Glutathione-capped *Syzygium cumini* carbon dot-amalgamated agarose hydrogel film for naked-eye detection of heavy metal ions

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**Abstract**

Development of a facile and sensitive analytical tool for the detection of heavy metal ions is still a challenging task because of interference from other chemical species. In this work, glutathione (GSH)-capped *Syzygium cumini* carbon dots (CDs) have been integrated with agarose hydrogel film and used as an amalgamated solid probe for sensing of different metal ions (Pb²⁺, Fe³⁺, and Mn²⁺). The synthesis of a solid sensing platform is based on the electrostatic interactions between GSH-capped *Syzygium cumini* CDs and agarose hydrogel. The developed hydrogel-based solid probe exhibited good linealities with the concentration ranges of metal ions from 0.005 to 0.075, 0.0075 to 0.1, and 0.0075 to 0.1 mM with detection limits of 1.3, 2.5, and 2.1 μM for Pb²⁺, Fe³⁺, and Mn²⁺ ions, respectively.

**Keywords:** GSH-capped CDs-hydrogel, Metal ions, UV-visible and fluorescence spectrometry

**Introduction**

Heavy metal ions have been considered as potential agents to contaminate various environments including water, soil, and air (Gong et al. 2016). Even at low concentrations, they exhibited a highly toxic nature and caused serious health problems in various living systems (Gong et al. 2016; Callender 2003; Roy 2010). Heavy metal ions are effectively accumulated in various living organisms and seriously damaged various organs/systems including the nervous, immune, reproductive, and gastrointestinal systems (Afkhami et al. 2013; Gumpu et al. 2015). Among the metals ions, cadmium, lead, chromium, mercury, and arsenic have been recognized as potential toxic agents to ecology (Pujol et al. 2014; Prabhakar et al. 2012; Kim et al. 2012; Bernalte et al. 2011). Therefore, it is highly desirable to develop a simple analytical strategy for the detection of the above metal ions in environmental water samples. Furthermore, various international organizations such as the World Joint Food and Agricultural Organization, the Health Organization, the Centre for Disease Control, the US Environmental Protection Agency, and the European Union have set the maximum permissible limit of their concentration in water by following the environment quality standards (Gumpu et al. 2015; WHO, Guidelines for Drinking-water Quality, 4th edition 2011; Directive, 2013/35/EU of the European Parliament and of the Council 2013; Standard methods for the examination of water and wastewater 2012). In view of this, the identification of trace-level metal ions plays a key role in the monitoring of toxic metal ions in various environmental and food samples.

To identify the above metal ions, various spectroscopic techniques including inductively coupled plasma mass spectroscopy (Wang et al. 2015), atomic absorption spectroscopy (Pohl 2009; Trindade et al. 2015; Kenawy et al. 2000), X-ray fluorescence spectrometry (Sitko et al. 2015), and neutron activation analysis and inductively coupled plasma optical emission spectrometric (Losev et al. 2015) have been used for the quantification of metal ions in
multifaceted matrices at nanomolar concentrations. However, these techniques are very costly and involved tedious sample preparations with skilled persons. Further, some of the techniques are needed to be coupled with chromatographic techniques for the separation and identification of metal ions from various environments (Array and Merkoci 2012). Therefore, it is essential to establish a simple visual analytical tool for the selective detection of the above metal ions in various environments (Cui et al. 2015).

Hydrogels are crosslinked 3D network structures that belong to soft materials. Recently, hydrogels have been integrated with various analytical applications including drug delivery and sensing of various chemical species (Ullah et al. 2015). To support this, hydrogel-based refractive delivery and sensing of various chemical species (Ullah et al. 2015). Moreover, Cu²⁺, Pb²⁺, and Ag⁺ ions were visually detected by fabricating hydrogels, and the method was able to detect metal ions even at a nanomolar concentration (Hong et al. 2011). To enhance the sensing ability of hydrogels, recently, various nanostructured materials and biomolecules have been incorporated into hydrogels and used as a probe for sensing of various chemicals species (Gogoi et al. 2015; Ye et al. 2012; Nam et al. 2018; Yan et al. 2017; Zhu et al. 2010). Apart from these reports, upconversion nanoparticles have also been used as probes for the detection of various metal ion (Gu and Zhang 2018; Gu et al. 2016a; Gu et al. 2016b).

