



Research article

Trace level monitoring of Cu(II) ion using CuS particles based membrane electrochemical sensor



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ABSTRACT

Cu(II) monitoring is a matter of great interest to researchers due to its toxicity and adverse environmental effects. Among different methods for detecting Cu(II), ion-selective electrode (ISE) is more advantageous as they are low-cost, easy to fabricate, and highly selective. Here, we report a simple, inexpensive, and reproducible procedure for the fabrication of Cu(II) ion-selective electrodes using CuS particles and polyvinyl chloride (PVC) as a matrix. CuS particles, obtained by chemical precipitation, were characterized using X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), and energy-dispersive X-Ray spectroscopy (EDX). Optimization of the membrane compositions was done to get a well-behaved sensor by varying amounts of CuS, PVC, and acetophenone (AP). A membrane composition of 0.4 g CuS, 0.5 g PVC, and 1.0 mL AP in 5.0 mL tetrahydrofuran (THF) gave a Nernstian slope of 27.31 mV per decade change of Cu(II) ion over a wide range of concentration down to 64 ppb (1×10^{-6} M). The sensor gave a fast response time of 25 s, and it indicated the endpoint in a potentiometric titration of Cu(II) with standard EDTA solution. A pH-independent potential response was obtained in the pH 4.0–6.0.

1. Introduction

Cu(II) is an essential trace element present in all land and marine organisms. It is a cofactor for various oxidative enzymes and plays an important role in different biological processes. World Health Organization (WHO) has set the limit of Cu(II) in drinking water at 2.0 mg/L [1, 2]. The increased accumulation of Cu(II) in the environment from numerous industrial sources poses a danger to public health. Excessive Cu(II) intake causes diseases such as gastrointestinal catarrh, Wilson disease, Menke's syndrome, hypoglycemia, dyslexia, and Alzheimer's [3, 4]. Thus, the determination of trace amount of Cu(II) has gained more attention as it directly affects human health and the environment.

Several instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-

MS), flow injection analysis, liquid chromatography, gravimetric, and voltammetric techniques are used for the determination of Cu(II) in environmental samples [5]. They can monitor and detect miscellaneous trace pollutants in the exposed environment, but unfortunately, their maintenance and operational cost is high [6, 7]. Thus, a portable, sensitive, and selective analytical technique is highly demanding. Electrochemical sensors or ion-selective electrodes (ISEs) can account for the aforementioned requirements to a greater extent [8, 9]. Such sensors even do not require sample pre-treatment conditions and can also be suitable for online analysis.

The critical part in designing an ion-selective electrode is finding a suitable and selective sensing element [10]. Various researchers have made numerous publications on neutral carrier and ion-exchange based ISEs [11, 12, 13, 14, 15, 16, 17, 18]. However, most of them suffer

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drawbacks such as narrow concentration range, high detection limit, and substantial interference effect of cations such as Fe^{3+} , Co^{2+} , Ni^{2+} , Sr^{2+} , Na^+ , Cs^+ and K^+ . CuS– Ag_2S all solid state Cu(II) ion-selective electrodes have been reported to give good response to Cu(II) ion [19, 20]. Such electrodes have been limited by the leaching of Cu(II) ion from the membrane and poor mechanical properties of the pellet [10, 19, 20]. This has given rise to the development of PVC matrix membrane ion-selective electrodes [21]. This idea has been further expanded by using nanoparticles trapped PVC membrane ion-selective electrodes to detect Cu(II) ion with mixed success in obtaining reproducible and reliable sensor response [7, 22, 23]. However, more study is needed to get information concerning nanoparticle characterization and its effect on the response and stability of the fabricated sensor.

Copper sulfide (CuS) nanoparticles have attracted tremendous interest due to their quantum size effect [24, 25, 26]. The constituents of CuS nanoparticles (Cu and S) are abundant in nature; they are non-toxic and cheap. It is alluring as it exists in different stoichiometric compositions with varying crystalline phases [24, 27, 28]. It behaves as a p-type semiconductor with a bandgap of 2 eV. The bandgap matches with ultraviolet and visible light energy so that CuS can be used in a wide range of applications such as electro-conductive electrodes, solar cell devices, IR detectors, Li-ion batteries, and other optoelectronic devices [29, 30].

