RESEARCH PAPER

Development of Nano Copper Sulfide (CuS) Structures for Electrochemical Detection of Vitamin C

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ABSTRACT

Copper Sulfide (CuS) has received significant interest due to its attractive physical and chemical properties. In this study, the development and characterization of nano CuS (a p-type semiconductor with a bandgap of 1.2~2 eV) for the detection of ascorbic acid (Vitamin C) is reported. Nano CuS was synthesized hydrothermally by studying the effects of cationic and anionic surfactants (CTAB and SDS). The as-synthesized nanostructures were characterized for surface morphology, chemical composition, and crystal structure. The developed CuS nanoparticles were then drop-cast on a graphite electrode and subjected to the electrochemical detection of ascorbic acid. Further, the deposition time of the analyte and the deposition potential of the electrode was evaluated. It was observed that the time required for ascorbic acid to deposit on the electrode was 20 seconds and deposition potential was found to be 0.34V. Besides, the effect of analyte concentration on the sensing ability of the nanomaterial was studied and a linear relationship between the two was observed. The working pH was found to be 9.4.

INTRODUCTION

Researchers are exploring numerous techniques to synthesize materials on a nanoscale owing to their great advantage of enhanced properties such as lightweight, increased strength, photocatalytic ability, and enhanced chemical catalytic activity [1]. These nanomaterials are suitable for diverse applications such as solar cells, nano-fabrics, sensors, cosmetics, and for the domains such as medical, nano-biotechnology, bio-engineering, defense, security etc., [1]. Research on the synthesis of metal chalcogenides such as CuS and their multi-faceted applications due to unique structural and optical properties, are gaining momentum. In recent years the quantum confinement effect attributed to their small crystallite size is explored [2].

Among the different chalcogenides, the copper-based chalcogenides such as nanoparticles (NPs) of Cu–S/Se, Cu–In–S/Se, and Cu–Zn–Sn–S/Se are opted for photovoltaic, optoelectronic, electrochemical, and photocatalytic applications [3]. CuS NPs, also known as Copper monosulfide NPs are incredibly attractive due to abundant availability of the constituent elements, non-toxicity, low cost, and applications in various fields [3,4]. CuS is a p-type semiconductor with phase dependent band gap varying from 1.1 to 2.0 eV [5,6]. The semiconducting nature of CuS backed by an outstanding electrochemical activity, rich valency, good chemical stability, metal-like conductivity, and ease of synthesis in various

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shapes at nanoscale makes it a potential candidate for electrochemical sensing applications [7,8].

Among several analytical methods of detecting biomolecules such as fluorescence, spectrometry, chemiluminescence, electrochemistry, etc., electrochemical detection is considered a simple, sensitive, fast, and cost-efficient method [9]. Among the electrochemical methods, voltammetry is known for the detection of ascorbic acid due to its ability to detect a specific component even at very low concentrations, fast analysis, inherent simplicity, and ease of application. Also, there is no need for sophisticated instruments and trained personnel for voltammetry [10]. Electrochemical biosensors find their use in a variety of fields including medical, biological, food, and environment due to their advantages such as enhanced sensitivity, portability, low cost, online detection, rapid response, and reusability [11].

CuS generally exists in the hexagonal crystalline phase having a P63/MMC space group and a primitive hexagonal unit cell with a = 3.8020 Å and c = 16.430 Å. CuS is active both spectroscopically at 620 nm in the UV-Vis region and electrochemically between - 0.4 V to -0.7 V at different scan rates in an alkaline solution [12]. Its properties depend on the morphologies such as nanowires, nanoplates, nanotubes, nanorods, nanoflakes, hollow spheres, and complex hierarchal structures [13]. There are numerous methods available for the synthesis of nano CuS such as solvothermal [14], microwave [15], ultrasonic irradiation [16], and thermolysis of single-source precursors in high boiling point solvents that act as surface passivating agents [17,18]. Among these, the hydrothermal method prompts rapid reaction due to the interaction at high pressure. It offers advantages, such as low-temperature operation, reproducibility, homogeneity, and product purity [19].

