Figure 2B. The crystalline nature has been characterized by XRD measurement. The XRD pattern of COL-AgNPs shows that the different peaks are at (111) 38.17, (200) 44.20, (220) 64.28, (311) 77.51, and (222) 81.81 planes.36 Among the different XRD planes, the absorbed (111) peak is more intense than that of the other planes. The intensity ratio between the (200) and (111) planes was calculated to be 0.6, which is relevant in showing that the (111) plane is predominant in the arrangement.

The crystalline size of COL-AgNPs was calculated by the following Scherer equation.23,36,37

$$D = (k \lambda) / (\beta \cos \theta)$$  

where $D$ is the crystalline size, $k$ is a shape factor (0.94 for a cube), $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half maximum (FWHM) of the peak, and $\theta$ is the Bragg angle. The crystalline size of COL-AgNPs was calculated to be 16.37 ± 0.15 nm.
Table 2. Features and Limitations of Reported Nanoparticles Synthesis and Their Application for the Detection of Iodide in the Literature

| Nanoparticles | Linear range (×10^{-6} M) | LOD (×10^{-6} M) | Sensing pH | Ref. |
|---------------|---------------------------|-----------------|------------|-----|
| tea-capped AgNPs | 0.1−50 | 60 | 60 | 7 |
| virgin silver nanoparticles | 0.76−199 | 320−1,320 | NR | 13 |
| steroidal 1,2,3-triazole | 32−50 | 200−2,000 | NR | 47 |
| Cu@Au nanoparticles | 0.5−80 | 5 to 9 | 500 | 48 |
| citrate-stabilized core−shell nanoparticles | 2.5−165 | 7.4 | 589 | 49 |
| COL-AgNPs | 0.5−80 | 5 to 9 | 500 | 50 |
| silver-coated gold nanobipyramids | 10−15 | 6.5 | 300 | 51 |
| COL-AgNPs | 0.5−80 | 6.5 | 60 | 52 |
| silver-coated gold nanobipyramids | 10−15 | 6.5 | 300 | 53 |
| COL-AgNPs | 0.5−80 | 6.5 | 60 | 54 |

- LOD: Limit of Detection
- pH: Sensing pH range
- Ref.: Reference number

- NR, no reaction.

where D is the crystallite size of the AgNPs, \( \lambda \) is the wavelength of X-ray wavelength, \( \beta \) is the full width half-length maximum of the (111) plane, \( \theta \) is the diffraction angle, and \( k \) is a constant. The average size of COL-AgNPs was calculated to be 20.32 nm by the Scherer equation, which fairly matched with the particle size obtained from the HR-TEM image.

3.1.4. Mass Spectral Studies. The mass spectrum of COL-AgNPs is shown (Figure S2). The fragment peaks are obtained at 525.18, 687.23, 848.34, 1008.27, 1169.27, 1320.63, 1420.43, 1632.54, 1805.69, 2250.35, 2500.02, 2750.34, 3000.56, 3455.76, 3690.35, 3750.63, 3954.54, 4257.84, and 4623.17 m/z (Figure S2). The obtained peaks are due to the fragmentation of COL (dimer, trimmer, tetramer, pentamer, hexamer, heptamer, and octamer). The obtained mass spectral results fairly matched with the previous report. This mass spectral result confirmed that the COL is present on the surface of AgNPs.

3.1.5. Effect of pH and Time. The effect of pH and time on COL-AgNPs in the presence of iodide was monitored with a UV−vis spectrophotometer using a phosphate buffer solution (0.2 M). The pH of COL-AgNPs was fixed from pH 3 to pH 12 and mixed with 1.48 × 10^{-6} M iodide. The SPR band was observed at pH 3, and when we increased the pH from 4 to 12, we have observed that the absorbance of the SPR band was enhanced from pH 4 to 7.2. Hence, COL-AgNPs are not stable in acidic pH because the acidic environment can convert the AgNPs to Ag⁺ ions. Therefore, the absorbances are less at pH 3 and 4 (Figure S3). When we go for natural pH, it is favored to form an AgI complex; this is the reason that the absorbance was enhanced when observed in neutral pH 7.2 (Figure S3). The absorbance dramatically decreased at pH 8 (Figure S3). The observed absorption decrease was attributed to the presence of excess OH⁻, which led to decreased absorption through the aggregation of NPs (Figure S3). Hence, we have optimized the pH 7.2 as a suitable pH for I⁻ sensing.