Herein, hydrogel-based visual strips have been fabricated for the detection of metal ions (Pb²⁺, Fe³⁺, and Mn²⁺) by incorporating glutathione (GSH)-capped fluorescent CDs into hydrogels. In this work, fluorescent CDs were fabricated from Syzygium cumini fruits by one-step hydrothermal treatment (Bhamore et al. 2016). Briefly, 15 mL of Syzygium cumini fruit juice was taken into a reaction flask that contains 85 mL of water. The reaction flask was inserted in autoclave reaction, and then carbonization was carried out at 180 °C for 6 h. The obtained black residue was dialyzed against Milli-Q-purified water for 6 h using a dialysis membrane (molecular weight cut off = 70 kDa). The isolated CDs were stored at 4 °C for further use. Further, the GSH was used as a capping agent for functionalizations of CDs. In this, 5 mM of 2.5 mL GSH was added to 20 mL of as-prepared CDs, and then the solution was stirred for 3 h.

Preparation of agarose hydrogel film

Agarose hydrogel was prepared by modifying the procedure described by Gogoi et al. Simply, 2.5% (w/v) of agarose solution was prepared by dissolving 0.25 g of agarose in 10 mL of 0.1 M NaOH solution. Then, the above solution was microwave heated at 180 °C for 30 s to dissolve the agarose. To form the film, the obtained solution was poured onto a petri dish and kept it for 12 h at room temperature.

Preparation of GSH-capped CD agarose hydrogel film

The GSH-capped CD-amalgamated agarose hydrogel was prepared by the following procedure. To this, 2.5% (w/v) of agarose was taken into a reaction beaker that contained 10 mL of GSH CDs and 1.0 M of NaOH solution (1:1 v/v). The solution was microwave heated for 30 s at 180 W. The hydrogel film was prepared by pouring the above solution into the petri dish and followed by drying at room temperature for 12 h.
Visual detection of metal ions

In order to examine the visual detection ability of prepared hydrogel towards metal ions, the GSH CD-agarose hydrogel film was cut into 2.0 × 2.0 cm and then the films were dipped separately into various metal ion solutions (Pb\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\), Cr\(^{3+}\), Hg\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Co\(^{2+}\) ions, 1.0 mM) and kept them stand for 12 h at room temperature. The dipped hydrogel films were dried, and their photographic images were measured by a digital camera. It was noticed that only Pb\(^{2+}\), Fe\(^{3+}\), and Mn\(^{2+}\) ions were significantly induced color changes of GSH CD-hydrogel film.

To establish a hydrogel film-based analytical strategy, various concentrations of Pb\(^{2+}\), Fe\(^{3+}\), and Mn\(^{2+}\) ions (0.005–1.0, 0.0075–1.0, and 0.0075–1.0 mM) were prepared and then the GSH CD-hydrogel films were treated with the above metal ion concentrations for 12.0 h at room temperature. The color changes of GSH CD-hydrogel films were measured by a digital camera and were measured by the ImageJ program by quantifying relative to the background of hydrogel film without the three metal ions.

Results and discussion

A green and one-step synthetic method was developed for the fabrication of GSH-capped CD agarose hydrogel film. The fabricated hydrogel film was used as a solid probe for visual detection of the three metal ions (Pb\(^{2+}\), Fe\(^{3+}\), and Mn\(^{2+}\)) (Scheme 1). Initially, fluorescent CDs were fabricated from *Syzygium cumini* fruits and then capped with GSH. To confirm the formation of CDs and GSH-capped CDs, the spectroscopic techniques (UV-visible, fluorescence, and FT-IR) were studied for the characterization of CDs and GSH CDs. Figure 1 shows the absorption spectra of CDs derived from *Syzygium cumini* fruits, GSH, and GSH-capped CDs. The UV-visible absorption spectra of the above compounds show maximum absorbance at 312, 299, and 316 nm for CDs, GSH, and GSH-capped CDs, respectively. The as-synthesized CDs exhibited absorption spectrum at 312 nm which is due to π-π* and n-π* transitions in CDs. The GSH-capped CDs showed tremendous excitation-dependent emission spectra by exciting at various excitation wavelengths. The distinctive red shift was observed in the emission wavelength upon the excitation at different wavelengths from 340 to 440 nm (Supporting Information of Figure S1). As shown in Supporting Information of Figure S2, the GSH-capped CDs exhibited fluorescence emission spectrum at 453 nm when excited at 370 nm with a quantum yield of 6.1%.