In this study, the hydrothermal synthesis of CuS nanoparticles and the impact of surfactants on the size and morphology are reported. Further, the as-synthesized nanoparticles were tested for electrochemical detection of ascorbic acid by
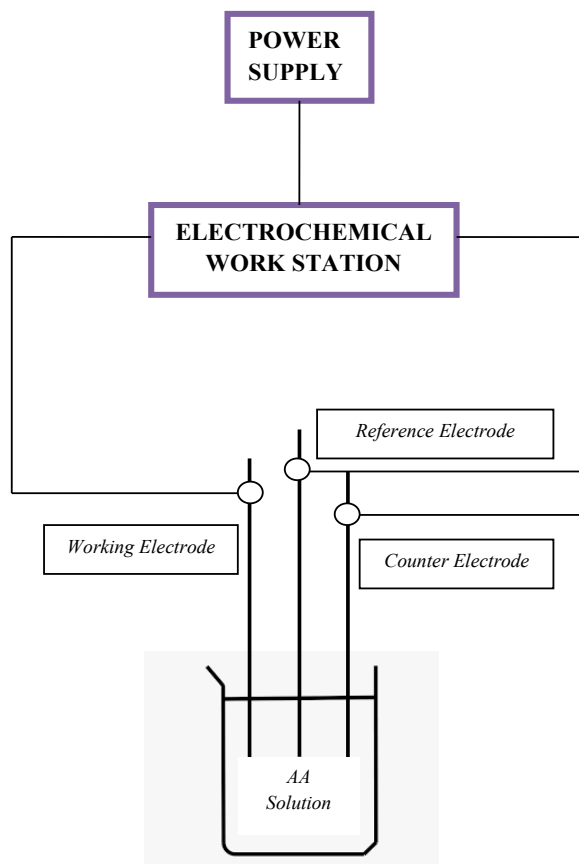
Fig. 1. Schematic of experimental setup for electrochemical

employing cyclic voltammetry.

MATERIALS AND METHODS

All the chemicals utilized were of analytical grade, purchased from Merck India Ltd., and were used as received without further purification. Cupric Sulphate ($CuSO_4.2H_2O$), Sodium Sulfide ($Na_2S.xH_2O$), Sodium Dodecyl Sulfate ($C_{12}H_{24}NaO_4S$), N,N,N,N-Cetyl Trimethyl Ammonium Bromide ($C_{19}H_{42}BrN$), and Acetone were used.

$CuSO_4$ and Na_2S were weighed in the mole ratio 1:2 and dissolved in 30mL of deionized water. 0.1g of SDS was added to the reactant solution under vigorous stirring to ensure that the reactants were well dispersed and the obtained solution transferred into a Teflon-lined autoclave. The above procedure was repeated by replacing the SDS with CTAB to study the impact of the surfactant. The autoclave was sealed and maintained at 120°C for 18 h. Later it was allowed to cool to room temperature, naturally. The as-obtained precipitate was centrifuged, washed sequentially with deionized water and acetone, and finally dried at 60°C for 2h in a hot air oven.

The sensing of ascorbic acid by the as-synthesized nanoparticles was carried out in an electrochemical sensing setup consisting of working, reference, and inert electrodes. The working electrode was fabricated by drop-casting the CuS solution on a graphite electrode. The working electrode was dipped in the electrolyte made of 2.5 mmol ascorbic acid solution (1 ml), phosphate buffer of pH 9 (8 ml), and 0.1M KCl solution (2 ml). Cyclic voltammetry was used to check the ability of nano CuS to detect ascorbic acid and to determine the voltage at which oxidation of ascorbic acid occurs. Fig. 1 is a schematic representation of the experimental setup. The oxidation of the ascorbic acid takes place at the working electrode and reduction takes place at the counter electrode. The potential developed due to this redox reaction is measured against the reference Ag/AgCl electrode. The effect of the concentration of ascorbic acid on the sensitivity of nano CuS was studied by varying the concentration of ascorbic acid and recording the respective peak values of current. The response of nano CuS to various concentrations was measured by adding 1 ml of 2.5 mmol ascorbic acid to the electrolyte solution, every 10 seconds. Optimum pH was determined by using buffer solutions of pH ranging from 3 to 9. These buffer solutions were prepared using 0.1 M HCl, 0.1 M Disodium Hydrogen Phosphate, and 0.1 M NaOH. The analyte was prepared by adding 8 ml of buffer solution to 2 ml of 0.1 M KCl and 5 ml of 2.5 mmol ascorbic acid. The optimum pH and concentration were determined at which the deposition time and deposition potential were measured.

All the synthesized samples were characterized on a Panalytical Powder Diffractometer with Cu Kα radiation (λ=1.5418 Å). The morphologies, sizes,
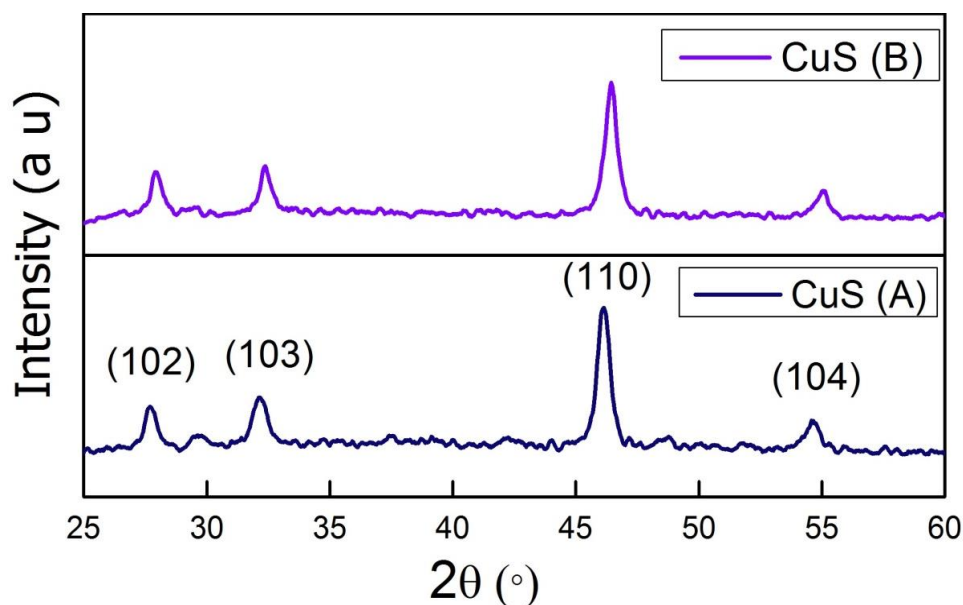

