

Synthesis and characterization of gold nanoparticles incorporated bentonite clay for electrocatalytic sensing of arsenic(III)

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Abstract. In the present manuscript, a simple and easy route to synthesize bentonite (bt) clay-supported gold nanoparticles (Au NPs) is reported (represented as Au-bt). Application of this new environmentally benign material in electrocatalytic determination of arsenite (As(III)) was studied. The successful synthesis and incorporation of Au NPs into the bt clay is supported by spectroscopic, microscopic and electrochemical methods. The synthesized Au-bt material was used to modify glassy carbon electrode (GC) by the evaporation of Au-bt aqueous suspension dropped on the surface of the GC (GC/Au-bt). Cyclic voltammetry and chronoamperometry studies of As(III) solutions were performed with this GC/Au-bt electrode which act as efficient platform for the electro-oxidation of As(III) to As(V) at a very low overpotential. Kinetic parameters were evaluated for the oxidation of As(III) at the GC/Au-bt platforms. A wide linear calibration range for the determination of As(III) from 1 to 1700 μM was obtained with high reproducibility and stability. A limit of detection, 0.1 μM was achieved with high sensitivity. Additionally, it showed a good selectivity for the determination of As(III) in the presence of copper(II) and other interfering ions suggesting a promising new route for trace level determination of As(III) in neutral conditions.

Keywords. Bentonite clay; gold nanoparticles; arsenite oxidation; electrocatalysis; oxidative determination.

1. Introduction

Nowadays, considerable attention is devoted for the development of new nanostructured materials for the construction of electrochemical sensing platforms (ESPs) since they exhibit well-recognized catalytic properties.^{1–3} These new nanostructured materials can be sourced from different constituents such as polymers,³ carbon based materials,⁴ silica,^{1,5} clays,^{6–8} etc. Among these materials, clays are widely used for the development of nanostructured materials because they are inexpensive, non-hazardous, easily available and very promising supports for the design and preparation of biocompatible electrocatalyst material.^{6,7} A large number of ion exchange sites available in clays is also beneficial for incorporation of electroactive species and nanoparticles (NPs).^{7,8} Use of clays for the modification of electrode surfaces is already well established and clay-modified electrodes (CMEs) are constantly getting great interest for the construction of sensors and biosensors.^{6,7,9} Thus, several CMEs have successfully been used as the

ESPs for various analytes. For example, very recently metal complex incorporated CMEs for oxidative determination of nitrite¹⁰ and isoniazid¹¹ was reported. Mousty and her group used organo-clay modified glassy carbon electrodes for electrochemical determination of mesotrione.¹² Zunic *et al.*, used organo-smectite clay coated glassy carbon electrode for the electrooxidation of p-nitrophenol.¹³

Arsenic, which is present in both organic and inorganic forms, causes adverse effect to human health because of its toxicity. Inorganic form of As mainly exists in water in two forms, arsenate (As(V)) and arsenite (As(III)) ions. As(III) is more soluble in water and more toxic in comparison to As(V).^{14,15} Even a very low concentration of arsenic present in water can cause skin diseases, cardiovascular diseases and cancer.¹⁵ World Health Organization (WHO) recommends a maximum limit of arsenic in drinking water as 10 $\mu\text{g dm}^{-3}$.¹⁶ Therefore, several analytical methods are exploited for the trace level determination of arsenic in water.^{14,15,17} Electro-analytical methods are advantageous over the other methods due to their fast, sensitive and selective determination.^{15,18–20} Different types of modified electrodes are used to sense arsenic, however, most of them utilize high acidic conditions.^{18,20} Therefore, in

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Dedicated to Prof. R. Ramaraj on the occasion of his 60th birth anniversary.

the present work, we synthesized a new nanostructured material based on bt clay and Au NPs and used this new material for the electrocatalytic oxidative determination of As(III) in neutral condition. To the best of our knowledge, Au NPs incorporated bt clay and its use in electroanalytical applications are barely reported.

