LETTER

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Development of an amperometric sensor for epinephrine determination using an Azure A/silver nanocluster modified electrode



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Abstract

A novel electrochemical sensor was developed for the detection of Epinephrine (EP) utilizing Azure A (AzA), a phenothiazine dye, and citrate-capped silver nanoparticles. The interaction between Azure A and silver nanoparticles facilitated the formation of AzA/silver nanoclusters through a self-assembled approach. The morphological analysis of AzA/silver nanoclusters was conducted using field-emission scanning electron microscopy (FESEM). The nanoclusters were then immobilized on a graphite electrode via a simple drop-casting method, resulting in a modified electrode. The electrochemical properties of the modified electrode were investigated using cyclic voltammetry and linear sweep voltammetry techniques. The modified electrode exhibited enhanced electrocatalytic oxidation of EP at a lower oxidation potential of 0.27 V. The electrochemical analysis demonstrated that the modified electrode functioned as an amperometric sensor, enabling the detection of EP within a concentration range of 4.6 × 10⁻⁷ to 3.6×10^{-3} M, with a correlation coefficient of 0.9950 and a detection limit of 2.2×10^{-7} M (S/N = 3). The modified electrode exhibited excellent selectivity, sensitivity, and a remarkably low detection limit, making it highly suitable for EP determination. Its ease of preparation further adds to the practicality and potential applications of this electrode.

Keywords Azure A, Chemically modified electrode, Silver nanoparticles, Epinephrine, Amperometric sensor

Introduction

Catecholamines are a class of important compounds that play a significant role in the central nervous system of mammals. They are released by the adrenal medulla in response to psychological stress or low blood sugar levels [1, 2]. Catecholamines, including Epinephrine (EP),

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also known as adrenaline, are widely used as medications for various conditions such as bronchial asthma, hypertension, myocardial infarction, and cardiac surgery [3]. Epinephrine, in particular, plays a central role during physical or mental stress and triggers the "fight or flight response" of the sympathetic nervous system (SNS) [4]. Epinephrine's presence in the body regulates important physiological functions such as blood pressure, heart rate, lipolysis, immune system response, and glycogen metabolism. It increases the breakdown of glycogen into glucose in the liver, thereby elevating blood sugar levels. Simultaneously, it initiates the breakdown of lipids in fat cells [5]. However, patients with Parkinson's disease, a degenerative neurological disorder characterized by tremors, muscle rigidity, dyskinesia, and postural instability, often exhibit low levels of Epinephrine [6, 7]. Additionally, changes in Epinephrine concentration in nervous



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tissues and body fluids have been identified as diagnostic markers for various diseases [8]. Consequently, quantitative determination of Epinephrine in body fluids such as plasma and urine is crucial, and electrochemical methods appear to be suitable due to its easy oxidation [9]. Among the different types of nanomaterials, metal nanoparticles have garnered considerable attention for developing amperometric sensors. This is due to their large specific surface area, excellent conductivity, and remarkable electrocatalytic activities [10]. Various electrodes have been modified with metal nanoparticles, including Platinum (Pt), Gold (Au), Palladium (Pd), Copper (Cu), Nickel (Ni), and Silver (Ag) nanoparticles [11–19]. Silver nanoparticles, in particular, have been extensively utilized to modify electrode surfaces due to their potential applications. For instance, they can be used to create surface-enhanced Raman scattering-active substrates [20].

In recent times, there has been extensive exploration of integrating redox mediators with metal nanoparticles to develop electrochemical sensors. Although counter intuitive, this approach offers similar advantages in terms of reducing the overpotential of electrode processes and increasing sensitivity [21-23]. In this context, various organic dye molecules have been utilized as redox mediators, incorporated onto electrode surfaces to enhance electron transfer rate, electrochemical properties, selectivity, and sensitivity [24, 25]. The integration of redox mediators such as dyes, metal oxides or metal hexacyanoferrates on the surface of noble metal nanoclusters have been used to improve the performance of the modified electrode ability by means of fast electron transfer rate, lowering the over potential and enhancing the sensitivity because they provide large surface area for them to adsorb on the surface of electrode in particularly in the neutral pH medium. Our recent work involved the development of an amperometric sensor for the detection of hydrogen peroxide by modifying the electrode with Azure A/gold nanoclusters [26].