Fig. 2. PXRD of CuS nanoparticles synthesized using different surfactants

and purity of the final product were determined by scanning electron microscope (Tescan-VEGA3 LMU) and EDS analysis.

RESULTS AND DISCUSSION

The hydrothermal reaction between $CuSO_4$ and Na_2S resulted in a black precipitate. The obtained product was subjected to powder diffraction and all the peaks in Fig. 2 were indexed to digenite CuS (JCPDS Card No. 06-0464) with a = 3.792 Å and c = 16.34 Å. From the pattern, it is evident that the product is pure due to the absence of peaks corresponding to the precursors, copper oxide, or other phases of copper sulfide. The sharp and pronounced diffraction peaks suggest that the as-synthesized products are crystalline in nature [20].

EDAX spectra further confirmed the presence of Cu and S peaks alone and quantitative analysis revealed that Cu and S are in a stoichiometric ratio of 1:2.

Fig. 3(A) depicts the SEM images of nano CuS structures synthesized using SDS as the surfactant and deionized water as the solvent. It can be seen that much-elongated rice millet-like nano architectures with aggregation are present. Further, these images show the uniform nanoparticle clusters with particle sizes ranging from 49-64 nm. The aggregation can be attributed to the surfactant SDS which aids in the self-assembly of nanoparticles. The end-to-end growth of nanoparticles resulted in the formation of clusters of nano CuS architectures. However,
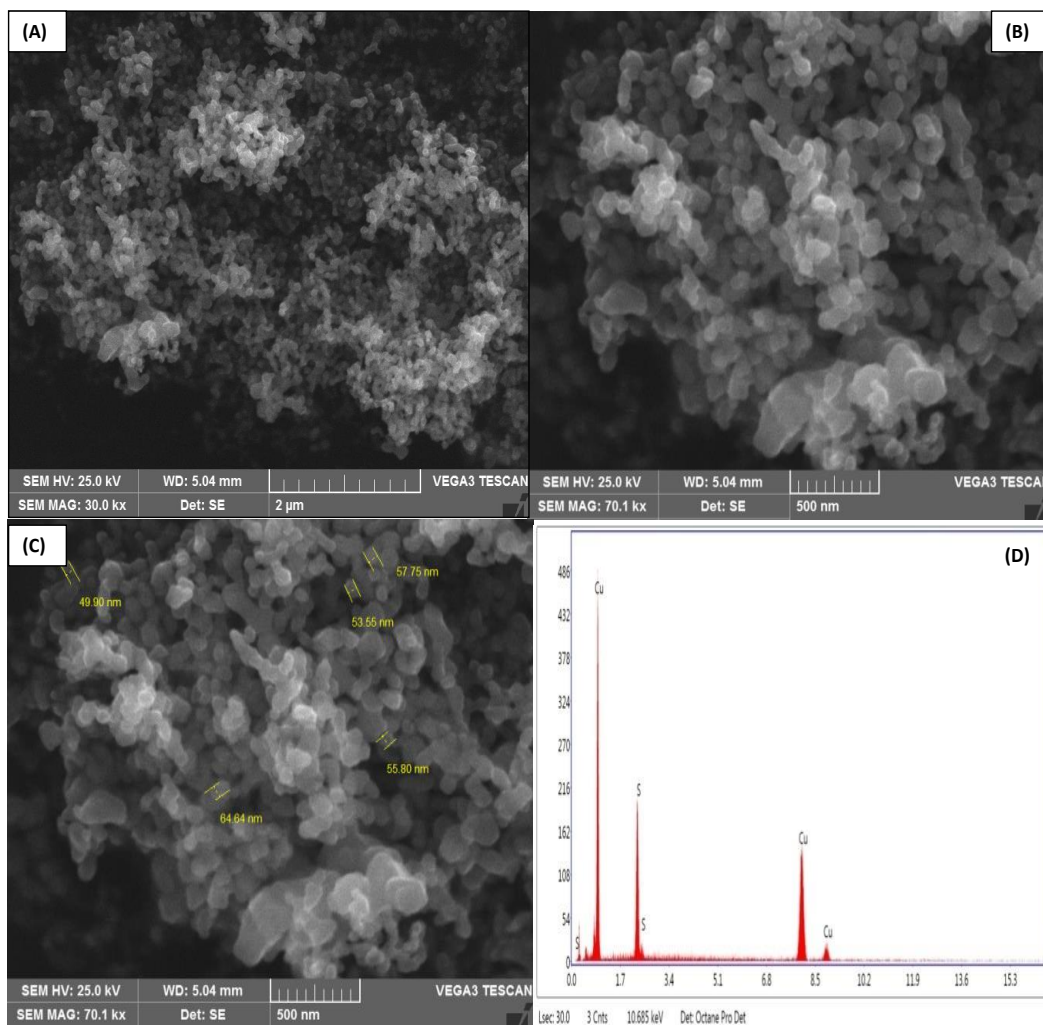