2. Experimental

2.1 Chemicals and reagents

Bentonite (bt) (Montmorillonite) was purchased from Himedia, India. Hydrogen tetrachloroaurate(III) (HAuCl_4) and sodium (meta)arsenite (NaAsO_2) were procured from Sigma-Aldrich (India). Poly(vinyl alcohol) (PVA) was purchased from S.D. Fine Chemicals (India). K_2HPO_4 and KH_2PO_4 were purchased from Qualigens, India and used for the preparation of phosphate buffer solution (PBS). All other chemicals were analytical grade and used as received. The experiments were carried out using triple distilled water unless otherwise mentioned.

2.2 Instrumentation

PerkinElmer Spectrometer (spectrum two) was used for FT-IR spectroscopic analysis. For X-ray diffraction (XRD) patterns a Philips PW-1710 ($\text{Cu-K}\alpha$ radiation, $\lambda = 0.154 \text{ nm}$) was used. UV-Vis absorption spectra of bt and Au-bt films were recorded by UV-Vis spectrophotometer (model 2802PC, Unico). Scanning electron microscopy (SEM) images of bt and Au-bt films were taken from Quanta 200 with an accelerating voltage of 20 kV. The bt and Au-bt films for UV-Vis and SEM studies were prepared by coating aqueous colloidal suspension of respective material on glass plate and allowed to dry at room temperature. The energy dispersive X-ray analysis (EDAX) of Au-bt was performed on Bruker EDAX instrument, operating at 10 kV. TECNAI 12 G2 FEI microscope, operated at 120 kV was used for collecting transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) images. For TEM analysis aqueous colloidal dispersion of the sample was prepared and coated on carbon coated copper grids. The interplanar spacing (d) values were calculated using Bragg's law. All the electrochemical measurements were carried out using CHI electrochemical workstation (Model CHI-660 C, USA) and a single compartment three-electrode cell system. Glassy carbon (GC) electrode (diameter = 3 mm) as working electrode, Pt wire as counter electrode and saturated calomel electrode (SCE) as reference electrode were used. Electrochemical impedance spectroscopy

was performed in the frequency range of 1 to 100 kHz with amplitude of 5 mV. All the electrochemical measurements were carried out at room temperature and prior to each experiment the sample was purged with N_2 gas for 10-20 min to remove dissolved oxygen.

2.3 Incorporation of Au NPs into bt

Au NP incorporated bt clay (Au-bt) was prepared using a simple chemical reduction method. Briefly, 2 wt% of bt was dispersed in water and then the gold precursor, HAuCl_4 was slowly added into the dispersed bt under stirring condition. This mixture was constantly stirred for 24 h at room temperature. After 24 h of stirring, an excess amount of NaBH_4 was added to it at ice cooled temperature and stirred vigorously for another 2 h to complete the reduction. During the addition of NaBH_4 , the color of the mixture changed from muddy yellow to wine red which confirmed the reduction of gold precursor to Au NPs. After that the Au-bt material was washed repeatedly with triple distilled water by centrifugation and filtration to remove any chloride ions and physically adsorbed gold precursors (if any). The washing procedure was repeated until the filtrate gave no precipitate with aqueous AgNO_3 solution to confirm the absence of Cl^- ions in the final product. Then the product was dried at 80°C for 4 to 6 h.

2.4 Preparation of the electrochemical sensing platforms (ESPs)

The GC electrode was mirror polished with micro polish alumina powder ($0.05 \mu\text{m}$) and ultrasonicated in triple distilled water for 15 min and then air dried. The clean GC electrode was coated with 10 μL of 0.05 wt% of Au-bt colloidal aqueous suspension prepared with 0.01 wt% PVA. Then the modified electrode was allowed to dry for 6-8 h at room temperature (GC/Au-bt) and used as the ESP. Similar procedure was applied for the preparation of GC/bt electrode for blank studies.