In this study, we focused on immobilizing Azure A (AzA), a phenothiazine dye, onto silver nanoparticles to create AzA/silver nanoclusters. We investigated the formation of AzA/silver nanoclusters and explored their potential application in electrochemical detection of EP (Epinephrine). The amperometric response of the AzA/silver nanoclusters modified electrode towards EP oxidation was thoroughly examined, and its analytical usefulness in determining EP levels in urine samples was also investigated.

Materials and methods

Chemicals

Azure A was procured from s.d. fine- Chemicals Limited, Mumbai, India, while epinephrine was obtained

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from Himedia, Mumbai, India. Silver nitrate, sodium borohydride, 2- propanol and trisodium citrate were acquired from Merck, New Jersey, USA. All remaining chemicals and reagents utilized in the study were of analytical grade. Double distilled water was used to prepare all solutions. A 0.1 M phosphate buffer solution (PBS) with a pH of 7.0 was consistently employed as the supporting electrolyte. Prior to the experiment, the solutions were deaerated by purging high purity nitrogen.

Instruments

All electrochemical measurements were performed using a CHI 660B electrochemical workstation (CH Instruments, USA) equipped with a conventional three-electrode cell configuration. The working electrode utilized was the AzA-functionalized GO modified electrode, while a platinum electrode served as the counter electrode. The reference electrode used was the Standard Calomel Electrode (SCE). Cyclic voltammetry and differential pulse voltammetry experiments were conducted in a static 50 mL phosphate buffer solution (PBS) with a pH of 7.0. Linear sweep voltammetry and chronoamperometric measurements were carried out under dynamic conditions in PBS at pH 7.0. To examine the nanoclusters, field-emission scanning electron microscope (FESEM) images were obtained using an FESEM instrument (Hitachi SE900, Japan) with an accelerating voltage of 15 kV.

Fabrication of AzA/silver nanoclusters modified electrode

The synthesis process for AzA/silver nanoclusters was similar to our previously reported method for AzA/gold nanoclusters [26]. Initially, citrate-capped silver nanoparticles were synthesized by reducing silver nitrate using a trisodium citrate solution and sodium borohydride as reducing agent [27]. A measured volume of the silver colloid was then mixed with a saturated solution of AzA in 2-propanol and stirred for 6 h. The resulting mixture was centrifuged, and the residue containing AzA/silver nanoclusters was subjected to multiple washes with distilled water to remove loosely adsorbed dye molecules. Scheme 1 provides a schematic representation of the nanocluster formation process. Subsequently, the AzA/silver nanoclusters were dispersed in 2-propanol using sonication. To prepare the AzA/silver nanoclusters modified electrode, the dispersed alcoholic solution of AzA/silver nanoclusters was drop-casted onto a graphite electrode impregnated with paraffin wax (PIGE). The resulting modified electrode, consisting of AzA/silver nanoclusters, was utilized for further experimental investigations.



Results and discussion

Physical characterization of AzA/silver nanoclusters

The formation of AzA/silver nanoclusters was studied by examining the interaction between citrate capped silver colloid and AzA solution using UV–visible absorption spectroscopy. The UV–visible absorption spectra of AzA with different amounts of silver colloid are depicted in Fig. 1A. The interaction of AzA with silver colloid was analogous to that of the interaction between gold colloid and AzA [26]. The spectrum 'a' exhibits two sharp absorption bands at 610 and 285 nm which are the characteristic absorption bands of AzA. Significant changes in the absorption intensities of AzA were observed on the addition of different amount of silver colloids at a given AzA concentration. It was seen that the intensities of the absorption bands at 610 and 285 nm (b-d) increased gradually while increasing the concentration of silver colloid in AzA solution. This absorption changes indicate a strong electrostatic interaction between cationic dye and SNPs. Thus, the silver nanoparticles, produced through the reduction of AgNO3 using trisodium citrate, exhibit a negative surface charge