The morphology and size of CDs derived from *Syzygium cumini* fruits were investigated by using HR-TEM and DLS. As shown in Fig. 2a, b, the size of the as-synthesized CDs was 2.1 ± 0.7 nm, which was calculated from the histogram graph of HR-TEM. The DLS data also confirm that the mean size of CDs was 3.1 ± 0.5 nm and GSH-capped CDs was 4.2 ± 0.3 nm (Supporting Information of Figure S3), which is well-matched with HR-TEM data. As displayed in Supporting Information of Figure S4, the zeta potential of GSH-capped CDs was observed at 47.1 mV. Importantly, it can be noticed that there are slight changes in the UV-visible absorption and fluorescence spectra of CDs and GSH CDs, suggesting the functionalizations of CDs with GSH molecules.

Further, the FT-IR spectra of CDs, GSH, and GSH-capped CDs are shown in Fig. 3. The peak at 3418 cm\(^{-1}\) represents the O–H stretching of CDs. The characteristic peaks at 2925 and 1400 cm\(^{-1}\) correspond to the –C–H stretching and bending of CDs. Similarly, the –C=O stretching of CDs was observed at 1625 cm\(^{-1}\). As shown in the GSH FT-IR spectrum in Fig. 3 (b), stretching of the N–H, S–H, and –C=O groups was observed at 3346, 2521, and 1715 cm\(^{-1}\), respectively. The C–H and O–H group bending was observed at 1398 and 923 cm\(^{-1}\), respectively. After capping with GSH, the –O–H/=–N–H stretching was observed at 3423 cm\(^{-1}\) and the stretching of –C=O peak was slightly shifted to 1633 cm\(^{-1}\) (Fig. 3 (c)), confirming the formation of GSH CD-hydrogel. These structural features play a significant role to incorporate GSH CD nanostructures into agarose hydrogels, which can be fabricated as a solid probe for visual detection of metal ions.

GSH-capped CD-agarose hydrogel as a visual sensor

In order to examine the distinctive analytical application of prepared hydrogel film, first, the visual detection ability of bare agarose hydrogel film and GSH-capped CD-agarose hydrogel film were studied by keeping 2.0 × 2.0 cm films (thickness ~ 0.3 mm) separately into various metal ion (Pb\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\), Cr\(^{3+}\), Hg\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\), and Co\(^{2+}\) ions, 1.0 mM) solutions. The color changes were monitored by taking photographic images by a digital camera (Fig. 4). It can be noticed that the bare agarose...
hydrogel film did not show any visual changes when treated with metal ions. However, the GSH-capped CD-agarose hydrogel film showed distinct color changes only with three metal ions (Pb²⁺, Fe³⁺, and Mn²⁺). The color of GSH CD-hydrogel film was changed to white, brown, and dark brown colors for Pb²⁺, Fe³⁺, and Mn²⁺ ions, respectively. These color changes are due to the formation of metal GSH CD-hydrogel complexes, which can be visualized with the naked eye. The other metal ions (Cr³⁺, Hg²⁺, Cu²⁺, Cd²⁺, and Co²⁺ ions) showed negligible color changes, indicating that GSH CD-modified hydrogel acts as a solid probe for visual detection of Pb²⁺, Fe³⁺, and Mn²⁺ ions.

**Sensitivity study for the visual detection of three metal ions with GSH-capped CD-agarose hydrogel film as a solid probe**