3. Results and Discussion

3.1 Characterization of Au-bt material

The synthesized Au-bt material was characterized by FT-IR, UV-Vis absorption spectra and X-ray diffraction studies (figure 1). FT-IR study (figure 1A) was performed to know the possible interaction of Au NPs with bt. FT-IR spectrum of bt (spectrum a of figure 1A) shows prominent peaks at 3697 and 3620 cm^{-1} due to $-\text{OH}$ stretching vibrations of Al-OH and Si-OH ,

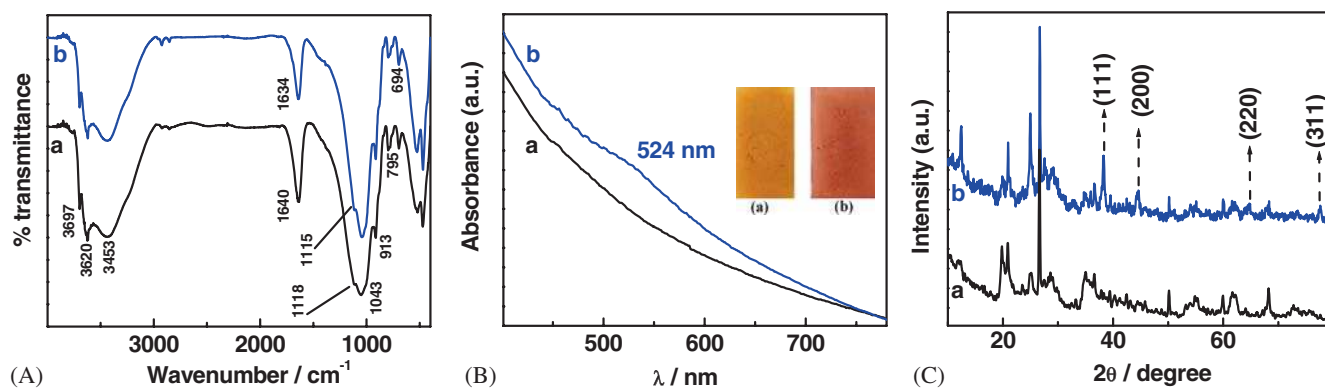


Figure 1. (A) FT-IR spectra; (B) UV-Vis absorption spectra (films of the respective samples); and (C) XRD pattern of (a) bt and (b) Au-bt materials. Inset of Figure (B) shows the digital photographs of (a) bt and (b) Au-bt film surface.

respectively, whereas the bending vibration of Al-OH is observed at 913 cm^{-1} . The Si-O stretching vibrations are observed at two different planes, i.e., in-plane vibration at 1043 cm^{-1} and out-plane vibration at 1118 cm^{-1} . Water adsorbed at the interlayer of the bt shows specific bands at 1640 and 3453 cm^{-1} due to -OH stretching and bending vibrations, respectively.^{8,10} The FT-IR spectrum of Au-bt material (spectrum b of figure 1A) also shows absorption bands very similar to the one observed for bt. However, slight shifts are observed in Au-bt, i.e., bands observed at 1640 and 1118 cm^{-1} of bt are shifted towards low wavenumbers, 1634 and 1115 cm^{-1} , respectively. This small shifts in IR bands suggest that Au NPs have only either a weak interaction with bt rather than any strong chemical binding or they are positioned physically inside the layered structure of bt. Figure 1B depicts the UV-Vis absorption spectra of bt (curve a of figure 1B) and Au-bt (curve b of figure 1B) films coated on glass plates. The UV-Vis spectrum of Au-bt (curve b of figure 1B) clearly shows a surface plasmon resonance (SPR) band at 524 nm whereas no peak is observed for bt (curve a of figure 1B) which indicates the successful incorporation of Au NPs into the bt layers. It should be noted that, the SPR band of Au-bt depends on their size and shape and it has been reported that spherical Au NPs of diameter $10\text{--}30\text{ nm}$ would give an absorption maximum around $520\text{--}530\text{ nm}$.²¹ As the SPR band of the present material (Au-bt) is observed at 524 nm , it is considered that the Au NPs present in bt may have a size between $10\text{--}30\text{ nm}$. The size of Au NPs inferred from UV-Vis spectrum is comparable from the average size of NPs calculated from the TEM images (*vide infra*). In order to confirm the immobilization Au NPs on the bt clay, powder XRD of bt and Au-bt was recorded and the corresponding patterns are shown in figure 1C. It also gives information about the crystalline nature and structure of the Au NPs present in bt matrix. XRD pattern