Fig. 1 A UV–visible spectra of AzA [0.02 mM] in aqueous solution containing different concentration of silver colloid [concentration of silver colloid: (a) 0 (b) 5.0×10^{-6} (c) 10.0×10^{-6} (d) 15.0×10^{-6} (e) 20.40×10^{-6} M]. **B** Raman spectra of (a) AzA and (b) AzA/silver nanoclusters. FESEM images of (**C**) silver nanoparticles and (**D**) AzA/silver nanoclusters

attributed to a loosely attached citrate layer [28]. Consequently, the cationic dye carries an opposing charge to the silver particle surface. Upon introducing silver nanoparticles to an AzA solution, the dye gets adsorbed onto the AgNP surfaces due to electrostatic attraction without any agglomeration. This results in the dense arrangement of dye molecules on the charged particle surface [29], thereby elevating the local concentration of AzA on the particle surfaces. Consequently, this enhances the effective absorption cross-sectional areas of AzA and prompts the creation of AzA/silver nanoclusters. Hence, the silver nanoclusters influences in the electron transfer rate of AzA redox reaction.

The synthesized AzA/silver nanoclusters from the electrostatic interaction of AzA and silver colloid were characterized by Raman spectroscopy studies. The Raman spectra of (a) pure AzA and (b) AzA/silver nanoclusters are shown in Fig. 1B. Reports exist regarding the computational and spectroscopic investigations of AzA, along with the assignment of Raman vibrational bands for the same [30]. The Raman shift for both AzA and AzA/silver colloid clearly confirms the adsorption of AzA on SNP. The intensities of the Raman vibrational bands for AzA/ silver nanoclusters were observed to be enhanced due to the presence of silver nanoparticle. The enhancement in the Raman shift is nothing but the surface enhanced Raman spectrum due to SNPs. This indicates the formation of AzA/silver nanoclusters and demonstrated that there occurs a strong interaction between the positively charged AzA molecule and negatively charged SNPs.

The surface characteristics of the synthesized silver nanoparticles and AzA/silver nanoclusters were examined using field-emission scanning electron microscopy (FESEM). Figure 1C displays the FESEM image of the silver nanoparticles, while Fig. 1D depicts the FESEM image of the AzA/silver nanoclusters. Analysis of the morphological features reveals that the silver nanoparticles, obtained through citrate reduction, exhibit a spherical shape with diameters ranging from 10 to 20 nm. These nanoparticles are observed to be well-separated from one another. However, upon the addition of AzA, the silver nanoparticles retain a similar size but undergo a transition into closely packed nanoclusters. The formation of these nanoclusters is attributed to the neutralization of surface charges, which occurs as a result of AzA adsorption onto the silver surfaces. This observation aligns with previous findings regarding the self-assembly interaction between colloidal gold and AzA [26].

Electrochemical characterization of AzA/silver nanoclusters modified electrode

Cyclic voltammetry was performed to characterize the electrochemical properties of the AzA/silver nanoclusters modified electrode. The cyclic voltammograms of (a) the bare electrode and (b) the AzA/silver nanoclusters modified electrode in 0.1 M phosphate buffer solution (PBS) at pH 7.0 were recorded and are presented in Fig. 2A. The bare electrode exhibited no detectable electrochemical activity within the specified potential range. In contrast, the AzA/silver nanoclusters modified electrode displayed a distinct pair of redox peaks at a formal potential of - 0.255 V. These cathodic and anodic peaks observed in the cyclic voltammograms of the modified electrode (curve 'b') in 0.1 M PBS can be attributed to the electrochemical redox reaction of the AzA molecule [26, 31], which was present on the surface of the silver nanoclusters.

To investigate the kinetic reaction occurring at the electrode surface, the electrochemical behavior of the AzA/silver nanoclusters modified electrode was recorded at various sweep rates in 0.1 M phosphate buffer solution (PBS) with a pH of 7.0. Figure 2B illustrates the cyclic voltammograms (CVs) of the AzA/silver nanoclusters modified electrode at different scan rates. It can be observed that both the anodic and cathodic peak currents increase as the scan rate is increased, indicating that the redox reaction is a surface-confined process [32, 33]. The inset of Fig. 2B shows the calibration plot of current versus scan rate, which demonstrates a linear relationship between the cathodic and anodic peak currents and the sweep rate.

