Preparation of topographically remarkable cobalt microspheres for colorimetric detection of dopamine and elucidation of its sensing mechanism

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Abstract

In this work, a new colorimetric probe is prepared and demonstrated for the detection of dopamine (DA), an important neurotransmitter. The proposed colorimetric probe is prepared using bovine serum albumin (BSA) modified cobalt hydroxide microspheres (CoMSPs@BSA) and subsequently explored for the selective colorimetric detection of DA. The sensing studies are monitored using UV–visible absorbance spectroscopy. Interestingly upon addition of DA, an intense blue color is formed suggesting the potential use of this probe for naked eye detection of DA. The mechanism behind the sensing is investigated using time dependent UV–visible absorbance spectroscopic study and cyclic voltammetry. These studies clearly indicate the ligand exchange reaction is responsible for the resultant blue color formation. Further using this colorimetric probe a concentration range from 5.3 to 211 μM DA could easily be detected. Limit of detection of this DA sensor is found to be 5×10^{-6} M. Similarly a linear relation is observed from the calibration graph plotted between the concentration and absorption intensity corresponding to ligand exchange of BSA by DA. Moreover, this sensing probe (CoMSPs@BSA) is found to be highly selective among a wide range of other commonly interfering biomolecules.

Graphic abstract Topographically remarkable cobalt microspheres are prepared using a simple method and explored for the colorimetric detection of dopamine. The sensing mechanism is elucidated using UV–visible spectroscopic and electrochemical studies.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-0972-8>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2019) 1:938 | <https://doi.org/10.1007/s42452-019-0972-8>

Received: 26 March 2019 / Accepted: 22 July 2019 / Published online: 30 July 2019

Keywords Biosensor · Bovine serum albumin · Cobalt microspheres · Colorimetric method · Dopamine · Nanostructures · Sensing mechanism

1 Introduction

The neurotransmitter, dopamine (DA) is one of the renowned potential biomarkers, which is primarily used to assess the mental health and social behavior of human beings [1]. The concentration of DA in human blood ranges from 26 to 40 μM , spinal fluid in the range of nM while in urine the upper reference limit is estimated to be 3.3 μM especially during pregnancy, intravenous dopamine consumption, carcinoid tumour and medicated conditions [2, 3]. More importantly, DA is the main constituent of food samples and the majorly prescribed drug for diseases like Parkinson disease, bronchial asthma, hypertension and cardiac surgery [4, 5]. Hence devising strategies for the selective detection and quantification of DA becomes important. Though the determination of DA is reported using several techniques like fluorimetry, high performance liquid chromatography (HPLC), electrochemical methods and chemiluminescence etc.; the colorimetric method is yet a simple, cheap method and offers naked eye detection [1, 6–8].

Generally noble metals are preferred for colorimetric sensing methods. Major drawbacks of using noble metals are their scarcity and higher cost [9]. In order to develop specific colorimetric probes, functionalization of such probes is found to be a more suitable option since

it offers highly selective optical signals. Usually, metal ions will portray the minor alteration in the receptor site through the optical spectra. In general, Fe(III), Co(II) and Ni(II) ions have less binding affinity towards the analytes and it is least preferred in sensor applications [10]. Being a bi-dentate ligand, DA coordinates to metal ions through its catechol group and cobalt complexes are promising for DA coordination. Baniyaghoob et al. studied the interaction mode of Schiff bases of cobalt complex with DA and reported a ligand exchange mechanism rather than a simple electron transfer reaction [11]. Similarly A. Bagheri and D. M. Boghaei analyzed the complexation of Co(II) with DA in water–ethanol system [12]. Comparably, the oxides of these metal ions are frequently used in colorimetry in presence of mediators where the metal acts as a catalyst and not an indicator of the analyte concentration [13, 14]. However, the modified $\text{Co}(\text{OH})_2$ based colorimetric sensor is not yet reported in literature to the best of our knowledge. The challenge of using cobalt hydroxide is its poor dispersibility that makes the analysis cumbersome. Modification and/or functionalization using surface binding groups will facilitate the dispersibility through steric or electrostatic repulsive interaction among the particles.

