Cu Nanoparticle-Based Solution and Paper Strips for Colorimetric and Visual Detection of Heavy Metal Ions

Trilochan Baral, Chitraniva Datta, and Subhojit Das*

ABSTRACT: The intrinsic toxicity of heavy metal ions to human health or other species calls for the need to develop an analytical tool for the easy and rapid detection of these ions based on inexpensive and stable nanomaterials. This article describes the potential utility of stable Cu nanoparticles (CuNPs) in the detection of toxic metal ions by solution and paper strip-based methods. For this, first, a dodecyl sulfate ion-stabilized CuNP (DS-CuNP) colloid was synthesized by a chemical reduction method. This was followed by treating the dispersion with heavy metal ions and monitoring the spectral change by spectrophotometric and colorimetric techniques. Among a host of metal ions, Hg$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$ have been found to significantly affect the surface plasmon resonance band of CuNPs by concomitantly altering the color of its solution. Notably, the brownish color of CuNP solution changed readily to milky white in the presence of Hg$^{2+}$. Furthermore, the fabricated brownish-yellow test paper strips containing DS-CuNPs transformed to a prominent white color in the presence of a few drops of Hg$^{2+}$ solution. This change in color of the paper strips could be visually detected by the naked eye. The experiments involving the detection of the various ions were carried out by optimizing the experimental conditions qualitatively as well as quantitatively. The limit of detection of the analytes (metal ions) has been found to be 10 $\mu$M. Routine analytical techniques like UV–vis spectroscopy, dynamic light scattering, transmission electron microscopy, and Fourier transform infrared spectroscopy formed part of the experiments.

INTRODUCTION

Heavy metals, particularly lead, cadmium, and mercury, pose serious risks to both the human body and the environment. These metals have, therefore, been thoroughly investigated, and international organizations such as the World Health Organization (WHO) examine their effects on human health on a regular basis. For instance, the general populace is primarily exposed to mercury via food, of which, fish is a major source of methylmercury exposure. It is believed that methyl mercury accumulates in the human body and destroys a variety of organs. Further, claims have also been made that mercury from dental amalgams cause a variety of diseases. Again, poor recycling of Cd-containing goods, such as Ni–Cd rechargeable batteries, which are being thrown away with domestic wastes, forms the primary source of Cd exposure. Lastly, human beings are exposed to lead through lead emissions from gasoline. It is anticipated that lead has neurotoxic effects at lower levels of exposure than previously thought. Based on the above facts, it may be stated that the detection of the mentioned ions becomes pertinent while also simultaneously rendering them harmless.

Until now, many methods for detecting heavy metal ions have been reported. Among them, the colorimetric assay of metal ions is increasingly popular. This is primarily because colorimetric approaches are convenient in most applications, as they can be easily determined by color change that can be visualized with the naked eye without requiring the use of any special equipment.