The influence of pH on the electrochemical behavior of the AzA/silver nanoclusters modified electrode was examined within the pH range of 3.0-9.0. The results depicted in Fig. 2C indicate that the peak currents increase with rising pH up to pH 7.0, beyond which the currents begin to decrease. The peak current and peak potential values of the modified electrode were recorded at various pH levels of the PBS using a scan rate of 50 mV s⁻¹. It was observed that the AzA/silver nanoclusters modified electrode displays pH-dependent voltammetric peak potentials. Specifically, both the cathodic and anodic peak potentials of the modified electrode shift towards more negative values as the pH of the buffer solution increases. Additionally, a plot of the formal potential against pH yields a linear relationship with a slope of 58 mV/pH which closely resembling the Nernstian slope for a $2e^{-}/2H^{+}$ transfer process as shown in Fig. 2D. Based on these findings, pH 7.0 was identified as the optimal pH for further investigations, considering that the modified electrode exhibited the best response at neutral pH. Moreover, as phosphate buffer is commonly used to maintain a pH around 7.0, it was employed as the buffer solution for all experiments.

The AzA/silver nanoclusters modified electrode was subjected to 100 continuous repetitive cycles in PBS at



Fig. 2 A Cyclic voltammograms recorded for the (a) unmodified electrode and (b) Azure A/silver nanoclusters modified electrode in 0.1 M PBS using a scan rate of 50 mV s⁻¹ with a reference electrode of SCE. **B** Electrochemical response of the AzA/silver nanoclusters modified electrode at various sweep rates $(10-100 \text{ mV s}^{-1})$. Inset: Correlation between peak current and sweep rate. **C** Influence of pH on the cathodic peak current of AzA/silver nanoclusters modified electrode. **D** Plot of formal potential of AzA/silver nanoclusters modified electrode vs pH

a sweep rate of 50 mV s^{-1} between the potential ranges of 0.2 to - 0.7 V. The stability of the modified electrode was investigated in this study. Figure 3A displays the cyclic voltammograms of the first and hundredth cycles of the modified electrode. It was observed that both the cathodic and anodic peak currents remained nearly unchanged, maintaining values close to their initial peak current. To assess the long-term stability of the modified electrode, voltammetric current decay was monitored over a period of 45 days, with measurements taken at regular intervals of 4 days. As depicted in Fig. 3B, the modified electrode exhibited a consistent and stable current response throughout the 45 day duration. Furthermore, the working stability of the modified electrode was examined by monitoring the current response every 30 min over an extended period of 10 h (inset of Fig. 3B). This analysis revealed a minimal decrease in the current response of the modified electrode, indicating its excellent working stability. Overall, these findings demonstrate that the modified

electrode maintains its stability and reliable performance over an extended period of time.

Electrochemical determination of Epinephrine

To assess the electrocatalytic activity of the AzA/silver nanoclusters modified electrode towards EP, cyclic voltammetric experiments were conducted. Figure 4A illustrates the cyclic voltammograms of the bare electrode ('a' and 'c') and the modified electrode ('b' and 'd') in the absence and presence of 1.6×10^{-5} M EP, respectively. It was observed that the electrocatalytic oxidation of EP was significantly enhanced at the modified electrode compared to the bare electrode. The modified electrode exhibited a substantial increase in oxidation peak current at a potential of 0.27 V and reduction peak at - 0.36 V, indicating favourable electrocatalytic oxidation of EP. Consequently, it was suggested that the modified electrode is suitable for the electrocatalytic oxidation of EP.