CuS nanoparticles in a polymer matrix show excellent applications [21, 31, 32, 33]. This paper describes an electrochemical sensor fabricated by using CuS particles in the matrix of polyvinyl chloride (PVC) and acetophenone (AP) plasticizer for selective and sensitive detection of Cu(II) ions. CuS particles were prepared by chemical precipitation routes using dimethylformamide (DMF) as a stabilizing agent. The effects of parameters such as membrane composition, pH of the solution, internal solution concentration, and response time have been studied. The selectivity coefficients were determined by using the match potential method. Finally, fabricated CuS ion-selective electrode (ISE) was used as an indicator electrode for the titration of Cu(II) ion with hexadentate ligands EDTA.

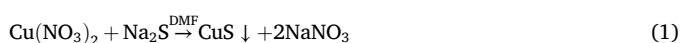
2. Experimental

2.1. Chemicals and reagents preparation

Analytical reagent grade copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), sodium sulfide (Na_2S), dimethylformamide (DMF), potassium nitrate (KNO_3), ferric chloride (FeCl_3), ethylene diamine tetraacetic acid (EDTA), Tetrahydrofuran (THF), Acetophenone, (AP), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), potassium nitrate (KNO_3), silver nitrate (AgNO_3), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$), ammonium nitrate (NH_4NO_3), and sodium nitrate (NaNO_3) were purchased from Sigma Aldrich, India. A commercial-grade polyvinyl chloride (PVC), laboratory-grade sodium hydroxide (NaOH), and nitric acid (HNO_3) were used. All the chemicals of required concentrations were prepared in double-distilled water.

2.2. Preparation of CuS particles

CuS particles were synthesized by chemical precipitation method using DMF as a stabilizing agent [26, 28, 30]. For this, 100 ml of 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution was mixed with 20 ml of DMF and stirred for 10 minutes. Then, 100 ml of 0.1 M Na_2S solution was added to the mixture dropwise with constant stirring for 3 hours and left overnight. The reaction mixture was decanted, and the precipitate was washed with distilled water, filtered through Whatman 42 filter paper, and dried in an oven at 60°C for 8 hours. Eq. (1) represents the precipitation of CuS particles.



2.3. Characterization of CuS particles

The crystalline phase of the synthesized CuS particles was characterized by a Bruker X-ray diffractometer using Cu- $\text{K}\alpha$ radiation having a wavelength (λ) of 1.5406 Å in the range of 2θ , 2θ , 2θ . The Fourier-transform infrared (FTIR) spectrum of the CuS particles was recorded on a Shimadzu tracer-100 spectrophotometer in the wavelength range of $400\text{--}4000\text{ cm}^{-1}$. UV-Visible spectrum of CuS dispersed in water was recorded on double beam Labtronics LT-2802 spectrophotometer in the wavenumber range of 200–400 nm. The surface morphology and elemental characterization of the synthesized CuS particles were observed by scanning electron microscopy (SEM) (Merlin, Zeiss Microscopy, Germany) and energy dispersive x-ray spectrophotometer (EDX) (Hitachi H-7100).

2.4. Preparation of CuS-PVC membrane and electrode

CuS-PVC sensor membrane was prepared by mixing CuS with PVC in the presence of AP as a plasticizer. The amount of PVC was fixed at 0.5 g, while the amount of CuS was 0.2, 0.3, 0.4, and 0.5 g. Each mixture of CuS and PVC was put into a Petri dish containing 10.0 ml of THF and 1.0 ml of AP. Finally, the mixture was homogenized and left overnight at room temperature for the evaporation of the organic solvent to get a thin CuS-PVC membrane.

An inner filling CuS-PVC membrane electrode was prepared by fixing the membrane in a polyethylene (PE) tube. The tube was filled with an internal solution of $\text{Cu}(\text{NO}_3)_2$, and a self-made miniaturized silver/silver chloride reference electrode (SSE) was inserted in the inner filling solution by adopting the established procedure [34]. The fabricated electrode was then equilibrated for 24 h in a 0.01 M $\text{Cu}(\text{NO}_3)_2$ solution for performance measurement. The cell assembly given below was used to calibrate the electrode

Ag/AgCl , $\text{Cu}(\text{II})$ (aq.), PVC membrane/test solution/SCE

The cell electromotive force (EMF) was measured by a digital multimeter (BK TEST BENCH 389).