Natural polymers and biomolecules are preferred for surface functionalization due to their ease of availability and excellent chelating properties. Bovine serum albumin

Scheme 1 Pictorial representation of the preparation of CoMSPs and elucidation of mechanism behind DA sensing process

(BSA) is a bio-ligand that is capable of stabilizing and dispersing metal hydroxides [15, 16]. Xu et al. used BSA to conjugate cobalt based Schiff base complexes and demonstrated them as a potential superoxide anion radical scavenger [17]. This study shows the versatility of BSA towards cobalt binding ability. Based on these ideas, a new colorimetric probe namely, $\text{Co}(\text{OH})_2$ -BSA is designed and explored for the selective detection of DA.

In this work, cobalt microspheres (CoMSPs) are prepared using a simple reduction process and then conjugated with BSA to yield CoMSPs@BSA, a new sensing probe. This is utilized further for the selective colorimetric determination of DA. The proposed strategy is based on a ligand exchange reaction and the mechanism is proved by spectroscopic and electrochemical techniques. The synthesis pathway used for the preparation of sensing probe and the proposed colorimetric DA sensor is presented in Scheme 1.

2 Materials and methods

2.1 Chemicals

Chemicals used in this work include $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (HiMedia Laboratories, Mumbai, India), bovine serum albumin (HiMedia Laboratories, Mumbai, India), hydrazine (Merck Chemicals, Mumbai, India), KOH (Sigma Aldrich, Bangalore, India) and dopamine hydrochloride (Sigma Aldrich, Bangalore, India). All these chemicals were of analytical reagent grade and used as such without further purification.

Millipore water having a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ obtained from Milli-Q system was used for the preparation of stock solutions and for electrochemical analysis.

2.2 Preparation of CoMSPs

CoMSPs were prepared from $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and hydrazine. Specifically, about 5 mL of 0.2 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was mixed with 15 mL of 5 M hydrazine and kept aside without any disturbance. There was copious formation of pink colored precipitate immediately after the addition of hydrazine. This was allowed to stand for 30 min for the completion of precipitation. Finally, the excess CoSO_4 and hydrazine present in the reaction mixture were removed by continuous centrifugation with large quantity of water. Centrifugation was repeated until the pH of solution changed to neutral ($\text{pH} = 7.0$). Interestingly the color of this solution is changed into turquoise. It was then re-dispersed in 45 mL of Millipore water and incubated for 2 days when the color of the solution changed to pale green. Then 5 mL of this solution was diluted to 20 mL and used further for colorimetric studies. Finally the resultant CoMSPs were characterized using spectroscopic and microscopic techniques.

2.3 Colorimetric detection of DA

Sensing studies were carried out using the following procedure. About 20 mg/mL solution of BSA was prepared and added to CoMSPs solution in 1:5 ratio. It was then shaken well for complete mixing. Similarly, for optimization studies two other concentrations of BSA viz. 10 mg/

mL and 30 mg/mL were also prepared. Through UV–vis spectroscopic analysis, 20 mg/mL BSA was found to be optimum and it was used for DA sensing studies (Electronic Supplementary Information [ESI]; Fig. S1). Different volumes of DA solution viz., 0 μ L, 10 μ L, 30 μ L, 50 μ L, 70 μ L, 100 μ L, 150 μ L, 200 μ L, 250 μ L, 300 μ L and 400 μ L were added from the stock solution to CoMSP@BSA and the corresponding absorbance values were recorded for each of these additions. Utmost care was taken to keep the final volume to be constant by compensating the remaining volume with water.