A linear current response was observed for the catalytic oxidation current of EP with the AzA/silver nanoclusters



Fig. 3 A CVs of the (a) 1st and (b) 100th cycle of AzA/silver nanoclusters modified electrode in 0.1 M PBS. (Sweep rate: 50 mV s⁻¹). B Current response of the AzA/silver nanoclusters modified electrode for a period of 45 days. (Inset: current response of the modified electrode vs time in min)



Fig. 4 A Cyclic voltammograms of (a) bare electrode, (b) bare electrode with 1.6×10^{-5} M EP (c) AzA/silver nanoclusters modified electrode and (d) AzA/silver nanoclusters modified electrode with 1.6×10^{-5} M EP in 0.1 M PBS (scan rate: 50 mV s⁻¹). **B** Calibration plot of EP determination

modified electrode, with a high correlation coefficient of 0.9950, upon successive addition of EP. The determination range for EP oxidation at the modified electrode was found to be 4.6×10^{-7} to 3.6×10^{-3} M, with a detection limit of 2.2×10^{-7} M, as depicted in Fig. 4B. Thus, it could be deduced that both Azure A and Ag nanoclusters contributed to the electrocatalytic oxidation of EP at the modified electrode. This could be attributed to the enhanced conductivity of Ag nanoclusters, which facilitated electron transfer. As a result, the electrocatalytic activity in terms of EP oxidation was superior to that of the Azure A modified and bare electrodes. The mechanism for the electrocatalytic oxidation of EP can be represented as shown in Scheme 2. The linear working range and detection limit obtained with the present sensor are better or comparable with earlier reports as shown in Table 1.

The electrocatalytic behavior of the AzA/silver nanoclusters modified electrode was investigated under dynamic conditions using linear sweep voltammetry. Figure 5A displays the linear sweep voltammograms obtained for the modified electrode in the absence ('a')



Scheme 2. Electrocatalytic oxidation mechanism of EP by AzA/silver nanoclusters modified electrode

Table 1
Analytical
parameters
for
EP
determination
using

various modified electrodes

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Electrode	рΗ	Linear range (µM)	Detection limit (µM)	Ref
Au-MWCNT-PANI-TiO ₂	7.0	0.077-4.9	0.16	[34]
NP Au films	7.0	20-190	2.40	[35]
NP Au–Ag films	7.0	10-100	5.05	[36]
MWCNTs	7.0	0.05-100.0	0.02	[37]
EDDPT/GO	7.0	1.5-600.0	0.65	[38]
Au-NR	7.0	10-150	2.80	[39]
Poly(fuchsine acid)	7.0	0.1-300	0.07	[40]
AzA/Ag nanoclusters	7.0	0.46-3600	0.22	This work

Au-MWCNT-PANI-TiO₂ multiwalled carbon nanotubes and polyaniline nanocomposite doped titanium dioxide on gold electrode, NP Au film nanoporous thin gold films, NP Au-Ag films nanoporous sponge like gold-silver electrode, MWCNTs Multiwalled carbon nanotubes, EDDPT/GO 2-(5-Ethyl-2,4dihydroxyphenyl)-5,7-dimethyl-4H-pyrido[2,3-d][1,3]thiazine-4-one/graphene oxide, Au-NR gold nanorod, AzA/Ag nanoclusters Azure A/silver nanoclusters

and presence ('b') of 2.4×10^{-5} M EP. It was observed that the catalytic oxidation of EP initiates at a potential of approximately 0.1 V and exhibits a significant increase in response with a maximum peak at 0.25 V, eventually reaching a plateau. Therefore, for the amperometric determination of EP, an applied potential of +0.3 V can be selected as the optimum potential for the AzA/silver nanoclusters modified electrode.

Following the evaluation of the electrocatalytic behavior of the AzA/silver nanoclusters modified electrode under dynamic conditions, chronoamperometric studies were conducted. Figure 5B illustrates the current-time response of the AzA/silver nanoclusters modified electrode for successive increments of 4.14×10^{-5} M of EP at an applied potential of 0.3 V. The results clearly demonstrate that the increase in anodic current is directly attributed to the concentration increase of EP. The inset of Fig. 5B presents the plot of catalytic oxidation against the concentration of EP, which exhibits a linear relationship with a correlation coefficient of 0.9960.