Environmental nanotechnology, which is arguably the most recent application of nanomaterials, is currently being used as novel instruments in environmental sensing and biomonitoring, pathogenic bacteria capture, wastewater treatment, and other applications. Colloidal nanoparticles (NPs) feature unique structural and optical properties, including quantum size effects, surface plasmon resonance (SPR), and high surface-to-volume ratio, making them suitable platforms for a wide range of materials applications. The detection of analytes utilizing nanomaterials is often based on a molecular interaction between the specified analytes and the surface of the NP, which is functionalized with appropriate surfactants. As label-free systems, NPs have excellent chemical and biological sensing capabilities. The availability of the finest...
colloidal metal nanostructures with finely modified surfaces makes them amenable for detection with high selectivity and sensitivity.\textsuperscript{15} Among the metal NPs, CuNPs are interesting candidates for biomedical applications,\textsuperscript{16} particularly biosensing, due to their visible SPR spectra and fluorescence features with a favorable quantum yield.\textsuperscript{17–21} Because CuNPs are prone to surface oxidation, engineering the surface passivation by tweaking the synthesis methods becomes appealing to keep them from oxidation.\textsuperscript{22–25} This makes surface-modified CuNPs promising candidates for colorimetric and fluorescence-based detection of analytes. Therefore, it becomes relevant to design a stable NP system having the potential to detect heavy metal ions at their minimum concentration (conc) levels and alter them to harmless substances. The designed platform should essentially be stable, cost-effective, and readily available. In this article, we report the synthesis of dodecyl sulfate ion-functionalized CuNPs—the resulting colloid being referred to as DS-CuNPs—and its use in the detection of heavy metal ions (as shown in Scheme 1). Dodecyl sulfate ion, an anionic part of the surfactant sodium dodecyl sulfate (SDS), could prevent the CuNPs from oxidation and aggregation by interacting with the tails suffering steric repulsion, thereby keeping the NPs stable, cost-effective, and readily available. In this article, we report the synthesis of dodecyl sulfate ion-functionalized CuNPs—the resulting colloid being referred to as DS-CuNPs—and its use in the detection of heavy metal ions (as shown in Scheme 1). Dodecyl sulfate ion, an anionic part of the surfactant sodium dodecyl sulfate (SDS), could prevent the CuNPs from oxidation and aggregation by interacting with the tails suffering steric repulsion, thereby keeping the NPs stable, cost-effective, and readily available. In this article, we report the synthesis of dodecyl sulfate ion-functionalized CuNPs—the resulting colloid being referred to as DS-CuNPs—and its use in the detection of heavy metal ions (as shown in Scheme 1). Dodecyl sulfate ion, an anionic part of the surfactant sodium dodecyl sulfate (SDS), could prevent the CuNPs from oxidation and aggregation by interacting with the tails suffering steric repulsion, thereby keeping the NPs stable, cost-effective, and readily available. In this article, we report the synthesis of dodecyl sulfate ion-functionalized CuNPs—the resulting colloid being referred to as DS-CuNPs—and its use in the detection of heavy metal ions (as shown in Scheme 1). Dodecyl sulfate ion, an anionic part of the surfac...
investigated from selected area electron diffraction (SAED) the anionic moiety plays a role in binding with NPs. In order to determine of NPs was carried out using the surfactant SDS, wherein solution is crucial before they are used. As such, functionalization to the face-centered cubic (fcc) crystal lattice of CuNPs. Further, that the particles were crystalline in nature was shown in Figure 3b. The SAED pattern was obtained by focusing an electron beam on a region of a collection of particles. Analysis of the diffraction pattern revealed the presence of planes (111), (200), and (220), and these are due to broadening of spectral lines. The detection of metal ions using CuNPs involved a gradual attenuation of the SPR band of the NPs when the concentration of cations was increased. For instance, the attenuation of the SPR band of the NPs when the addition of Hg$^{2+}$ cation from 2.6 × 10$^{-2}$ to 64.2 × 10$^{-2}$ µM, the SPR band was found to undergo a steady fall marked by broadening of spectral lines. It may be mentioned that the concentration and hence the absorbance of the original DS-CuNP solution gradually kept on decreasing, upon increasing the Hg$^{2+}$ concentration, on account of the rise in its volume from starting at 3 mL to ending at 8.4 mL. The disappearance of the SPR band was marked by a concomitant change from a reddish-brown color of the DS-CuNP colloid to milky-white. Additionally, the electrostatic repulsion among the ionized SDS micelles plays a role in the formation of small, evenly distributed CuNPs. The interaction between the dodecyl sulfate ion and CuNPs can prevent the particles from increasing their size during the growth as well as from undergoing aggregation.