2.4 Electrochemical studies

Electrochemical studies were performed to analyze the oxidation state associated with three different systems namely CoMSPs, CoMSPs@BSA and CoMSPs@BSA-DA. These studies were carried out using 0.1 M KOH aqueous solution as an electrolyte by drop casting 5 μ L of the respective material onto a pre-polished glassy carbon electrode (GCE). In case of time dependent studies carried out for analyzing the functional group interaction with CoMSPs, bare GCE was employed by using the respective system as the electrolyte. The corresponding cyclic voltammograms were recorded and analyzed. Platinum wire was used as a counter electrode and Ag/AgCl was used as a reference electrode for the electrochemical studies. All these experiments were carried out at room temperature and rest of the conditions if applied were mentioned in the respective diagram.

2.5 Instrumentation

UV–visible spectroscopic measurements were recorded using Perkin Elmer UV Win Lab 6.0.3.0730/1.61.00 Lambda 650 spectrophotometer. SEM images were analyzed by using Vega-3 TESCAN equipment. Electrochemical studies were carried out using Biologic instrument model SP–240 provided with EC Lab software. Electron paramagnetic resonance (EPR) spectra were recorded using Bruker EMX Plus instrument and Fourier transform infrared (FTIR) analysis was performed using Bruker Optik GmbH spectrometer. Furthermore X-ray diffraction (XRD) studies were carried out using Cu K α radiation having a wavelength of 1.540 Å as a source of X-ray within 2 θ range between 10° and 90° using XPERT-PRO multipurpose X-ray diffractometer procured from the Netherlands. Mass spectral analysis was carried out using liquid chromatography—ion trap mass spectrometer in the positive ion mode with the help of Electrospray ionization mass spectrometer, LC Q Fleet obtained from Thermo Fischer Instruments Limited, USA.

Fig. 1 XRD pattern of as-prepared cobalt microspheres (CoMSPs)

3 Results and discussion

3.1 Structural and morphological characterization of CoMSPs

Basically in this work, CoMSPs are synthesized using a simple reduction method and functionalized with BSA. The resultant material namely, CoMSPs@BSA is used as a probe for the colorimetric detection of DA. Apart from acting as a probe, BSA enables the dispersibility of the micrometer sized spheres. During the preparation of CoMSPs, various color changes are observed before and after pH alteration which corresponds to the formation of different products. The initial product formed immediately after hydrazine addition is pink in color which is the octahedral form of cobalt(II) hydroxide. On ageing it has further changed to blue color due to the intercalation of water molecules to form tetrahedral Co²⁺ arrangement [18]. Upon prolonged ageing, it turns into green color which arises due to the optical appearance of α -Co(OH)₂ [19]. In our case, the final resultant product is green in color and its corresponding XRD pattern is shown in Fig. 1. XRD pattern clearly shows the prominent peaks at 2 θ values of 11.91°, 27.02°, 32.88°, 35.03°, and 58.92° that can be assigned to (003), (006), (012), (015) and (110) planes of α -Co(OH)₂ respectively. These peak positions and associated planes agree very well with the values reported in literature [19, 20]. Formation of low intense and broad peaks indicate that α -Co(OH)₂ is less crystalline and particularly the plane at 35.03° corresponds to the two dimensional reflection of the unit cell that are turbo-statically stacked. These observations confirm the presence of α -hydrotalcite like phase in CoMSPs [18]. Due to this slippery of unit cell and to counter balance the positively charged Co(OH)_{2-x}, the

Fig. 2 SEM images of CoMSPs before (A) and after (B) modification with BSA

interstitial spaces of α -Co(OH)₂ are generally occupied with the ionic species or water molecules [20].

The texture and structural arrangement of CoMSPs are analyzed using SEM and the corresponding images are shown in Fig. 2. It is observed that the individual particles are spherical in shape comprising of several flakes which are systematically arranged. Overall the appearance of CoMSPs resembles a flower like structure (Fig. 2A). The shape of these microparticles is homogeneous and possesses uniform size. The average diameter of these MSPs is measured to be $\sim 1 \mu\text{m}$. Figure 2B shows the SEM image of CoMSPs after modification with BSA. This image vividly indicates that functionalization with BSA didn't alter the morphology much but the particles are aggregated together probably due to the highly viscous BSA which brings the particles together in solution.