In order to establish the analytical platform for the three metal ions individually, different concentrations of the three metal ions (Pb²⁺, 0.005–1.0 mM; Fe³⁺, 0.0075–1.0 mM; Mn²⁺, 0.0075–1.0 mM) were taken separately into sample vials and then treated with GSH-capped CD-agarose hydrogel (2.0 × 2.0 cm, thickness ~ 0.3 mm) for 12 h. The metal ion-treated hydrogel film strips were taken out, and then their color changes and color intensities were measured for the quantification of the three metal ions (Fig. 5). The color changes (Pb²⁺ ion → white,
Fe$^{3+}$ ion→brown, and Mn$^{2+}$ ion→dark brown) were progressively increased with increasing concentration of metal ions, which can be noticed with the naked eye. The color intensities of metal ion-treated hydrogel films were measured (before and after immobilization to GSH CD-hydrogel film) by analyzing them with the ImageJ software, and then calibration graphs were constructed between color intensities and the concentrations of the three metal ions. As a result, good linearities were observed between the color intensities and the concentration ranges of 0.005–0.075 mM for Pb$^{2+}$ ion and 0.0075–0.1 mM for Fe$^{3+}$ and Mn$^{2+}$ ions with a correlation coefficient of 0.9891, 0.9915, and 0.9873 for Pb$^{2+}$, Fe$^{3+}$, and Mn$^{2+}$ ions, respectively (Fig. 6). The detection limits were 1.3, 2.5, and 2.1 μM for Pb$^{2+}$, Fe$^{3+}$, and Mn$^{2+}$ ions, respectively (LOD = 3.3 × standard deviation of blank/slope ($n = 3$)). Additionally, the accuracy and precision of the as-synthesized GSH CD-hydrogel film for Pb$^{2+}$, Fe$^{3+}$, and Mn$^{2+}$ ions were mentioned in Supporting Information of Table S1. These results indicate that GSH CD-agarose hydrogel film acts as a promising solid probe for visual detection of Pb$^{2+}$, Fe$^{3+}$, and Mn$^{2+}$ ions.
Fig. 5 Photographic images of GSH CD-agarose hydrogel films treated with different concentrations of Pb$^{2+}$ (0.005–1.0 mM), Fe$^{3+}$ (0.0075–1.0 mM), and Mn$^{2+}$ (0.0075–1.0 mM).

Fig. 6 Calibration graph plotted between the color intensities of hydrogel films and different concentrations of a Pb$^{2+}$ ion in the range of 0.005–0.075 mM, b Fe$^{3+}$ ion in the range of 0.0075–0.1 mM, and c Mn$^{2+}$ ion in the range of 0.0075–0.1 mM.
without the aid of sophisticated instruments, which avoids tedious sample preparations. As shown in Table 1, GSH CD-agarose hydrogel film as a probe was compared with gold (Au) interdigitated electrodes, Au nanoparticles (Au NPs), AT-cut Au-coated quartz crystal, graphene quantum dots (GQDs) and Au NPs, L-tyrosine silver NPs (Ag NPs), and poly-L-α-glutamic acid (PGA) for Pb^{2+} ion (Cui et al. 2016; Teh et al. 2014; Niu et al. 2018; Annadhasan et al. 2014; Hu and Elioff 2018). For Fe^{3+} ion, various fluorometric methods were based on GQDs, sulphur-doped carbon dots (C-dots) and carbon quantum dots (CQDs), cranberry CDs, citric acid and (NH₄)₂HPO₄ CDs, alginic acid (AA) and ethane diamine (EDA) CDs (Zhang et al. 2019; Xu et al. 2015; Wu et al. 2018; Zulfajri et al. 2019; Chandra et al. 2016; Liu et al. 2015). Various colorimetric methods based on 4-mercaptobenzoic acid (4-MBA) and melamine (MA)-modified Ag NPs, L-tyrosine Ag NPs and β-cyclodextrin Ag NPs, NH₂-MIL-125(Ti)/carbon paste electrode (CPE) photoirradiation cathodic stripping voltammetry (CSV) method, and carboxymethyl cellulose (CMC)/Tb(III) nanocomposite fluorometric method were compared with GSH CD-agarose hydrogel film for Mn^{2+} ion (Annadhasan et al. 2014; Xu et al. 2014; Ye et al. 2018; Hu et al. 2014). Furthermore, GSH CD-hydrogel film as a detection probe was used for standard samples of 1 mM of Pb^{2+}, Fe^{3+}, and Mn^{2+} and treated the same as described for the prepared solutions (Pb^{2+}, Fe^{3+}, and Mn^{2+}, 1 mM), and as shown in Supporting Information of Table S2, the obtained data of standard samples were well matched with the prepared metal ion solutions.

**Conclusions**

In conclusion, a simple synthetic protocol was established for the fabrication of GSH CD-agarose hydrogel film for the visual detection of three metal ions (Pb^{2+}, Fe^{3+}, and Mn^{2+}) without the aid of any analytical instrument. The GSH-capped CDs were successfully incorporated into the agarose hydrogel system and characterized by various spectroscopic techniques. These three metal ions effectively induced color changes (Pb^{2+} ion → white, Fe^{3+} ion → brown, and Mn^{2+} ion → dark brown color) of GSH CD-agarose hydrogel film, which can easily be observed with the naked eye. This color intensities of hydrogel film exhibited good linealities in the range of 0.005–0.075 mM for Pb^{2+} ion and of 0.0075–0.1 mM for Fe^{3+} ion.