2.5. CuS-PVC electrode response characterization

The cell assembly thus prepared was used for direct potentiometry measurements of Cu(II) ion concentration in the range of 10^{-6} M to 10^{-1} M . A saturated calomel electrode (SCE) was used as an outer reference electrode, and cell EMF was measured within $\pm 2.0\text{ mV}$ accuracy in all the measurements. The cell assembly of Ag/AgCl , $\text{Cu}(\text{II})$ (aq.), sensor membrane/test solution/SCE was used to measure the Nernstian response of thus fabricated CuS-PVC membrane electrode. The cell EMF dependency on pH of the Cu(II) ion solution was measured in the pH range 1–8 at a fixed Cu(II) ion concentration of $1.0 \times 10^{-3}\text{ M}$. The pH of the test solution was adjusted by dropwise addition of an appropriate volume of either 2 M HNO_3 or 2 M NaOH solution for lowering and raising the pH of the test solution.

The CuS-PVC membrane electrode response time was evaluated by effecting a tenfold increase of Cu(II) ion concentration and recording the cell EMF every 5s till 80s. A plot of measured cell EMF against elapsed time was made to determine the time taken by the sensor to produce an equilibrium cell EMF.

Potentiometric titration between the Cu(II) solution and a standard EDTA solution was monitored using the fabricated Cu-PVC membrane as an indicator electrode combined with an external SCE reference. Both electrodes were connected through a salt bridge of potassium nitrate in agar-agar gel. Cell EMF was measured after the addition of a known volume of EDTA (10^{-2} M).

Finally, the selectivity coefficient of the membrane electrode was calculated by the match potential method [5]. The concentration of

interfering ions (secondary ion) producing the same potential change effected by Cu(II) ion (primary ion) was estimated by using Eq. (2)

$$K_{A,B}^{pot} = (\Delta a_A/B) \quad (2)$$

Where Δa_A is the concentration difference of primary ion producing an EMF change equivalent to Nernstian slope, B is the concentration of interfering ions producing EMF change equivalent to Nernstian slope. The interfering ions used for the purpose were Co^{2+} , Ni^{2+} , Cd^{2+} , K^+ , NH_4^+ , Na^+ .

3. Results and discussion

3.1. Characterization of CuS particles

Figure 1 shows the X-ray diffraction pattern of CuS particles. The obtained diffraction patterns at $2\theta = 29.83, 32.20, 48.52, 52.91,$ and 59.70 correspond to the (102), (103), (110), (108), and (116) planes of CuS, respectively [35, 36, 37]. The diffraction patterns and interplanar spacing of the CuS particles was in good agreement with the standard hexagonal structure of CuS (JCPDS 06-0464). An average crystallite size of the CuS particles was estimated using Debye-Scherrer Eq. (3) [38]:

$$D = k\lambda/\beta\cos\theta \quad (3)$$

Where D is average crystallite size, k is Scherrer constant, λ is the wavelength of X-ray, β is peak width of half maximum, and θ is Bragg diffraction angle.

For the most intense peak at $48.52^\circ 2\theta$, substituting a value of 0.94 for k , and 0.63 for β gave crystallite size of 13.2 nm. Therefore, the X-ray diffraction pattern confirmed the formation of CuS particles in the nano range.

FTIR spectrum of CuS particles is depicted in Figure 2. The peaks observed at 478 cm^{-1} and 669 cm^{-1} were attributed to Cu-S stretching. These bands were in agreement with the peak reported in the literature [39].

UV-Visible spectrum of CuS particles dispersed in water is shown in Figure 3. The spectrum exhibited an absorption band edge centered at about 300 nm, which is blue-shifted. The blue shift in the absorption band edge shows that the smaller crystallite size of CuS particles exhibit a remarkable quantum size effect on its optical properties [24]. The absorption peak is consistent with a smaller crystallite size of the synthesized particles [24].