Further EDAX analysis provides an arbitrary idea about the elemental composition of CoMSPs in which apart from cobalt, other species like nitrogen, oxygen and sulfur are also present (ESI; Fig. S2). Their corresponding atomic weight percentage to molecular weight ratios are calculated to be 0.93, 2.39, 0.27 and 0.07 respectively (ESI; Fig. S2). These values correspond to the empirical formulae of the proposed compound. Hence apart from one cobalt and two oxygen atoms, trace amounts of nitrogen and sulphur are also present due to the intercalated SO_4^{2-} and NO_3^- ions. FTIR spectrum (ESI; Fig. S3) of the resultant CoMSPs confirms further the presence of cobalt hydroxide. In case of CoMSPs, appearance of a transmittance band at 667 cm^{-1} corresponds to Co–O–H while that at 550 cm^{-1} corresponds to Co–O bond. Similarly the peak at 1638 cm^{-1} is ascribed to bending vibration of water and the peak at 3454 cm^{-1} is due to the presence of interlayer H_2O molecules and Co–OH group [18, 21]. Absence of any peaks in the region between 900 and 930 cm^{-1} rules out

the possibility of existence of hydrazine in the adsorbed form [22]. These results clearly show that the resultant compound is pure and comprises only of Co(OH)₂.

Since there is a possibility of cobalt salts to form complexes with hydrazine, it is essential to determine the exact molecular weight of the as-prepared compound. Mass spectroscopy is an ideal tool for the determination of exact molecular weight of the resultant compound. In order to ensure the absence of complex formation with hydrazine and to predict the exact composition, mass spectrum of the as-prepared compound is recorded. Electron-spray ionization mass spectrometry (ESI–MS) results display the formation of a base peak at $m/z = 93.56$, which is closely matched with our calculated $m/z = 92.947$ (ESI; Fig. S4). These results correlate very well with XRD, EDAX and FTIR analyses discussed earlier and confirm that CoMSPs is actually composed of α -Co(OH)₂.

3.2 Colorimetric sensing of dopamine

As-prepared CoMSPs are explored further for the colorimetric sensing of DA by functionalizing with BSA. The amount of BSA loading was optimized through monitoring the concentration dependent absorption intensity and subsequently by determining the selectivity. The UV–vis spectrum of unmodified CoMSPs has shown two absorbance peaks at 590 nm and 645 nm (ESI; Fig. S5(a)) corresponding to d–d transition states [23]. After modification with BSA, an additional low intense peak is formed at 370 nm [ESI; Fig. S5(b)] suggesting the conjugation of CoMSPs with BSA. This is supported by the observation of Xu et al. that BSA after conjugation with cobalt shows an absorbance within 300–500 nm wavelength region and it is often weakly conjugated with cobalt atom [17]. Also, while adding DA to this BSA conjugated CoMSPs, a

Fig. 3 **A** Photographic images depicting the color change after the addition of DA (79 μM) to (a) CoMSPs@BSA, (b) CoMSPs alone, (c) BSA alone and (d) cobalt sulfate alone containing solutions respectively. **B** Photographic image corresponding to the addition of DA to unmodified CoMSPs results in the formation of a black precipitate

Fig. 4 **A** UV-vis spectra recorded using BSA functionalized CoMSPs for the successive addition of DA for various concentrations viz.,: (a) 0, (b) 5.3, (c) 15.8, (d) 26.3, (e) 36.8, (f) 52.6, (g) 79, (h) 105.3, (i) 131.6, (j) 158 and (k) 211 μM respectively. **B** A calibration plot for the quantification of DA based on its absorbance value obtained for each addition. **C** Photographic images displaying the blue color formation corresponding to change in DA concentration as shown in figure (A)

deep blue color solution is formed and the corresponding peak maximum is observed at 615 nm. Visual appearance of these colour changes are clearly seen from the photographic images shown in Fig. 3.