Fig. 3. SEM images of CuS nanoparticles with SDS as surfactant. SEM image at a magnification of (A) 2μm (B) 500nm (C) 500 nm with dimensions (D) EDS of CuS nanoparticles

the exact shape of the nanoparticles could not be determined due to excess agglomeration [21]. The XRD pattern of the as-obtained CuS nanoparticles shown in Fig. 2 (A) can be indexed as a dijenite phase (JCPDS Card No. 2-1292).

Fig. 3(B) shows the SEM images of nano CuS structures synthesized with CTAB as the surfactant and deionized water as the solvent. The nanoparticles are found to be uniform with particle sizes ranging from 17 – 40 nm. However, the aggregation is not much pronounced as in the case of SDS. CTAB, being a cationic surfactant, caps CuS and inhibits the lateral growth of CuS clusters helping to reduce agglomeration of nanoparticles. Aggregation of nanoparticles is strongly due to Van der Waals forces of attraction and π-π interaction. Hence, obtaining a stable dispersion is a challenge [22]. The fine and mostly monodispersed particles reveal that the growth of nanoparticles was restricted by CTAB [23]. CTAB thus facilitates the homogeneous formation of stable nano CuS structures with well-defined morphology [24]. The XRD pattern of the as-prepared CuS nanoparticles is shown in Fig. 2 (B). All the peaks of the CuS nanoparticles can be indexed as dijenite phase

(JCPDS Card No. 23-960) with lattice constants of a = 11.11 Å and c = 16.36 Å.

A noteworthy change is the reduction in the size of the nanoparticles when CTAB was employed as the surfactant. The aforementioned differences are correlated to the structure, size, and type of the surfactant. CTAB, due to its long chain, methyl branches, and cationic nature, prevents aggregation by restricting nanoparticles from being in close vicinity to each other. While the small size and the anionic nature of SDS cause the cupric ions to come closer to each other making the particles appear larger [21].

Electrochemical behavior of ascorbic acid indicates that it can either be in oxidized form (L-dehydroascorbic acid) or reduced form (L-ascorbic acid) obeying the equilibrium as follows [22]:

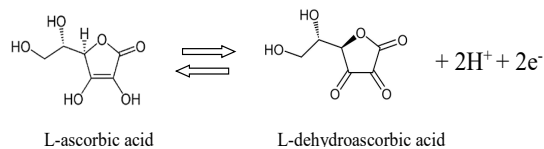L-ascorbic acid ⇌ L-dehydroascorbic acid $+ 2H^+ + 2e^-$

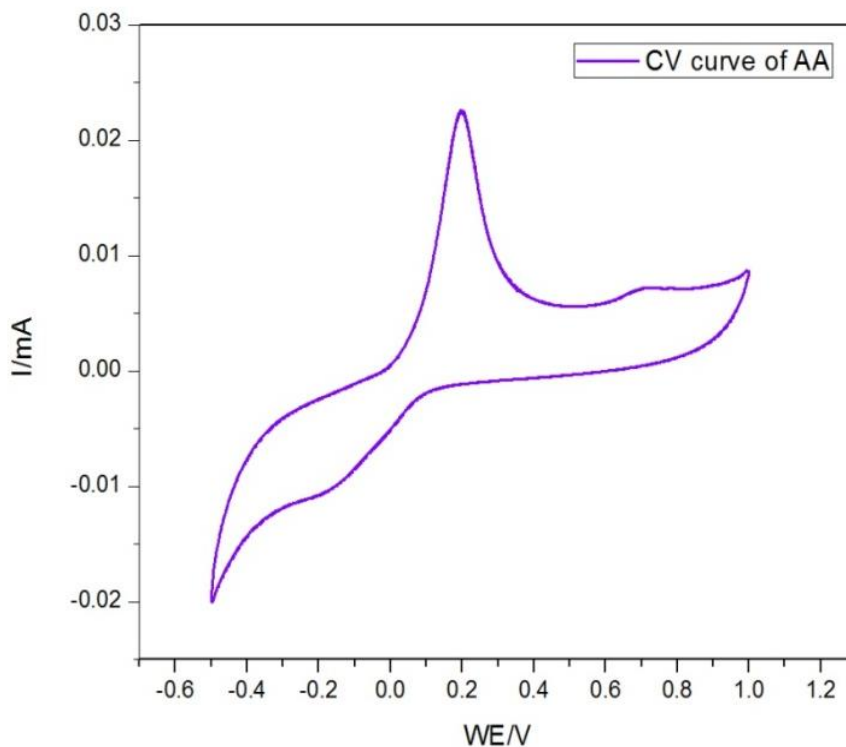Fig. 4 shows the cyclic voltammogram obtained