The detection of metal ions using CuNPs involved a gradual attenuation of the SPR band of the NPs when the concentration of cations was increased. For instance, the absorption spectra obtained during additions of definite amounts of Hg$^{2+}$ into a DS-CuNP solution (taken 3 mL) led to diminishing of the SPR band. The spectra so-obtained are displayed in Figure 5a. Upon progressively increasing the concentration of Hg$^{2+}$ cation from 2.6 × 10$^{-2}$ to 64.2 × 10$^{-2}$ µM, the SPR band was found to undergo a steady fall marked by broadening of spectral lines. It may be mentioned that the concentration and hence the absorbance of the original DS-CuNP solution gradually kept on decreasing, upon increasing the Hg$^{2+}$ concentration, on account of the rise in its volume from starting at 3 mL to ending at 8.4 mL. The disappearance of the SPR band was marked by a concomitant change from a reddish-brown color of the DS-CuNP colloid to milky-white. Further, predictably, a plot of the absorption at $\lambda_{\text{max}}$ ≈ 580 nm was found to be nearly identical, with apparent shifts in the stretching frequencies of certain specific bonds. Spectral changes were observed for SDS associated with CuNPs with respect to pure SDS. The stretching vibration $\nu$($\text{S=O}$) showed a shift from 972 to 1065 cm$^{-1}$, while $\nu$($\text{SO}_{3}^{-}$) shifted from 1205 to 1225 cm$^{-1}$. The shifts occurred to a higher-frequency side on going from SDS to SDS-CuNPs. Further, for the C–H bond, the asymmetric stretching frequency showed a change of several wavenumbers from 2957 to 2963 cm$^{-1}$, while the symmetric stretching appearing at 2850 cm$^{-1}$ remained barely unchanged in the DS-CuNP sample. This interpretation of observed spectral features of both samples is in alignment with the findings of a previous report. According to the FTIR investigations, the coordinative attachments between the O-atoms of sulpho groups of SDS and the surface of the NPs allow the anionic moiety to stabilize the resulting CuNPs.

It is worthwhile to consider the mechanism of coordination between SDS and CuNPs. SDS is known to exist in the form of micelles in an aqueous medium, with the long hydrophobic chains pointed toward the core and the hydrophilic heads directed to the outer surface. The sulfate groups on the outer surface of micelles can efficiently coordinate with CuNPs thereby imparting stability to the NPs. Additionally, the electrostatic repulsion among the ionized SDS micelles plays a role in the formation of small, evenly distributed CuNPs. The interaction between the dodecyl sulfate ion and CuNPs can prevent the particles from increasing their size during the growth as well as from undergoing aggregation.

The detection of metal ions using CuNPs involved a gradual attenuation of the SPR band of the NPs when the concentration of cations was increased. For instance, the absorption spectra obtained during additions of definite amounts of Hg$^{2+}$ into a DS-CuNP solution (taken 3 mL) led to diminishing of the SPR band. The spectra so-obtained are displayed in Figure 5a. Upon progressively increasing the concentration of Hg$^{2+}$ cation from 2.6 × 10$^{-2}$ to 64.2 × 10$^{-2}$ µM, the SPR band was found to undergo a steady fall marked by broadening of spectral lines. It may be mentioned that the concentration and hence the absorbance of the original DS-CuNP solution gradually kept on decreasing, upon increasing the Hg$^{2+}$ concentration, on account of the rise in its volume from starting at 3 mL to ending at 8.4 mL. The disappearance of the SPR band was marked by a concomitant change from a reddish-brown color of the DS-CuNP colloid to milky-white.
of CuNP sol [values noted from Figure 5a], as a function of Hg$^{2+}$, exhibited a nearly linear relationship, as portrayed in Figure 5b. Initially, a steep decline in absorbance could be observed up to about $35 \times 10^{-2} \mu$M; however, after that point, the decline was slow. It could also be noted from the plot that the lowest Hg$^{2+}$ concentration that was able to effect a change in CuNP absorbance was as small as 1 $\mu$M. Such a spectral change noticeable from UV-vis spectra, though small, is only of academic relevance, for no visual color change could be detected with a meager 1 $\mu$M Hg$^{2+}$ concentration. The practical limit for the visual detection of color change of the original CuNP colloid was found to be that using 10 $\mu$M Hg$^{2+}$.

Additionally, on fitting a trendline to the data, a best-fit straight line with a negative value of slope was obtained. The declining slope and a gradual fall in absorbance is possibly indicative of the minuscule nature of changes brought about on every injection of Hg$^{2+}$, in addition to the effect of dilution.