in the 2θ range of $10\text{--}80^\circ$ of bt (pattern a of figure 1C) shows the typical diffraction peaks related to bt clay⁸ whereas the XRD pattern of Au-bt (pattern b of figure 1C) in the same region shows some additional diffraction peaks along with bt peaks. The additional diffraction peaks which are observed at 2θ values 38.3° , 44.4° , 64.5° and at 77.5° are related to the planes of (111), (200), (220) and (311) reflections for the crystalline Au NPs, respectively.⁷ The d values are calculated to be 2.351 , 2.037 , 1.445 and $1.299\text{ \AA}$. These calculated d values agree well with the reported values for metallic Au (JCPDS File No. 04-0784). Therefore the XRD pattern of Au-bt clearly indicates that metallic Au NPs have been successfully incorporated into bt clay matrix.

Surface morphology of bt and Au-bt were characterized by SEM and TEM analysis (figure 2). SEM images of bt film (figure 2a) shows homogeneous morphology with regular pores whereas the SEM images of Au-bt film (figure 2b) shows similar surface morphology along with the presence of spherical Au NPs. Thus, the presence of Au NPs in SEM image of Au-bt film confirms successfully incorporation of Au NPs into the bt matrix. The energy dispersive X-ray analysis (EDAX) of Au-bt material (Figure S1 in Supplementary Information (SI)) shows peaks for Au which also reveals the presence of Au NPs. TEM images of Au-bt material are shown in figure 2c and 2d along with its selected area electron diffraction (SAED) pattern (inset of figure 2c). It can be clearly seen that the spherical shaped Au NPs of different sizes are distributed in the clay matrix. Based on the TEM image measurements, the average diameter of Au NPs is calculated to be in the range of $10\text{--}30\text{ nm}$. From SAED pattern (inset of figure 2c), it can be noticeably seen that the characteristic rings in the electron diffraction patterns associated with the known fcc planes, (111), (200), (220), (311) and (222) of Au.²² Based on the SAED pattern, the d values are estimated as 2.293 , 2.045 , 1.346 , 1.193 and $1.128\text{ \AA}$, respectively.

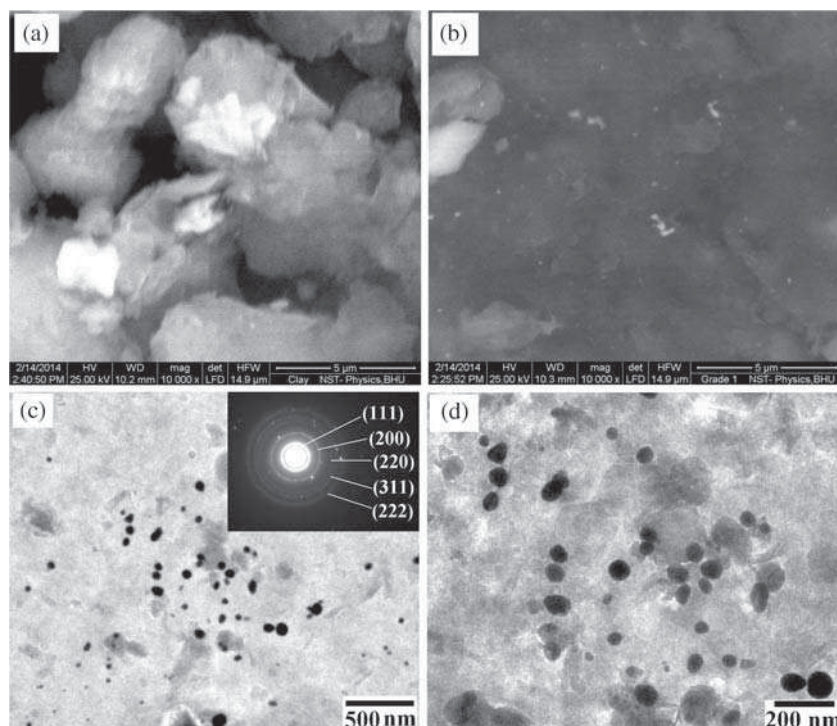


Figure 2. SEM images of (a) bt, and (b) Au bt film; TEM images of Au-bt at different magnifications (c and d); inset of image c shows the corresponding SAED ring pattern.