In case of colorimetric sensing studies, different concentrations of DA ranging from 0 to 211 μM were added to CoMSPs@BSA and the corresponding UV-vis spectra recorded are shown in Fig. 4A. It can be seen that upon incremental addition of DA, the intensity of peak at 615 nm increased in proportion to concentration as evident from the intensification of blue color as shown in Fig. 4C. The mechanism behind the blue color formation is explained in the later section. The limit of detection (LOD) associated with DA sensing carried out using this method

is found to be 5 μM . A plot of concentration versus the intensity [obtained by calculating the difference in absorbance intensity and initial absorbance intensity without DA addition ($I - I_0$)] (Fig. 4B) has shown a linear concentration dependence suggesting an efficient colorimetric sensor for DA detection.

Control experiments were also performed to confirm the role of CoMSPs and BSA towards the color formation. Addition of DA to CoMSPs alone results in the formation of a black precipitate whereas addition of DA to BSA and CoSO_4 didn't show any color change as shown in Fig. 3. Hence the blue color formation is due to the synergetic effect of three compounds viz., CoMSPs, BSA and DA where the role of each of them is inevitable. The concentration of

BSA was optimized before DA addition in order to obtain a better UV–vis response (ESI; Fig. S1). These studies depict that the increment or decrement of BSA concentration doesn't cause much change in intensity of peaks when a known DA concentration (79 μM) is used. However, a slight rise in absorbance value is observed for 20 mg/mL of BSA and it is chosen as the optimum BSA concentration throughout our studies.

3.3 Elucidation of sensing mechanism

In order to investigate the mechanism associated with sensing behavior, a time dependent UV–visible spectroscopic study was carried out between CoMSPs@BSA and DA over a period of 30 min at an interval of 3 min (Fig. 5). Initially, the absorbance peak observed at 615 nm increased rapidly for 9 min and thereafter it remains unchanged. After 18 min, there is no significant change in the absorbance value for the peak at 615 nm implies the saturation of BSA replacement with DA for the proposed sensor. During the course of time, it is quite interesting to observe a ratiometric behavior between the peaks formed at 370 nm (due to BSA conjugation with cobalt) and 615 nm (new peak due to DA bonding with cobalt). The intensity of absorbance at 370 nm decreases correspondingly with the incremental increase in absorbance at 615 nm. This clearly depicts that the conjugated BSA is replaced by DA.

Cyclic voltammetry offers a simple mode of investigating the electron transfer reactions associated with metals, and their corresponding oxidation states. In order to

Fig. 5 UV–vis absorbance spectroscopy based time dependent study carried out between CoMSPs@BSA and DA (79 μM) which depicts the ligand exchange mechanism. Time duration was varied as, (a) 0, (b) 3, (c) 6, (d) 9, (e) 12, (f) 15, (g) 18, (h) 21, (i) 24 and (j) 27 min respectively. Here “↓” denotes decrement of conjugated BSA absorption peak noted at 370 nm and “↑” denotes increment of peak intensity at 615 nm corresponding to DA binding

Fig. 6 Cyclic voltammograms recorded using glassy carbon electrode modified with (a) CoMSPs, (b) CoMSPs@BSA and (c) CoMSPs@BSA-DA in 0.1 M KOH at a scan rate of 50 mV/s. Inset: Enlarged view of the peak corresponding to Co_3O_4 to Co(OOH)

determine the oxidation state of the proposed systems, the cyclic voltammograms of CoMSPs, CoMSPs@BSA and CoMSPs@BSA-DA modified GCEs are recorded in aqueous 0.1 M KOH solution at a scan rate of 50 mV/s and the respective plots are shown in Fig. 6. CoMSPs (Fig. 6a) show an oxidation peak at 0.3 V which corresponds to Co(II)/(III) conversion according to the following equation [24, 25]:

While CoMSPs@BSA and CoMSPs@BSA-DA systems have shown the characteristic behavior of Co(III)/(IV) redox system exhibiting the anodic peak at 0.45 V. This oxidation potential corresponds to the equation given below:

This ensures the change in oxidation state of CoMSPs by adding BSA and subsequently this induces change in oxidation state of CoMSPs to another higher oxidation state more probably to +3 after modifying with BSA. The oxidation state remains same even after DA addition.