As an auxiliary experiment that was carried out to check if dilution alone were responsible for the drop in CuNP absorbance and the nature of the observed spectra, we added liquid water, sans Hg$^{2+}$, to CuNP sol, and the spectra were recorded (Figure S2). The spectra so-obtained were found to be different from those in Figure 5a. Although a decline of the absorbance value of the CuNP solution (starting 3 mL) upon dilution is apparent, one could observe that the nature of the spectral lines on going from a spectrum corresponding to the concentrated solution to the one for a dilute solution remained the same. Besides, a rapid line broadening that was observed for a Hg$^{2+}$-treated sample was missing in the dilution experiment spectra. Needless to mention that, in addition to the broadening of the band, the attenuation of the SPR peak was predominantly higher for the Hg$^{2+}$-CuNP solution than for the dilute solution of CuNPs (results summarized in Table S1), when identical volumes of Hg$^{2+}$ solution and water were added to CuNP colloid. Lastly, the color of the final dilute CuNP solution (8.4 mL) appeared bluish (possibly due to the oxidation of CuNPs to Cu$^{2+}$), whereas, as mentioned above, Hg$^{2+}$-CuNP solution eventually turned white. This suggests that Hg$^{2+}$ indeed had a role in dampening the CuNP plasmon band and bringing about a change in the solution color.

It is also imperative to state here that a chemical reaction between mercuric ion and zerovalent copper atom is possible according to the following equation.

$$
\text{Cu}^{0} + \text{Hg}^{2+} \rightarrow \text{Cu}^{2+} + \text{Hg}^{0}
$$

From the standard reduction potential values $E^0_{\text{Cu}^{+}/\text{Cu}} = 0.34$ V and $E^0_{\text{Hg}^{2+}/\text{Hg}} = 0.80$ V (at 25 °C), taken from standard textbooks, the $E^0$ was calculated to be $E^0 = 0.80 - 0.34 = 0.46$ V. The positive value of $E^0$ suggests that the above reaction is favorable. This certifies that the reduction in the absorbance value of CuNPs marked by a change in its color upon mixing with Hg$^{2+}$ is due to the aforementioned redox reaction. Furthermore, formation of CuNP aggregates is also possible owing to the occurrence of chemical reactions in the medium.

![Figure 5](https://example.com/figure5.png)

Figure 5. (a) UV–Vis spectra of DS-CuNP sol in the presence of varying concentration of Hg$^{2+}$ (Legend: value $\times 10^{-2} \mu$M). (b) Plot of maximum absorption of CuNPs at $\lambda_{\text{max}}$ against [Hg$^{2+}$].

![Figure 6](https://example.com/figure6.png)

Figure 6. DLS profiles of DS-CuNPs (a) before and (b) after treatment with Hg$^{2+}$. 

![Table S1](https://example.com/tableS1.png)
The formation of such aggregates could also be one of the reasons for the broadening of the spectral band. Further, dynamic light-scattering (DLS) measurements were conducted to probe the size distribution of particles, particularly the hydrodynamic diameter of nanostructures. Figure 6a,b shows the particle size distribution plots of DS-CuNPs and Hg^{2+}-treated DS-CuNPs. It may be mentioned here that the latter sample was the one prepared by having the highest [Hg^{2+}] in the medium of CuNPs, as mentioned under UV–vis results. It could clearly be noticed that the DS-CuNPs possessed a hydrodynamic diameter of 20–30 nm. However, for the Hg^{2+}-DS-CuNP sample, the hydrodynamic diameter was observed at 200–250 nm. This hints at the possible formation of aggregates of CuNPs upon mixing DS-CuNPs with Hg^{2+}. DLS spectra of control samples consisting of SDS-Hg^{2+} solution and pure SDS solution, provided in Figure S3a,b, showed the size distribution for both samples as 1 nm. These supporting data helped us to figure out that no aggregates had formed between a mixture of SDS micelles and Hg^{2+} and that the size of SDS-Hg^{2+} is the same as pure SDS. Hence, it could be stated that the observations from DLS studies were in accord with UV–vis studies so long as the formation of aggregates of CuNPs in the presence of mercury cation is considered.