**Table 1** Evaluation for the detection of Pb^{2+}, Fe^{3+}, and Mn^{2+} ion using GSH CD-agarose hydrogel film with various other established methods

| Method                        | Probe                                | Linear range (μM) | LOD (μM) | References                  |
|-------------------------------|--------------------------------------|-------------------|----------|----------------------------|
| Pb^{2+}                       | Electrochemical                      | 0.01–0.1          | 0.00661  | Cui et al. 2016            |
|                               | Quartz crystal microbalance with dissipation monitoring | 0.046–3          | 0.014 | Teh et al. 2014            |
|                               | Fluorescence                         | 0.05–4            | 0.0167   | Niu et al. 2018            |
|                               | Colorimetric                         | 0.016–0.1         | 0.016    | Annadhasan et al. 2014     |
|                               | Fluorescence                         | 66–261            | 0.098    | Hu and Elioff 2018         |
|                               | **Colorimetric- hydrogel film**      | 5.0–75            | 1.3      | Present method             |
| Fe^{3+}                       | Fluorescence                         | 3.5–670           | 1.6      | Zhang et al. 2019          |
|                               | Fluorescence                         | 1.0–500           | 0.1      | Xu et al. 2015             |
|                               | Fluorescence                         | 100–1000          | 0.177    | Wu et al. 2018             |
|                               | Fluorescence                         | 30–600            | 9.55     | Zulfajri et al. 2019       |
|                               | Fluorescence                         | 20–200            | 20       | Chandra et al. 2016        |
|                               | Fluorescence                         | 0–50              | 10.98    | Liu et al. 2015            |
|                               | **Colorimetric hydrogel film**       | 7.5–100           | 2.5      | Present method             |
| Mn^{2+}                       | Colorimetric                         | 0.5–10            | 0.05     | Zhou et al. 2012           |
|                               | Colorimetric                         | 0.016–0.5         | 0.016    | Annadhasan et al. 2014     |
|                               | Photoirradiation CSV                 | 0.01–10           | 0.004    | Xu et al. 2014             |
|                               | Fluorescence                         | 0.1–1000          | 0.046    | Ye et al. 2018             |
|                               | **Colorimetric hydrogel film**       | 7.5–100           | 2.1      | Present method             |
Fe\textsuperscript{3+} and Mn\textsuperscript{2+} ions with a correlation coefficient of 0.9891, 0.9915, and 0.9873 for Pb\textsuperscript{2+}, Fe\textsuperscript{3+}, and Mn\textsuperscript{2+} ions, respectively, with increasing concentrations of the three metal ions. The detection limits were 1.3, 2.5, and 2.1 μM for Pb\textsuperscript{2+}, Fe\textsuperscript{3+}, and Mn\textsuperscript{2+} ions, respectively. The fabricated GSH CD-agarose hydrogel film acts as a promising solid probe for the visual detection of the three metal ions, which can be used as a portable on-site solid probe for the detection of the three metal ions in environmental samples without any complicated sample preparations.

### Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s40543-020-00208-8.

**Additional file 1:** Supporting Information of Glutathione capped Syzygium cumini Carbon Dots Amalgamated Agarose Hydrogel Film for Naked-eye Detection of Heavy Metal Ions

**Abbreviations**

CDs: Carbon dots; DLS: Dynamic light scattering; FT-IR: Fourier transform infrared; GSH: Glutathione; HR-TEM: High-resolution transmission electron microscopy; NaOH: Sodium hydroxide; UV: Ultraviolet

**Authors’ contributions**

JRB carried out this work at the Applied Chemistry Department, S. V. National Institute of Technology, Surat, 395007, India. T-JR discussed the analytical characteristics of the prepared hydrogels. SKK supervised the entire work and edited the manuscript. All authors read and approved the final manuscript.

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**Availability of data and materials**

All the experiments were carried out at the Applied Chemistry Department, SVNIT, Surat, India. Analytical data (UV-visible, FT-IR, DLS, and fluorescence) were measured, which are available at the Applied Chemistry Department, SVNIT, Surat. All the data are available from the corresponding author (Dr. Suresh Kumar Kailasa) of this manuscript. HR-TEM images were measured at the Central Salt and Marine Chemicals Research Institute, Bhavnagar, Gujarat. Research data have been provided in the manuscript and supporting information files.

**Competing interests**

The authors declare that they have no competing interests.

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