Fig. 4. Plot of current vs. voltage of working electrode (WE) (cyclic voltammogram of Ascorbic Acid (AA))
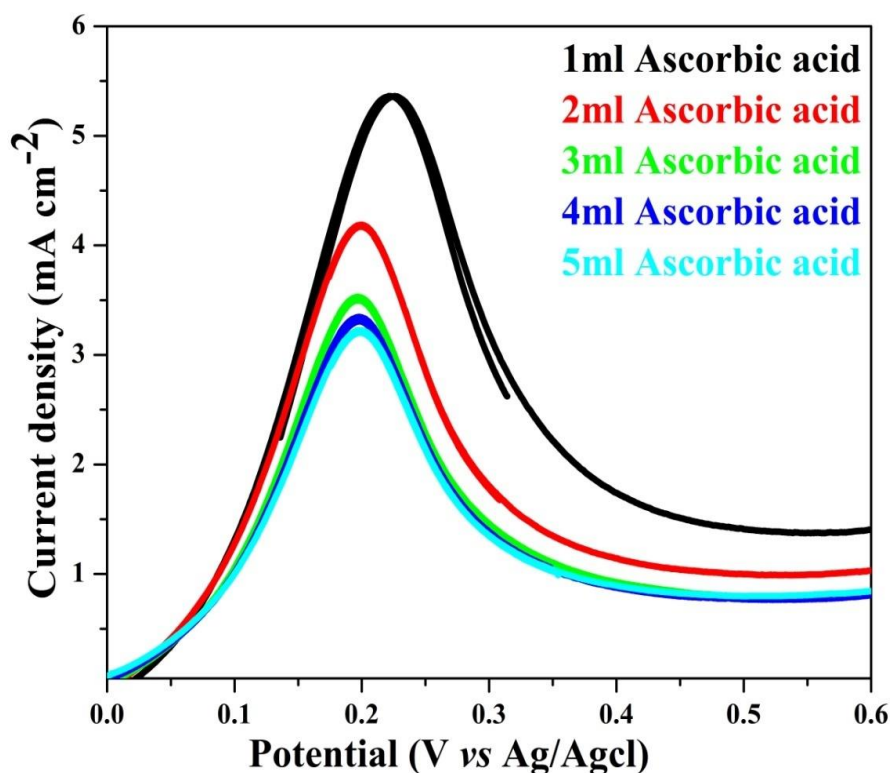
Fig. 5. A series of oxidation peaks for different concentrations of Ascorbic Acid at the working electrode

at a scan rate of 10 mVs^{-1}. The peak occurring at 0.2 V [23,24] confirms the detection of ascorbic acid by the CuS nanostructures. This peak represents the oxidation of ascorbic acid as indicated by the forward reaction of equation (1). Also, the absence of a reduction peak, as evident from the figure, further confirms the irreversibility of electrochemical oxidation of ascorbic acid [25,26].

Effect of concentration of ascorbic acid on the peak current

The ability of the nano CuS to detect ascorbic acid is correlated to the current registered by the working electrode. Variation in current is due to the variation in the concentration of ascorbic acid. In an experiment, the current flowing through the working electrode dipped in the analyte was monitored. The concentration of the ascorbic acid was varied by adding 1 ml of 50 ppm ascorbic acid to the stock solution as described in Section 2.1. A series of oxidation peaks for different concentrations of the analyte are shown in Fig. 5. A strong response is obtained at the analyte concentration of 5 ml ascorbic acid. Further, the relationship between the electrode current and concentration of the targeted species was obtained

and the resultant graph is shown in Fig. 6. A plot of average currents against the concentration of ascorbic acid indicates linearity as depicted in Fig. 7 [27].

A direct correlation between current (I) and concentration (C) is seen, allowing for the CuS nanoparticles to act as biosensors without any signal modification as indicated by equation (2). The statistical analysis and the fitted curve shown in Fig. S1, is enclosed in the supporting information.

$$I = 0.00548C + 0.0056$$

The concentration of ascorbic acid can be determined by equation (1) of the trend line in Fig. S1 relating the peak current I and concentration C of ascorbic acid. The error induced in the calculation of slope and intercept is of the order of 10^{-3} which is as shown in Table 1 and Table 2 presents the analysis of variation (ANOVA), which are presented in the supporting information.