The d values obtained from SAED ring patterns are in good agreement with the d values obtained from XRD analysis (*vide supra*).

3.2 Electrochemical Characterization of GC/Au-bt

Figure 3 shows the cyclic voltammetry (CV) responses of GC/bt and GC/Au-bt ESP recorded between 0.0 and 1.2 V in PBS (0.1 M, pH 7.0) at a scan rate of 100 mVs^{-1} . The CV response of GC/Au-bt (figure 3b) clearly shows distinct oxidation/reduction peaks which

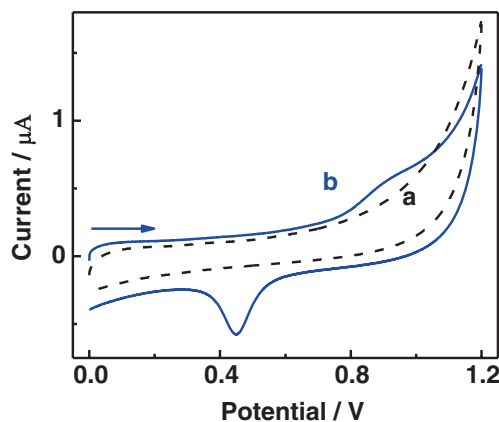


Figure 3. CV response of (a) GC/bt and (b) GC/Au-bt ESP at a scan rate of 100 mVs^{-1} in PBS, 0.1 M, pH 7.0.

are not observed at GC/bt (figure 3a), indicating the presence of Au NPs at the GC/Au-bt ESP. The peak observed at 0.90 V can be attributed to Au oxide formation and on the reverse scan, the peak at 0.45 V can be attributed to the reduction of Au oxide layer formed during the forward scan.²³

The peak currents increase with the increase in scan rate (figure S2 in SI). A plot of anodic peak current (observed at 0.90 V) vs. square root of scan rate deviates from the linear behavior at high scan rates (inset (i) of figure S2), suggesting a possible surface process. In addition, the anodic peak current is found to be linearly dependent to the scan rate (inset (ii) of figure S2) indicating that the observed redox process is related to the surface confined species.²³

3.3 Electrocatalytic oxidation of As(III)

Figure 4 shows the CV responses of GC/bt electrode and GC/Au-bt ESP in the absence (a and b) and presence of $500.0 \text{ } \mu\text{M}$ As(III) (a' and b') in PBS (0.1 M, pH 7.0). GC/bt electrode (figure 4a and 4a') does not show any redox behavior in the absence and presence of As(III), whereas in the absence of As(III) the GC/Au-bt (figure 4b) shows redox behavior associated with Au NPs as discussed in the previous section, 3.2. At GC/Au-bt, in the presence of $500.0 \text{ } \mu\text{M}$ As(III) (figure 4b'),

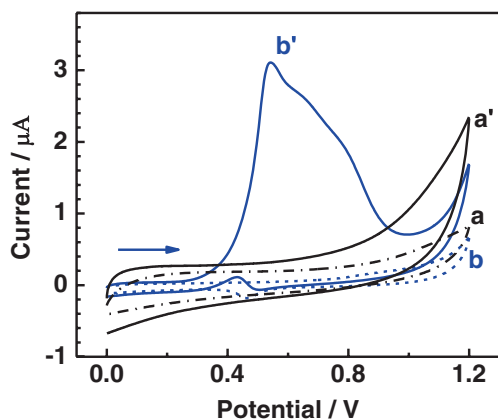


Figure 4. CV responses of GC/bt (a, a') and GC/Au-bt ESP (b, b') in PBS, 0.1 M, pH 7.0 in the absence (a, b) and presence (a', b') of 500.0 μM As(III). Scan rate: 20 mVs^{-1} .

a clear sharp increase in oxidation peak current at 0.54 V is observed. This observation clearly demonstrates the catalytic effect of the prepared GC/Au-bt ESP for As(III) oxidation.