Further a detailed electrochemical study is performed to obtain an idea about the functional groups involved in binding with metal ions. Since DA is an electro-active compound, it is easy to access the mode of binding through electrochemical studies. Even though BSA has a complicated structure, electrochemical studies will provide insight information about the changes occurring in the concerned system.

Our motive is to find out the functional groups involved in metal binding for the three systems viz., CoMSPs, CoMSPs@BSA and CoMSPs@BSA-DA. These components are employed as the electrolyte and their corresponding redox behavior was analyzed using CV

Fig. 7 **A** CVs recorded at a scan rate of 50 mV/s using bare GCE in (a) CoMSPs, (b) CoMSPs@BSA and (c) CoMSPs@BSA, which are used as the electrolytes. **B** Time dependent study: CVs of bare GCE in CoMSPs@BSA-DA as an electrolyte

by employing bare GCE as a working electrode. It can be seen from Fig. 7A that no significant peak is observed for CoMSPs (a), whereas CoMSPs@BSA system (b) has shown a new peak at 0.76 V. In order to understand the characteristics of this peak, CV of bare GCE was recorded in BSA (20 mg/mL) solution and the corresponding voltammogram is shown in Fig. S6. It is interesting to observe the anodic peak for free BSA in aqueous solution (Fig. S6) at 0.59 V rather than 0.76 V. This implies the altered electronic behavior of BSA after conjugation with CoMSPs. CV response of bare GCE in CoMSPs@BSA-DA (c) solution has shown the well known quasi reversible oxidation peak at 0.2 V (quinone form of DA) and the reduction peak at 0.1 V (back to dihydroxy form) [26, 27]. These redox peaks correspond to the existence of dopamine in unbound state. Here, after the addition of DA, the peak at 0.76 V increased which is due to the electrochemical oxidation of dopamine over a wide range of potentials.

Further to understand the sensing mechanism, a time dependent study was carried out between CoMSPs@BSA and DA at a time interval of 5 min. The corresponding cyclic voltammograms are shown in Fig. 7B. Interestingly after $t = 5$ min, the current intensity values associated with these two peaks (0.2 V and 0.76 V) are reduced. The peak at 0.76 V begins to diminish and at the point where the blue color formation starts (at $t = 20$ min), there is no more peak residues. Accordingly, the significant peak for locating the mode of DA binding with CoMSPs is at 0.2 V which slowly decreased during the first scan and disappears completely from the third scan ($t = 10$ min). At $t = 10$ and 15 min, there is no peak at 0.2 V which is due to the combination of two possibilities: (1) either few molecules are oxidized during the first scan and the number of reduced molecules available for the second scan becomes less or (2) the hydroxyl groups are involved in metal binding. Control experiments with DA alone showed the presence of this peak even after 7 scans reveals that the hydroxyl group of DA is involved in the metal binding (ESI; Fig. S7).

While analyzing the CV recorded at 15 min time duration, the color of the solution begins to change into blue and at $t = 25$ min, there is a new peak formation at 0.58 V. This peak position is comparable with that of 0.59 V corresponding to the earlier observation for solution containing only BSA. This clearly indicates that as a result of ligand exchange, BSA is replaced and the appearance of new peak at 0.58 V is due to free BSA in the solution. It is difficult to determine the binding site of BSA with CoMSPs using CV studies due to its complicated structure. Regarding its structural interpretation, BSA is composed of essentially 583 amino acids and categorized into three domains namely I, II and III. Further each of these domains is subdivided into two sub domains namely A and B. BSA often involves in complexation with metals through its α -helical structure. Based on the previous report by Xu et al. on the analysis of binding phenomenon between cobalt based metal complexes and BSA, the most probable binding site is identified to be "N" atom of α helical structure in BSA [17, 28].