Effect of pH of buffer solution on the electrochemical detection of ascorbic acid

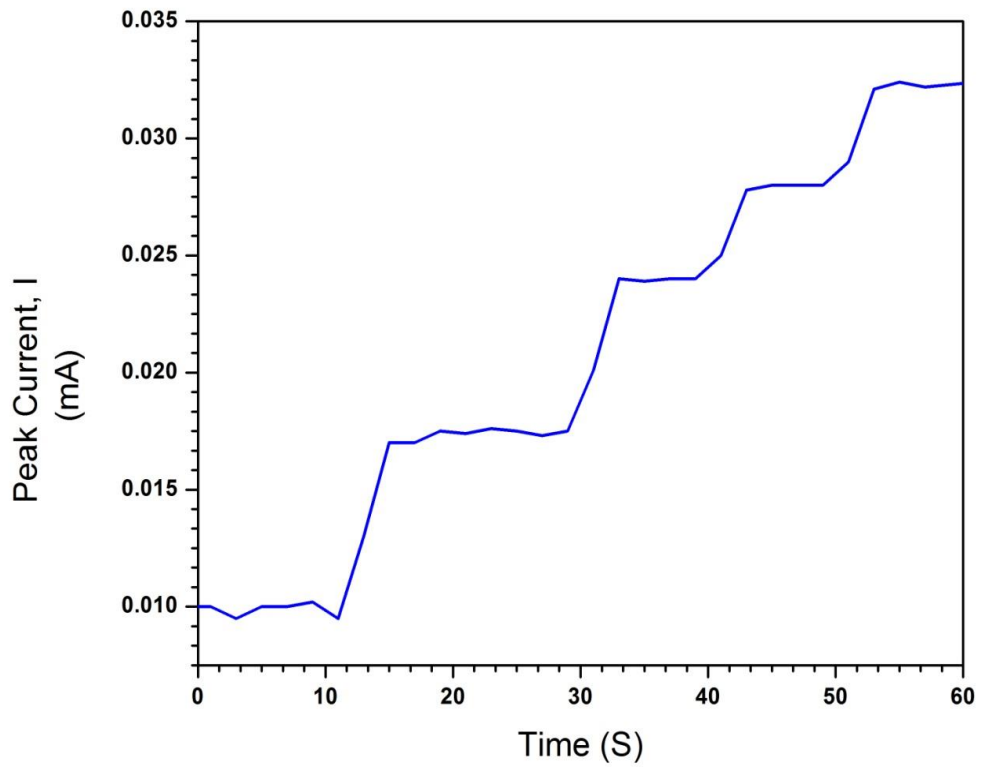One of the key parameters that influence the