The bandgap of CuS particles was calculated by using the following Eq. (4) [40].

$$\alpha h\nu = A(h\nu - E_g)^r \quad (4)$$

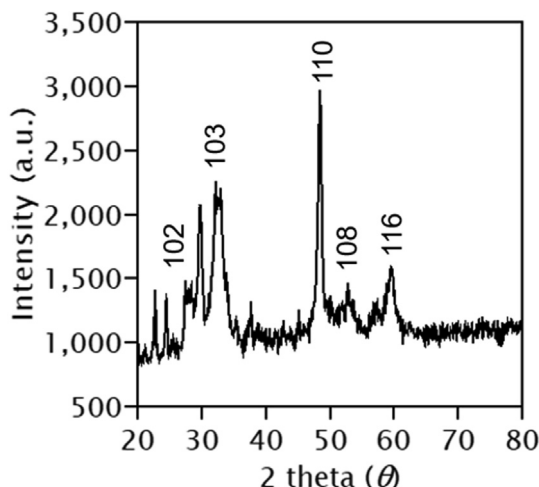


Figure 1. XRD pattern of CuS particles.

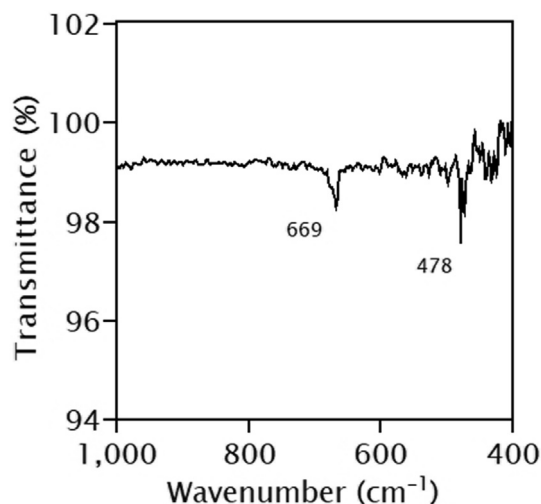


Figure 2. FTIR of CuS particles.

Where α is the coefficient of absorption, h is the Planck's constant, E_g is the optical energy gap of material, ν is the frequency of light, A is constant, r depends on the nature of the electron transition ($1/2$ for direct transition and 2 for indirect transition band gaps), and $h\nu$ is the energy of the photon. By extrapolating the plot of $(\alpha h\nu)^2$ with energy as shown in Figure 3b, the bandgap energy of CuS particle was calculated as 3.8eV, which is higher than that of bulk CuS (2.2eV) and as expected for nanoparticles. The larger bandgap is due to the quantum size confinement effects, and there is wide variation in the reported band gap values of CuS nanoparticles [24, 28, 41].

3.2. SEM-EDX analysis

The SEM image of the synthesized CuS particles is shown in Figure 4a, which is a representative image taken over several locations. The image shows the granular shape with some degree of agglomeration. The average size ranged from 80 to 750 nm in diameter. The irregular size distribution could be attributed to the uncontrolled nucleation of CuS.

EDX patterns were used to evaluate the composition and purity of the resulting CuS particles, as shown in Figure 4b. It shows the presence of Cu and S peaks with the presence of O peaks. The existence of oxygen is taken as impurities due to surface contamination. The average atomic ratio of Cu:S, calculated from the quantification of the peaks (O element excluded), gave the value of 24.5:20.9. This indicates that the surface of the samples was rich in Cu. The deviation of atomic ratio from 1:1 was believed to be originated from the absorption of excessive Cu(II) on the surface of the nanoparticles.

3.3. Response of the CuS-PVC membrane

Four CuS-PVC membranes with different compositions were prepared to evaluate the best performance of the membrane. The ratio of CuS, PVC, THF, and acetophenone were varied as shown in Table 1 to make a membrane of CuS entrapped in the matrix of PVC.