The results of DLS measurements were corroborated by a TEM investigation of an Hg^{2+}-treated DS-CuNP solution (with highest [Hg^{2+}], mentioned above). It could be observed from Figure 7a that a large number of structures, mostly spherical in shape and sizes on the order of 250 nm or higher, had formed in the solution. These superstructures, on magnification, revealed the existence of tens of hundreds of NPs in close proximity to each other [Figure 7b,c], akin to NP agglomerates, but with the exception that the NPs are somewhat detached from each other, giving unaggregated structures. It seems also that some particles underwent coalescence with others, forming somewhat bigger particles here and there. We conjecture that it could be because of the presence of these unaggregated superstructures and larger particles in the medium that broadening of the UV–vis band might have occurred, progressively with the rise in [Hg^{2+}] in CuNP solution. This also justifies the cause for the nonevolution of a band or shoulders in the longer wavelength region, an observation identical to that of a previously reported study.29 Thus, UV–vis, DLS, and TEM measurements collectively confirm the formation of superstructures or aggregates consisting of CuNPs as the building blocks, when in the presence of Hg^{2+}.

Identical to the detection of Hg^{2+}, the experiments relating the determination of Cd^{2+} and Pb^{2+} ions revealed the diminishing of the SPR band of DS-CuNPs when the concentration of the metal ions was increased. The results of the analyses involving the two cations are presented in Figure 8. It is noticed from the figure that the amounts of metal ions required for affecting the SPR is way higher than that using Hg^{2+}. Further, physical interactions between the cationic species (Cd^{2+}, Pb^{2+}) and CuNPs might be a possible reason for the resultant change in the NP SPR band, unlike Hg^{2+}, which is able to chemically react with CuNPs.

In both the cases involving Pb^{2+} and Cd^{2+} ions, precipitation of CuNPs resulted in a final observation of solution color—white or greyish-white, as shown in Figure 9. The same figure also depicts the photographs of solutions corresponding to treatment of DS-CuNPs with a series of other heavy metal ions. All in all, the colorimetric detections of the ions Hg^{2+}, Pb^{2+}, and Cd^{2+} were prominent using CuNPs. The limit of detection was found to be 10 μM for Hg^{2+} and relatively higher for Cd^{2+}/Pb^{2+}.

Interestingly, the sensing experiment of Hg^{2+} using DS-CuNPs suspended on a paper led to remarkable results. Precisely, test paper strips containing CuNPs, when dipped into different heavy metal ion solutions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ca^{2+}), showed no significant changes for the metal solutions of Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ca^{2+}. However, when a few drops of Hg^{2+} were added to the brownish-yellow test paper strip, decoloration of the paper resulted in a spectrum of colors ranging from yellow to pale yellow and milky-white, by varying [Hg^{2+}] (Figure 10 & Figure S4). As mentioned above, a redox reaction between Hg^{2+} and Cu^{0} is possibly responsible for bringing about a color change to the paper strip, on exposure to a Hg^{2+}-containing solution. In stark contrast, the reduction potential values of Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ca^{2+} are lower than those of Cu^{2+}/Cu, for which auto oxidation—reduction is not favorable. It is for this reason that these ions fail to affect any color change to the paper strips. However, it might be possible that, at higher concentrations, these ions could change the color of paper strips. But, that change would be ascribed to physical interactions between the metal ions and CuNPs and not because of a chemical reaction.

### CONCLUSIONS

We have reported the synthesis of a stable CuNP dispersion by a chemical reduction method using dodecyl sulfate ion as a surface passivating agent. The particles were characterized using routine techniques like UV–vis spectroscopy, Fourier transform infrared spectroscopy, dynamic light scattering, and
transmission electron microscopy. The as-prepared DS-CuNP colloid was treated with a host of heavy metals, which indicated that DS-CuNPs are highly selective and sensitive toward Hg\(^{2+}\) ions. The detection limit was in the range of 10 \(\mu\)M. Further, test paper strips containing the CuNPs facilitated the detection of Hg\(^{2+}\) by a visual change in its color. The method is robust in that it involves the use of a low-cost, easy detection and easily disposable paper strips. We believe that this method would offer a new approach for the detection of heavy metal ions in aqueous, biological, and environmental samples, for an evolving point-of-care detection of toxic metal ions.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03687.