The oxidation peak appears in both forward and reverse scans (figure 4b) indicating the high efficiency oxidation of As(III) by the Au-bt material. The observed overpotential (0.54 V) for As(III) oxidation at GC/Au-bt is very much lower than those reported in the previous reports at various types of ESPs.^{20,24,25}

Electrochemical impedance spectroscopy (EIS) was performed in the presence and absence of As(III) to confirm the electrocatalytic efficiency of Au-bt material for the oxidation of As(III). The EIS outcomes (Nyquist diagrams) of GC/Au-bt ESP at an applied potential of 0.6 V in the absence (curve a) and presence of various concentrations (b to k) of As(III) in PBS (0.1 M pH 7.0) are shown in figure S3 (SI). In the absence of As(III), GC/Au-bt ESP shows a semicircle with large diameter. However, gradual increase in the concentration of As(III) decreases the diameter of the semicircle gradually. This outcome of EIS in the presence of various concentrations of As(III) confirms the electrocatalytic oxidation of As(III) at GC/Au-bt ESP.²⁵

3.4 Evaluation of kinetic parameters of As(III) oxidation

The CV of GC/Au-bt ESP at various scan rates ranging from 20 to 300 mVs^{-1} in the presence of 100.0 μM As(III) was performed (figure 5). The catalytic oxidation current for As(III) was found to be linearly dependent with the square root of scan rate (inset (i) of figure 5), implying that the transport of As(III) at GC/Au-bt electrode is controlled by diffusion.^{24,25} Besides, the catalytic oxidation peak potential (E_{pa}) for As(III)

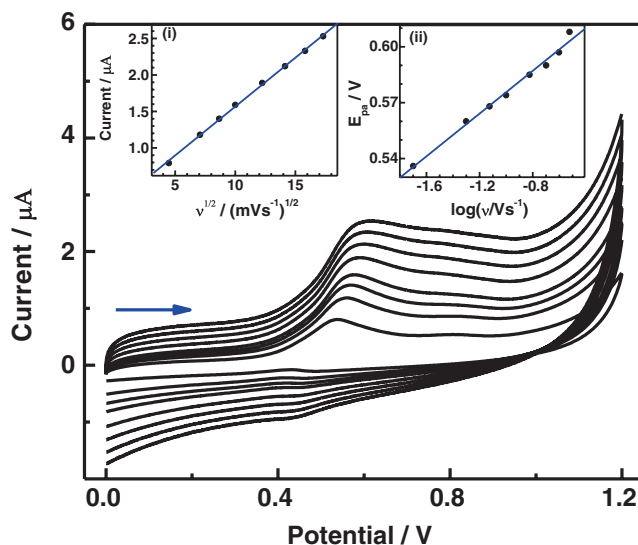


Figure 5. CV responses of GC/Au-bt ESP for the oxidation of 100.0 μM As(III) at different scan rates. Inset (i) shows the plot of the oxidation peak currents against the square root of scan rates and inset (ii) shows the plot of the oxidation peak potential against the log of scan rate.

oxidation is also shifted towards positive potential values on increasing the scan rate (figure 5). For a totally irreversible diffusion controlled process, the Tafel slope (b) can be obtained using equation (1) which provides information on the rate determining step.

$$E_{\text{pa}} = \text{Constant} + (b/2) \log(v) \quad (1)$$

Inset (ii) of figure 5 shows the plot of variation of oxidation peak potential against $\log(v)$. On the basis of equation (1) and the slope value of E_{pa} vs. $\log(v)$ plot, the calculated b value is found to be 110 mV. The obtained b value at GC/Au-bt ESP for the electrocatalytic oxidation of As(III) signifies the involvement of one electron transfer process in the rate determining step.^{24,25}

The catalytic oxidation of As(III) at the surface of the GC/Au-bt ESP was also studied by chronoamperometry and depicted in figure 6. Figure 6A shows the chronoamperograms for different concentrations of As(III) in the range of 200–1000 μM which shows a linear increase in current sampled at 45 s against the concentration of As(III) (inset of figure 6A).