The effect of time on COL-AgNPs with the iodide graph is shown in (Figure S4). We have monitored the absorption of COL-AgNPs after the addition of 1.48 × 10^{-6} M (pH 7.2) at different time intervals. The absorption was increased from 1 to 10 min and then became constant from 10 to 60 min (Figure S4). These results confirmed that 10 min is sufficient to react iodide with AgNPs. Hence, we have optimized the 10 min reaction time as the optimized incubation to form AgI.

3.2. Spectrophotometric Detection of Iodide. The interaction between iodide and COL-AgNPs was monitored by a UV−vis spectrophotometer. The UV−vis spectrum of COL-AgNPs exhibits the SPR band at 400 nm (Figure 4, curve a), and the color of the solution is brownish yellow. After the addition of 0.498 μM iodide, the absorption was decreased at 400 nm, and, interestingly, a new hump appeared at 422.2 nm (Figure 4, curve b). With the second addition 0.999 μM iodide, we let to decrease the absorption of COL-AgNPs at 400 nm.

The obtained hump at 430 nm becomes sharp (Figure 4, curve c). While adding 1.48 μM iodide (Figure 4, curve d), the SPR band completely vanished, and the hump becomes a well-resolved peak at 422.2 nm with a decrease in absorbance. The next addition led to shifting the wavelength of the resolved peak obtained at 422.2 nm. However, the SPR band completely vanished (Figure 4, curves e−h, inset (i)). The color of the solution also changed from brownish yellow to colorless (Figure 4, inset (ii)). It is expected that the disappearance of the SPR band and appearance of a new peak at 422.2 nm is due to the formation of AgI. The obtained
AgI peak at 422.2 nm perfectly matched with previous reports.\(^7,\text{13}\) Therefore, the solution color and UV–vis spectral changes confirmed the formation of AgI. Based on the decrease in the SPR band of COL-AgNPs, we have calculated the concentration of iodide. The detection limit was calculated to be \(108.5 \times 10^{-9} \text{ M (S/N = 3)}\), and good linearity was obtained from 498 nM to 2.28 \(\mu\text{M}\) iodide. Further, we have predicted the mechanism for the formation of AgI from COL-AgNPs with the help of HR-TEM images and DPV data.

The UV–vis spectrum of 0.5 M iodide (Figure S5) shows the absorption band at 226 nm. On the other hand, the UV–vis spectrum of 1% COL solution exhibits the absorption broad band at 280 nm (Figure S6). We have added the different concentrations of iodide into the COL solution and monitored their absorption spectral changes (Figure S7). Interestingly, after the addition of different concentrations from 7.4 to 43.1 \(\mu\text{M}\) iodide, we did not observe any spectral changes of COL, but the iodide peak at 226 nm was increased. These results revealed that the there is no interaction between the COL and iodide. Therefore, the interaction was obtained between the AgNPs and iodide. Therefore, we conclude that added COL here acts as a stabilizing agent to protect the interaction between the AgNPs and iodide. Therefore, we conclude that the interaction was obtained between the AgNPs and iodide. Therefore, we conclude that added COL here acts as a stabilizing agent to protect the AgNPs from aggregation.

### 3.3. HR-TEM of COL-AgNPs in the Presence of Iodide

We have characterized the COL-AgNPs after the addition of 1.48 \(\times 10^{-6}\) M iodide by HR-TEM (Figure 5). The HR-TEM image COL-AgNPs in the presence of iodide shows the slightly aggregated and smallest particles. The particle size was calculated to be 4.61 \(\pm 0.12\) nm. The obtained small particles were expected due to the etching effect of iodide ions on the COL-AgNPs.\(^7\) The aggregated particles size is 3.6-fold lower than the size of COL-AgNPs.\(^\text{3} \)Further, the UV–vis spectral data of COL-AgNPs added with iodide produces a new peak at 422.2 nm. Figure 5 (inset (i)) shows the HR-TEM image of COL-AgNP in the presence of 1.48 \(\times 10^{-6}\) M iodide. The particle size was observed to be 4.61 nm. Interestingly, we have observed the lattices. The lattice distance was estimated to be 0.35 nm, which is higher than that of the lattice of COL-AgNPs (Figure 3, inset). Further, the observed lattice distance of 0.35 nm perfectly matched with the previous reports of AgI.\(^\text{4} \)\(^1\)\(^2\)