Fig. 6. Plot of Peak Current vs. Time for 1 ml of 50 ppm added at every 10 seconds interval
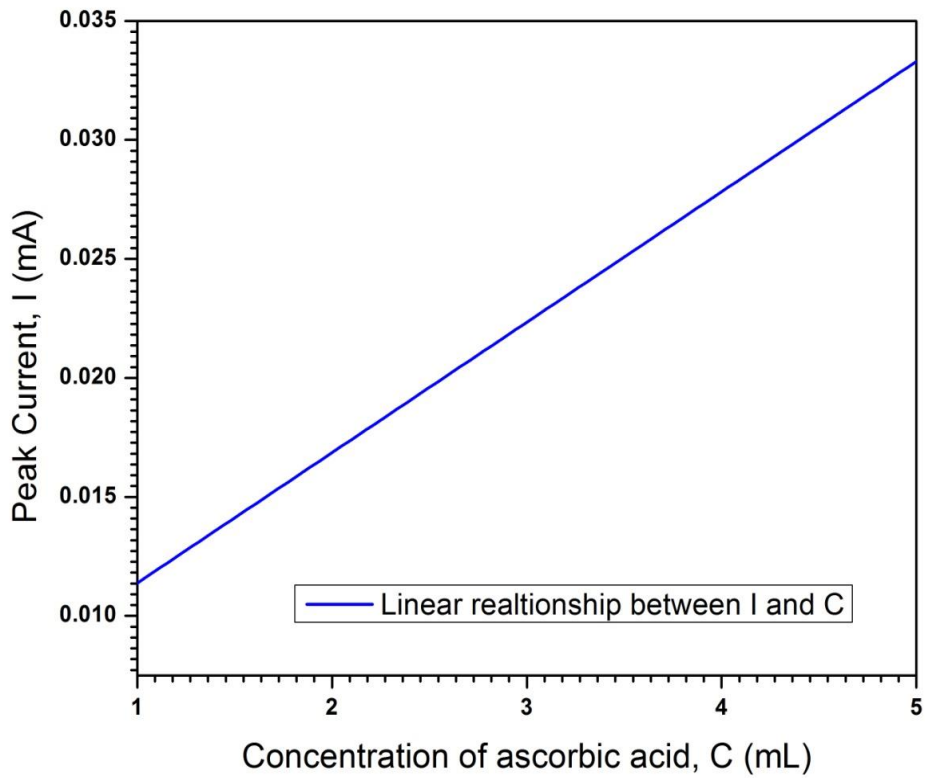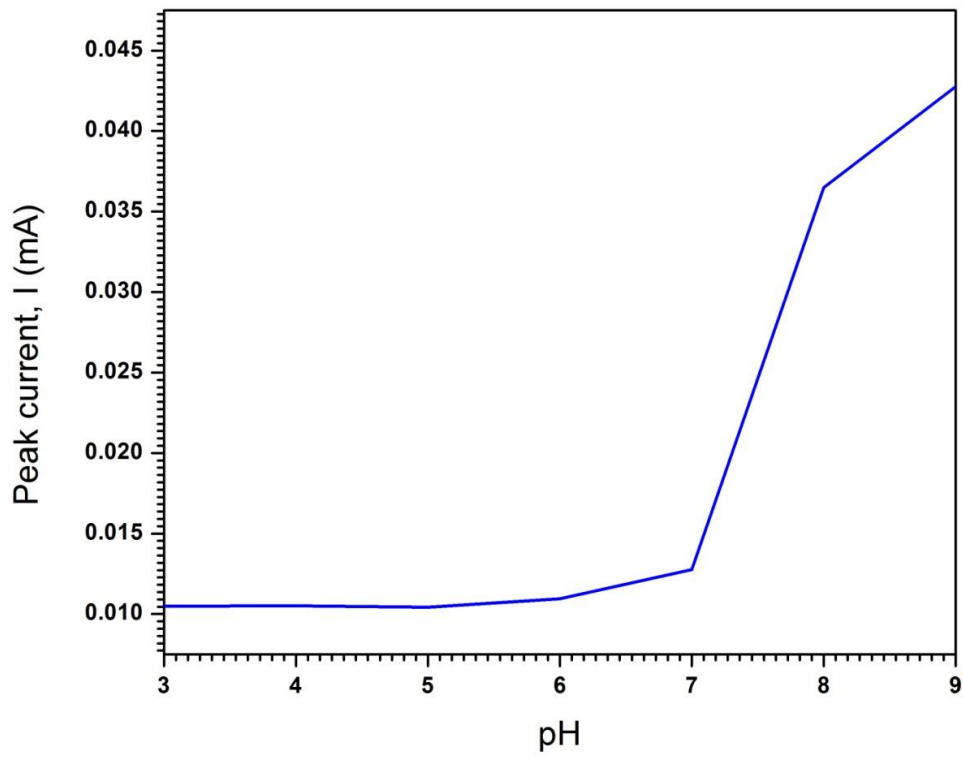

Fig. 7. Calibration plot

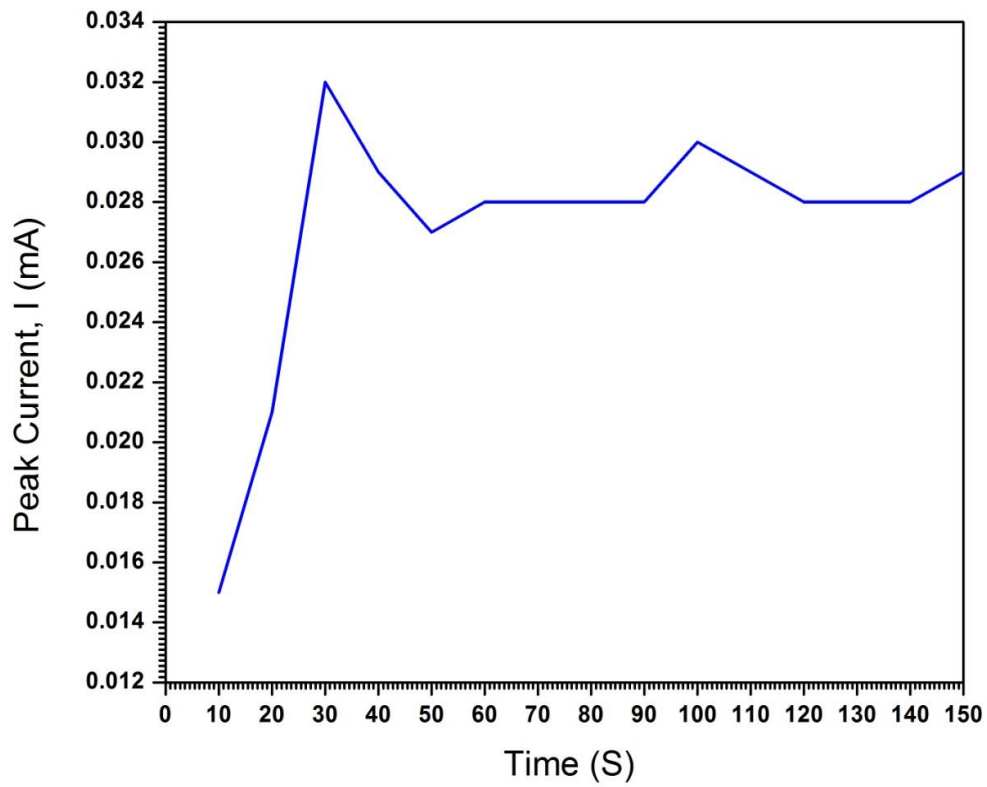Fig. 8. Plot of Peak Current vs. pH of buffer solution