Further from chronoamperometric measurements, one can determine the diffusion coefficient (D) of the analyte, As(III) at the ESP using the Cottrell equation (2).

$$I = nFAD^{1/2}C/(\pi t)^{1/2} \quad (2)$$

where C is the bulk concentration of the analyte. The plots of I vs. $t^{-1/2}$ for various As(III) concentrations show a linear behavior (figure 6B). Inset of figure 6B

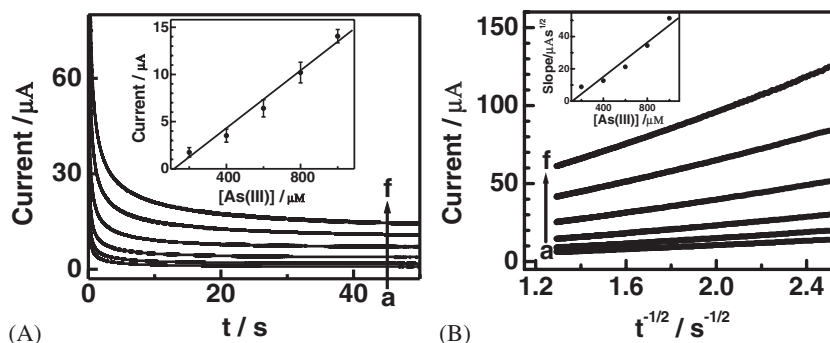


Figure 6. (A) Chronoamperometric responses for GC/Au-bt ESP at different concentrations of As(III) [a $\rightarrow$ f correspond to 0, 200, 400, 600, 800 and 1000 μM of As(III)]. Inset shows the variation of chronoamperometric current measured at 45 s against As(III) concentrations. (B) Plots of oxidation current vs. $t^{-1/2}$ at different concentrations of As(III). Inset shows the plot of slope of the resulting straight lines as shown in B against the added As(III) concentration.

shows the plot of the slopes of the resulting straight lines vs. As(III) concentration. From the slope of this plot (inset of figure 6B) and using the Cottrell equation (2), the average value of D is calculated to be $6.98 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This value is comparable to the literature value for oxidation of As(III).^{25,26}

3.5 Electrocatalytic determination of As(III)

The electrocatalytic oxidation peak current of As(III) at GC/Au-bt ESP can be used for the determination of As(III) in water samples. Figure 7 shows CV response for various concentrations of As(III) at GC/Au-bt ESP in 0.1 M PBS (pH 7.0) at 20 mVs^{-1} .

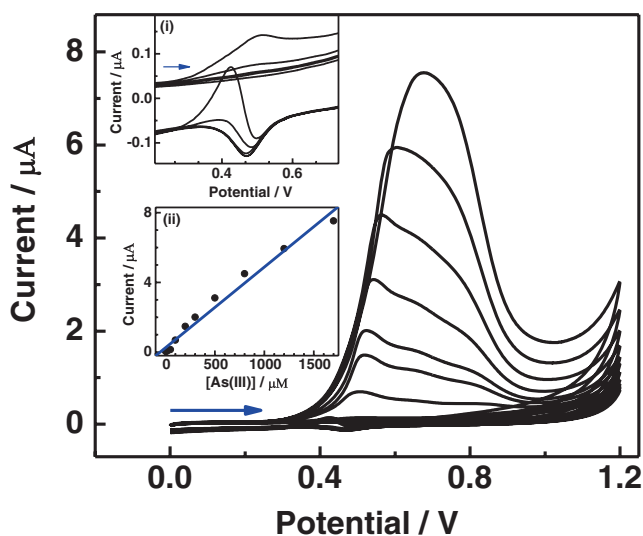


Figure 7. CV response of different concentrations of As(III) at GC/Au-bt ESP in 0.1 M PBS (pH 7.0) at a scan rate 20 mVs^{-1} . Inset (i) shows enlarged view at low concentrations of As(III) and insert (ii) shows the corresponding calibration plot.