Moreover, we have analyzed the element by EDX. The EDX spectrum of COL-AgNPs in the presence 1.48 \(\times 10^{-5}\) M iodide is shown in Figure 5 (inset (ii)). The EDX spectrum revealed the strong signals of silver at 3 KeV and iodide at 4 KeV. These results strongly confirmed the formation of AgI. Further, these results perfectly match with previous reports.\(^\text{43}\) Further, nitrogen, carbon, and oxygen signals are due to the presence of the COL ligand. The excess carbon and copper signals are obtained from the copper grid. UV–vis spectral data (Figure 4), COL-AgNPs color changes (Figure 4, inset (ii)), differential pulse voltammetry data (Figure 7), HR-TEM images in Figure 5 (inset (i)), and EDX spectral results (Figure 5, inset (ii)) strongly confirmed the formation of AgI. Further, the abovementioned results perfectly match with previous reports.

### 3.4. Effect of Interferences

The effect of a coexisting ion is very pertinent for a new detection method for iodide. We have taken common interferences of \(\text{Br}^–\), \(\text{F}^–\), \(\text{Cl}^–\), \(\text{NO}_2^–\), \(\text{NO}_3^–\), \(\text{H}_2\text{PO}_4^–\), \(\text{SO}_4^{2–}\), \(\text{CN}^–\), acetate (\(\text{AC}^–\)), \(\text{CO}_3^{2–}\), \(\text{SCN}^–\), \(\text{Na}^+\), \(\text{K}^+\), \(\text{Fe}^{2+}\), \(\text{Al}^{3+}\), and \(\text{Fe}^{3+}\). Interestingly, the presence of 1.22 \(\times 10^{-2}\) M (825-fold) of the above mentioned common potential interference did not interact with the detection of 1.48 \(\times 10^{-6}\) M iodide (Figure 6A,B). However, the \(6.0 \times 10^{-7}\) M concentration of other metal ions including \(\text{Zn}^{2+}\), \(\text{Ni}^{2+}\), \(\text{Mg}^{2+}\), \(\text{Cu}^{2+}\), and \(\text{Mn}^{2+}\) did not interfere with the detection of (405-fold) 1.48 \(\times 10^{-6}\) M iodide. Further, the color of the solution of COL-AgNPs (Figure 6C,D) did not change after the addition of interferences. However, even the addition of 1.48 \(\times 10^{-6}\) M iodide led to changing the color of the AgNP solution from yellow to colorless.

These results confirmed the use of the obtained COL-AgNPs as a novel probe for the highly selective detection of iodide. Even the presence of 825- and 405-fold higher concentrations of abovementioned interferences did not interfere with the detection of 1.48 \(\times 10^{-6}\) M iodide.

### 3.5. Electrochemical Studies of COL-AgNPs with Iodide

Further, we have studied the interaction between COL-AgNPs and iodide by a differential pulse voltammetry (DPV) technique (Figure 7). Exhibited by the DPV of COL-AgNPs is the presence and absence of iodide. The COL-AgNPs exhibited the oxidation peak of Ag\(^0\) at 0.22 V (Figure 7, curve a).\(^44\)\(^45\) It is well known that the oxidation peak of Ag\(^0\) will be shifted to the lower potential, and the current intensity can be enhanced when AgNPs interact with iodide.\(^44\)\(^44\)\(^44\) The DPV of COL-AgNPs shows the Ag\(^0\) oxidation peak at 0.22 V. Interestingly, the addition of 0.5 \(\mu\text{M}\) iodide led to shifting the peak from 0.22 to 0.09 V (Figure 7, curve b). The second addition of iodide (2 \(\mu\text{M}\)) shows no peaks at 0.22 and 0.09 V (Figure 7, curve c). The new peak that appeared at 0.793 V is due to the conversion of AgI from Ag\(^0\) (Figure 7).\(^7\)\(^46\) The appearance of a new peak at 0.793 V revealed the excess of iodide. This result perfectly matches with the previous report.\(^7\) The electrochemical study has confirmed the formation of AgI after the addition of iodide into COL-AgNPs.