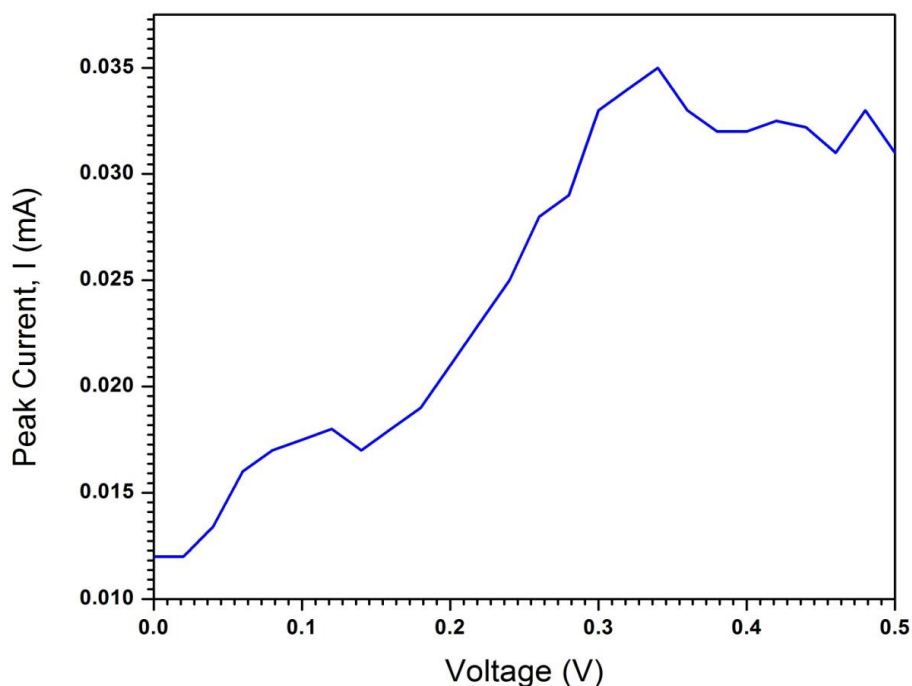Fig. 9. Plot of Peak Current vs Deposition Time

Fig. 10. Response of Peak Current for various Deposition Potentials

response of the electrode in the electrochemical detection of ascorbic acid is the pH of the buffer solution [28]. The pH of the buffer solution or the supporting electrolyte was varied from 3 to 9 to study its effect on the oxidation peak current of ascorbic acid. Fig. 8 shows the oxidation peak currents registered at different pH. The onset of current is observed at a pH of 7 and the peak is observed at a pH of 9 in the considered range of pH. Thus, the pH of the electrolyte solution was chosen to be 9 for all the further studies [29].

The effect of deposition time on the peak current was examined in the time range of 0-150 seconds at the optimized pH of 9 and a concentration of 5 ml of ascorbic acid solution. The peak current was observed at 20 seconds as shown in Fig. 9. Hence 20 seconds was taken as the deposition time for measuring the deposition potential. The electrochemical sensing ability of the nano CuS is affected by another important factor, the deposition potential [30]. The potential was varied from 0 V to 0.6 V and the corresponding response of the working electrode in terms of current was recorded as indicated in Fig. 10. The highest current was measured at 0.3V. This indicates that ascorbic acid observes maximum deposition onto the nanocomposite electrode at this voltage and is designated as deposition potential.

CONCLUSION

In summary, CuS nanoparticles were synthesized hydrothermally by studying the effects of surfactants on size and morphology. CuS nanoparticles were synthesized at a hydrothermal temperature of 120°C and a duration of 18 hours. The use of SDS as a surfactant resulted in the agglomeration of nanoparticles giving large clusters of size range 49 – 64nm. However, a particle size of 17 – 40 nm was obtained when CTAB was used as the surfactant. The nanoparticles obtained were elongated in shape. The as-synthesized nanoparticles were used for electrochemical detection of ascorbic acid by drop-casting on a graphite electrode. Cyclic voltammogram recorded the ascorbic acid oxidation peak at 0.2V confirming the ability of the nanoparticles to detect Vitamin C (ascorbic acid). The sensitivity of the nano CuS towards ascorbic acid was studied and a direct correlation was obtained indicating the use of nano CuS as a biosensor without the need for signal amplification. The concentration of ascorbic acid and pH of the buffer solution necessary for the optimum electrochemical response were found to be 5ml and 9 respectively. At this optimum concentration and pH, the deposition time and deposition potential were found to be 20 seconds and 0.3V respectively.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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