FTIR study also supports the binding of DA with cobalt atom wherein CoMSP-DA and CoMSP@BSA-DA share similar peaks at 2926, 2851, 1375, 1117 and 1045 cm^{-1} corresponding to $\nu(\text{N-H})$, $\nu(\text{C-H})$, $\nu(\text{CH}_2)$, $\nu(\text{C-O})$ and $\nu(\text{C-N})$ respectively (ESI; Fig. S3). The existence of a new peak at 1117 cm^{-1} strongly supports the binding of DA with cobalt atom [29–31].

3.4 Selectivity studies

Though many different techniques proposed for colorimetric sensing including electrochemical method and that too with the advantage of availability in portable form, the selectivity is a major issue. This seeks an alternative method for naked eye sensing like colorimetric and fluorescence methods for molecule identification and its quantitative determination. Here, the conjugated system, CoMSPs@BSA based probe is subjected to selectivity studies for a number of biomolecules like cysteine, hydrogen

Fig. 8 **A** UV-Vis spectra recorded for selectivity study of the proposed DA sensor over other common biomolecules such as: (a) cysteine (Cys), (b) hydrogen peroxide (H₂O₂), (c) glutathione (GSH), (d) cholesterol (Chol), (e) serine, (f) DA, (g) ascorbic acid (AA), (h) uric acid (UA), (i) glucose (Gluc), (j) tyrosine (Tyr) and (k) histidine

(His) respectively. **B** Photographic images depicting the selectivity of DA over (a) cysteine, (b) hydrogen peroxide, (c) glutathione, (d) cholesterol, (e) serine, (f) DA, (g) ascorbic acid, (h) uric acid, (i) glucose, (j) tyrosine and (k) histidine respectively

peroxide, glutathione, cholesterol, serine, ascorbic acid, uric acid, glucose, tyrosine and histidine. The concentration of each of these analytes is 30 times higher when compared to DA concentration and their corresponding UV-vis spectra are shown in Fig. 8A. From these studies, it is found that except DA, other analytes do not show any interfering peaks at 615 nm indicating the efficiency of the proposed biosensor in terms of selectivity and specificity. A visible color change can be seen from the photographic images shown in Fig. 8B. Even though cysteine and histidine form yellow color, these analytes do not affect the signal of interest in the absorbance spectra. Thus UV-vis spectra recorded for the corresponding analytes and the color change showed that the proposed system is highly selective to DA over other commonly interfering bio-analytes. The DA concentration measurement range and the higher selectivity associated with the proposed colorimetric sensor make it a promising sensor matrix for the determination of DA.

4 Conclusions

A topographically remarkable CoMSPs are prepared by simply adjusting the pH during the synthesis. Surface property of these CoMSPs is altered by conjugation with BSA and a naked eye sensing strategy was developed for the detection of DA using this modified CoMSPs. The binding mechanism between CoMSPs@BSA and DA was determined using spectrophotometric and cyclic voltammetric studies. Further, the systematic colorimetric detection of DA is carried out for different concentrations of DA and the corresponding sensing parameters like LOD and detection

range are calculated. Selectivity studies show that the sensing probe CoMSPs@BSA is highly specific for DA when compared to the other commonly interfering molecules in biological system. These studies clearly demonstrate the proposed probe is a better working system and a suitable alternative for the high cost noble metal based sensors for the colorimetric detection of DA.

Acknowledgements SVS acknowledges senior research fellowship (SRF) received from Council of Scientific and Industrial Research (CSIR), India to pursue her Ph.D. Authors are thankful to Central Instrumentation Facility (CIF) of CSIR-CECRI, Karaikudi for providing various equipments for necessary characterization and analyses.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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