Based on the results obtained from UV–vis spectral, HR-TEM image lattice, EDX spectral, and electrochemical studies, we have given the possible mechanism for the formation of AgI(Scheme 1).

### 3.6. Real Sample Analysis

The COL-AgNPs was successfully applied for the detection of iodide in water samples (tap water, river water, and pond water) and urine, blood serum, and food (Kelp) samples. The water, blood serum, and urine samples did not have iodide content. Then, we spiked a known amount of iodide to the real sample, which led to the decrease of the SPR absorption band. A good recovery was observed from 97 to 99.7% of those spiked with iodide. The summarized result is shown in Table 1. These results confirmed that the COL-AgNPs are a good probe for the detection of iodide in environment water, urine, blood serum, and food samples.

### 3.7. Development of a Paper-Based Kit for On-Site Monitoring of Iodide

The preparation procedure for COL-AgNP-coated wax-printed paper is given in the experimental section. Tap water samples of 20 \(\mu\text{L}\) containing known concentrations of iodide were dropped onto the wax paper. For example, 20 \(\mu\text{L}\) of (a) 0, (b) 0.498, (c) 0.998, (d) 1.48, (e) 1.9, (f) 2.44, (g) 2.91, and (h) 3.38 \(\mu\text{M}\) iodide (Figure 6A,B). However, the \(6.0 \times 10^{-7}\) M concentration of other metal ions including \(\text{Zn}^{2+}\), \(\text{Ni}^{2+}\), \(\text{Mg}^{2+}\), \(\text{Cu}^{2+}\), and \(\text{Mn}^{2+}\) did not interfere with the detection of (405-fold) 1.48 \(\times 10^{-6}\) M iodide. Further, the color of the solution of COL-AgNPs (Figure 6C,D) did not change after the addition of interferences. However, even the addition of 1.48 \(\times 10^{-6}\) M iodide led to changing the color of the AgNP solution from yellow to colorless.

Further, the absorbance of modified wax-printed paper was quantitized by the microplate reader; each printed well was cut
into a 2 cm² area then the cut area was fixed into a separate well of a 16-well microplate, and the absorbance was recorded at 405 nm wavelength. We have measured 15 times in the well area. Good linearity was observed from 0 to 3.38 × 10⁻⁶ M iodide (Figure 8B) (R² = 0.9905).

The results confirmed that our paper-based platform kit provides advantage including low cost, a simple experimental step, test screening, and a good performance for achieving real-sample on-site monitoring of iodide in biological and environmental samples. When compared with the other reported nanoparticles for the detection of iodide, the present method has several advantages, including 10 min reaction time, low LOD, and environmental sensing pH. Six different real samples were tested and a paper based kit was developed (Table 2).

4. CONCLUSIONS

We have developed a one-pot synthesis of COL-AgNPs at room temperature. The synthesized COL-AgNPs were well characterized by UV–vis, FT-IR, XRD, HR-TEM, mass, and DPV methods. Then COL-AgNPs were used as probes for detection. After the addition of iodide into the COL-AgNPs, the color of the solution changed to colorless, and noticeable SPR band changes were observed as well as the formation of AgI. The possible mechanism also was discussed. Finally, the 825-fold excess of common interferences including Br⁻, F⁻, Cl⁻, NO₃⁻, NO₂⁻, H₂PO₄⁻, SO₄²⁻, CN⁻, acetate (AC⁻), CO₃²⁻, SCN⁻, Na⁺, K⁺, Fe³⁺, Al³⁺, and Fe²⁺ and 405-fold excess of common interferences Zn²⁺, Ni²⁺, Mg²⁺, Cu²⁺, and Mn²⁺ did not interfere with the detection of 1.48 × 10⁻⁶ M iodide. This method was successfully applied for the detection of iodide in biological (blood and urine), food (kelp), and environmental (tap, river, and pond water) samples. For the first time, we have developed a paper-based kit for on-site monitoring of iodide, which was successfully validated with a microplate-reader technique.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01144.

UV–vis spectra of AgNO₃, COL, mixture of AgNO₃ and COL, and COL-AgNPs, mass spectrum of COL-AgNPs, effect of pH, Time effect, UV–vis spectrum of I⁻, UV–vis spectra of I⁻ (1% COL), UV–vis spectra of COL in the presence of different concentrations of I⁻ (PDF)

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Notes

The authors declare no competing financial interest.

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