Characterization methods, TEM images, UV–vis spectra, DLS profiles of samples, and experimentation scheme for Hg\(^{2+}\) sensing (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Subhojit Das — Department of Chemistry, National Institute of Technology Agartala, Tripura 799046, India; 
[orcid.org/0000-0003-3754-6616](https://orcid.org/0000-0003-3754-6616); Email: sdas.chem@nita.ac.in

**Authors**

Trilochan Baral — Department of Chemistry, National Institute of Technology Agartala, Tripura 799046, India

Chitraniva Datta — Department of Chemistry, National Institute of Technology Agartala, Tripura 799046, India

**Figure 8.** UV–Vis spectra of DS-CuNPs in the presence of (a) Cd\(^{2+}\) and (b) Pb\(^{2+}\) solutions of different concentrations (Legend: concentrations of metal ions expressed in \(\mu\)M units).

**Figure 9.** Photograph of DS-CuNP solution after being treated with different metal ions (conc \(\approx\) 10 \(\mu\)M).

**Figure 10.** Test paper strips treated with a range of concentration of Hg\(^{2+}\) solution.
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank CRF, NIT Agartala for providing the instrumental support. S.D. thanks A. Hajra, IIT Guwahati, for helping with the TEM results.

■ REFERENCES

(1) Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B. B.; Beeregowda, K. N. Toxicity, mechanism and health effects of some heavy metals. Interdiscip. Toxicol. 2014, 7, 60–72.
(2) Ferner, D. J. Toxicity of heavy metals. eMed. J. 2001, 2, 1.
(3) Hu, X. F.; Lowe, M.; Chan, H. M. Mercury exposure, cardiovascular disease, and mortality: A systematic review and dose-response meta-analysis. Environ. Res. 2021, 193, 110538.
(4) Mutlu, A.; Lee, B. K.; Park, G. H.; Yu, B. G.; Lee, C. H. Long-term concentrations of airborne cadmium in metropolitan cities in Korea and potential health risks. Atmos. Environ. 2012, 47, 164–173.
(5) Wani, A. L.; Ara, A.; Usmani, J. A. Lead toxicity: a review. Interdiscip. Toxicol. 2015, 8, 55–64.
(6) Nolan, E. M.; Lippard, S. J. Tools and Tactics for the Optical Detection of Mercuric Ion. Chem. Rev. 2008, 108, 3443–3480.
(7) Tseng, C.; Chang, H.-Y.; Chang, J.-Y.; Huang, C.-C. Detection of mercury ions based on mercury-induced switching of enzyme-like activity of platinum/gold nanoparticles. Nanoscale 2012, 4, 6823–6830.
(8) Cheng, X.; Li, Q.; Qin, J.; Li, Z. A new approach to design ratiometric fluorescent probe for mercury(II) based on the Hg^{2+}-promoted deprotection of thioacetals. ACS Appl. Mater. Interfaces 2010, 2, 1066–1072.
(9) Xiang, Y.; Wang, Z.; Xing, H.; Wong, N. Y.; Lu, Y. Label-free fluorescent functional DNA sensors using unmodified DNA: A vacant site approach. Anal. Chem. 2010, 82, 4122–4129.
(10) Lee, J.-S.; Han, M. S.; Mirkin, C. A. Colorimetric detection of mercuric ion (Hg^{2+}) in aqueous media using DNA-functionalized gold nanoparticles. Angew. Chem., Int. Ed. 2007, 46, 4093–4096.
(11) Li, T.; Li, B.; Wang, E.; Dong, S. G-quadruplex-based DNAzyme for sensitive mercury detection with the naked eye. Chem. Commun. 2009, 3551–3553.
(12) Zhang, F.; Zeng, L.; Yang, C.; Xin, J.; Wang, H.; Wu, A. A one-step colorimetric method of analysis detection of Hg^{2+} based on an in situ formation of Au@HgS core–shell structures. Analyst 2011, 136, 2825–2830.