The presence of various coexisting species commonly found alongside EP can potentially impact its determination using cyclic voltammetry technique. To assess this, the determination of EP was performed in the presence of several common species such as NaCl, KCl, $Ca(NO_3)_2$, glucose, lysine, cystine, glycine, and citric acid. It was determined that these species did not interfere with the accurate determination of EP. However, the presence of ascorbic acid (AA), which often coexists with EP, can have an influence on its determination. To address this issue, the AzA/silver nanoclusters can be coated with Nafion, a negatively charged polymer [41, 42]. By employing this approach, the proposed electrode can effectively detect EP even in the presence of high concentrations of AA.

To assess the prolonged stability of the modified electrode, the current response towards the determination of 2.4×10^{-5} M EP was recorded at regular intervals of every 4 days over a period of 45 days as shown in Fig. 5C. It was observed that the electrode exhibited only a negligible decrease in current at the end of the 45 day period, indicating its excellent stability. Additionally, the working performance of the modified electrode was evaluated



Fig. 5 A Linear sweep voltammograms of AzA/silver nanoclusters modified electrode in the absence (a) and presence (b) of 2.4×10^{-5} M EP in 0.1 M PBS. [Stirring rate: 300 rpm]. **B** Amperometric response of the AzA/silver nanoclusters modified electrode for the successive additions of 4.14×10^{-5} M EP in 0.1 M PBS. [Stirring rate: 300 rpm; Operating potential: +0.3 V]. Inset: Calibration plot of amperometric current response of AzA/silver nanoclusters modified electrode towards 2.4×10^{-5} M EP determination for a period of 45 days. (Inset: current response of the modified electrode *vs* time in min)

by measuring the current response for EP oxidation at 30 min intervals over an extended duration of 10 h (inset of Fig. 5C). The consistent and stable current response observed during the oxidation of EP further confirms the electrode's capability for long-term usage. The modified electrode was stored in air-tight container at 4 °C while not in use.

Real sample analysis

To assess the practicality of the developed amperometric sensor, real samples were analyzed using the modified electrode. In this study, the electrode was used to determine EP in two different human urine samples. Prior to the measurements, the urine samples were diluted tenfold using 0.1 M PBS of pH 7.0, without undergoing any pretreatment. A known concentration of EP was spiked into the urine samples, and differential pulse voltammetry (DPV) measurements were recorded. The obtained results, indicating the quantitative recoveries, are presented in Table 2. The results demonstrate satisfactory

Added (10 ⁻⁵ M)	Found (10 ⁻⁵ M)	Recovery (%)
25	25.05	100.2
50	50.2	100.4
25	25.15	100.6
50	49.6	99.2
	Added (10 ⁻⁵ M) 25 50 25 50	Added (10 ⁻⁵ M)Found (10 ⁻⁵ M)2525.055050.22525.155049.6

recoveries, highlighting the effectiveness of the modified electrode for EP analysis in real urine samples.

Conclusions

In conclusion, we have presented a novel method for synthesizing Azure A capped silver nanoclusters and utilized them to fabricate a modified electrode for amperometric sensing of EP. The synthesized nanoclusters were characterized using FESEM, revealing their spherical shape

with a diameter range of 10-20 nm and closely packed arrangement. The AzA/silver nanoclusters modified electrode was thoroughly characterized using cyclic voltammetry and linear sweep voltammetry. Optimization studies were conducted to determine the ideal scan rate and pH conditions for the modified electrode. The electrode exhibited excellent electrocatalytic activity for EP determination, with a lower oxidation potential of 0.27 V. The concentration range of EP detection spanned from 4.6×10^{-7} to 3.6×10^{-3} M, yielding a high correlation coefficient of 0.9950 and a low detection limit of 2.2×10^{-7} M (S/N=3). Successful determination of EP in spiked urine samples was achieved using the AzA/silver nanoclusters modified electrode. Additionally, the developed electrode offers advantages of cost-effectiveness, ease of fabrication, and stability. Furthermore, it holds potential for analyzing other biologically significant compounds.

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Author contributions

Conceptualization, Methodology, Investigation, writing-original draft preparation, CP; Formal analysis, data curation, SA, writing-review and editing, RSB; Supervision, SSN.

Data Availability

The data supporting these findings are within the article.

Declarations

Ethics approval and consent to participate Not applicable.

Competing interests

The authors declare no competing interests.

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