With each addition of As(III), the anodic oxidation current continuously increases and it shows a linear response from 1.0 to 1700 μM of As(III) (inset (ii) of figure 7). The sensitivity and detection limit (based on three times the standard deviation (S) of blank) for determination of As(III) at GC/Au-bt ESP is found to be $56.34 \mu\text{A mM}^{-1} \text{ cm}^{-2}$ and 0.1 μM , respectively. The sensitivity is higher than those reported based on cobalt oxide nanoparticle-modified GC electrode²⁴ and comparable to poly(taurine)/nano gold modified electrode.²³ The analytical characteristics such as detection limit, detection potential and linear calibration range of the GC/Au-bt ESP are compared with other electrochemical methods for As(III) determination and listed in table S1 (in SI).^{20,23–25,27–31} It can be seen that the proposed GC/Au-bt ESP displays relatively low detection limit and covers a wide linear range for determination of As(III), demonstrating the superiority of the proposed sensor.

3.6 Selectivity, stability and reproducibility

In the electrochemical estimation of As(III) in aqueous solutions, Cu(II) is a well-known interfering species which can seriously affect the quantitative determination of As(III).²⁷ Therefore, to check the influence of Cu(II) ions which may exist in water samples, interference study for As(III) detection was carried out in presence of Cu(II) ions. Figure S4 (in SI) shows the CV response of 250.0 μM As(III) (curve a of figure S4) in the presence of two fold excess concentration, 500.0 μM of Cu(II) ions (curve b of figure S4) at GC/Au-bt ESP. Presence of Cu(II) exhibits no noticeable change in the current response of As(III) oxidation. In addition, the selectivity for As(III) determination at GC/Au-bt ESP is also examined in presence of two

fold excess concentration of other competing metal ions such as Pb^{2+} , Hg^{2+} , Cd^{2+} , Mg^{2+} , Zn^{2+} and Ca^{2+} and it is found that these metal ions did not interfere. These results indicate the remarkable advantage of the present method since the quantitative determination of As(III) by several electrochemical methods are highly affected by the presence of heavy metal ions.^{19,31} These results clearly indicate the selective oxidation As(III) at GC/Au-bt ESP. The reproducibility and fouling effect on GC/Au-bt ESP was checked by carrying out 10 continuous CV measurements for As(III) at 200.0 μM and the relative standard deviation of the measurements is found to be 7.8% indicating negligible fouling effect. This result confirms the high stability of the GC/Au-bt ESP in comparison with some recent reports.^{27–30} The reproducibility was again checked by five different GC/Au-bt ESPs for 200.0 μM As(III). The relative standard deviation of these five different GC/Au-bt ESPs was found to be 2.1%. The storage stability of the GC/Au-bt ESP was investigated by measuring the CV response of As(III) before and after storing it in 0.1 M PBS (pH 7.0). After storage in 0.1 M PBS (pH 7.0) for ten days, the GC/Au-bt electrode retained 91% of the initial current response. These results indicate that the proposed GC/Au-bt ESP has good selectivity, reproducibility and stability for the electrochemical determination of As(III).

4. Conclusions

Au NPs incorporated Bentonite (bt) material was synthesized, characterized and then successfully utilized for the construction of a novel electrochemical sensing platform (ESP) for As(III) determination in neutral (pH 7.0) solution. The proposed ESP shows greatly improved electrochemical behavior compared to bare GC and GC/bt electrodes for As(III) oxidation. The linear calibration range and the detection limit for As(III) were found to be 1.0 to 1700 μM and 0.1 μM , respectively. Kinetic parameter such as diffusion coefficient of As(III) was also evaluated. It is believed that this new nanostructured Au-bt material can be used for the sensitive and selective determination of As(III) in real water samples.

Supplementary Information

Additional information such as EDAX of Au-bt (figure S1), CV responses of GC/Au-bt ESP at different scan rates (figure S2), Nyquist plots for GC/Au-bt ESP in the absence and presence of As(III) (figure S3), CV responses obtained for As(III) in presence of Cu(II) at

GC/Au-bt ESP (figure S4) and comparison of analytical characteristics (table S1) are given in the supplementary information. The electronic supplementary information is available at www.ias.ac.in/chemsci.

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