(13) Liu, C.-W.; Hsieh, Y.-T.; Huang, C.-C.; Lin, Z.-H.; Chang, H.-T. Detection of mercury(II) based on Hg^{2+}–DNA complexes inducing the aggregation of gold nanoparticles. Chem. Commun. 2008, 2242–2244.
(14) Wang, H.; Wang, Y.; Jin, J.; Yang, R. Gold nanoparticle-based colorimetric and “turn-on” fluorescent probe for mercury(II) ions in aqueous solution. Anal. Chem. 2008, 80, 9021–9028.
(15) Li, Y.; Wu, P.; Xu, H.; Zhang, Z.; Zhong, X. Highly selective and sensitive visualizable detection of Hg^{2+} based on anti-aggregation of gold nanoparticles. Talanta 2011, 84, 508–512.
(16) Alzahrani, E.; Ahmed, R. A. Synthesis of copper nanoparticles with various sizes and shapes: Application as a superior nonenzymatic sensor and antibacterial agent. Int. J. Electrochem. Sci. 2016, 11, 4712–4723.
(17) Jia, X.; Li, J.; Wang, E. Cu nanoclusters with aggregation induced emission enhancement. Small 2013, 9, 3873–3879.
(18) Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically precise colloidal metal nanoclusters and nanoparticles: Fundamentals and opportunities. Chem. Rev. 2016, 116, 10346–10413.
(19) Khlebtsov, N. G.; Dykman, L. A. Optical properties and biomedical applications of plasmonic nanoparticles. J. Quant. Spectrosc. Radiat. Transfer 2010, 111, 1–35.
(20) Xu, M.; Obodo, D.; Yadavalli, V. K. The design, fabrication, and applications of flexible biosensing devices. Biosens. Bioelectron. 2019, 124–125, 96–114.
(21) Guo, Y.; Cao, F.; Lei, X.; Mang, L.; Cheng, S.; Song, J. Fluorescent copper nanoparticles: recent advances in synthesis and applications for sensing metal ions. Nanoscale 2016, 8, 4852–4863.
(22) Ahmed, M. Synthesis and structural analysis of copper (II) glutathione complexes via Cu-S linkage. World Appl. Sci. J. 2014, 29, 1357–1362.
(23) Prabhash, P. G.; Nair, S. S. Synthesis of copper quantum dots by chemical reduction method and tailoring of its band gap. AIP Adv. 2016, 6, 055003.
(24) Wang, C.; Ling, L.; Yao, Y.; Song, Q. One-step synthesis of fluorescent smart thermo-responsive copper clusters: A potential nanothermometer in living cells. Nano Res. 2015, 8, 1975–1986.
(25) Cui, M.; Song, G.; Wang, C.; Song, Q. Synthesis of cysteine-functionalized water-soluble luminescent copper nanoclusters and their application to the determination of chromium(VI). Microchem. Acta 2015, 182, 1371–1377.
(26) Begleitsova, N.; Selifonova, E.; Chumakov, A.; Al-Alwani, A.; Zakharievich, A.; Chernova, R.; Glukhovskoy, E. Chemical synthesis of copper nanoparticles in aqueous solutions in the presence of anionic surfactant sodium dodecyl sulfate. Colloids Surf. A: Physicochem. Eng. Asp. 2018, 552, 75–80.
(27) Gawande, M. B.; Goswami, A.; Felpin, F.-X.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R. S. Cu and Cu-based nanoparticles: Synthesis and applications in catalysis. Chem. Rev. 2016, 116, 3722–3811.
(28) Cheng, X.; Zhang, X.; Yin, H.; Wang, A.; Xu, Y. Modifier effects on chemical reduction synthesis of nanostructured copper. Appl. Surf. Sci. 2006, 253, 2727–2732.
(29) Giorgi-Coll, S.; Marín, M. J.; Sule, O.; Hutchinson, P. J.; Carpenter, K. L.H. Aptamer-modified gold nanoparticles for rapid aggregation-based detection of inflammation: An optical assay for interleukin-6. Microchem. Acta 2020, 187, 13.