The response of the membrane towards Cu(II) ion concentrations was evaluated in a direct potentiometry. For this, the internal filling solution of $1 \times 10^{-3}\text{ M Cu(NO}_3)_2$ solution was used, and the external solution was varied from 1.0×10^{-6} to $1.0 \times 10^{-1}\text{ M}$ by the standard addition method [8]. The plots of cell EMF of all four CuS-PVC membrane as a function of the concentration of Cu(II) thus obtained are shown in Figure 5. The cell EMF of a Cu(II) ion-selective membrane can be given by Eq. (5),

$$E_{cell} = E'_0 + 0.0295 \log [Cu^{2+}] \quad (5)$$

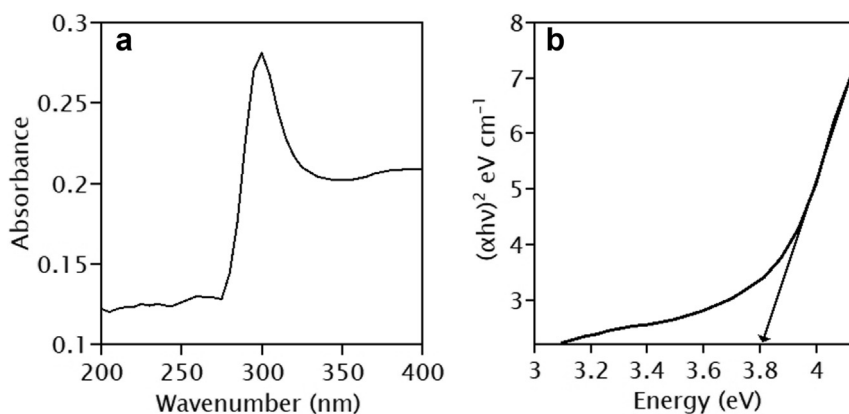


Figure 3. a) UV-Vis Spectra of CuS particles b) Bandgap energy plot.

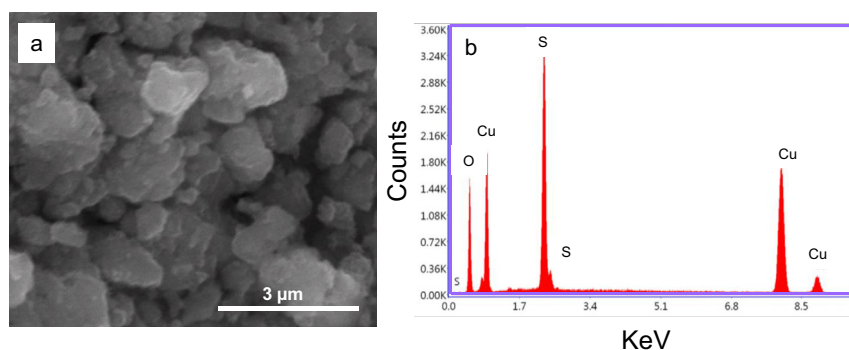


Figure 4. a) SEM image of CuS particle and b) Its EDX mapping.

Table 1. Composition of different membranes of CuS in PVC matrix.

Membrane No.	CuS (g)	PVC (g)	Acetophenone (mL)	THF (mL)
1	0.2	0.5	1	10
2	0.3	0.5	1	10
3	0.4	0.5	1	10
4	0.5	0.5	1	10

Figure 5 shows the EMF of the cell increases with decrease in Cu(II) ion concentration that is dictated by the constant, E'_0 which includes the contributions of both the reference electrodes. The linear concentrations range and slope, evaluated by linear regression analysis, for different

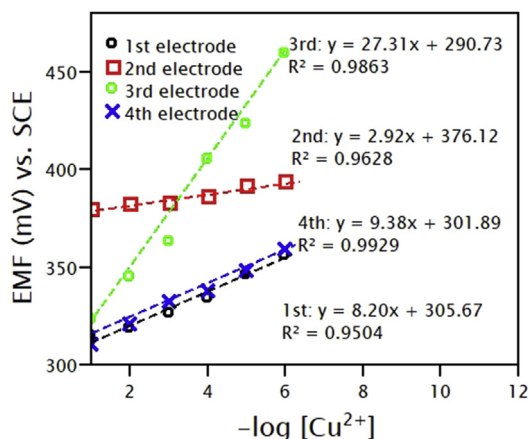


Figure 5. Cell EMF vs. concentration of Cu^{2+} curve for all the membrane electrodes.

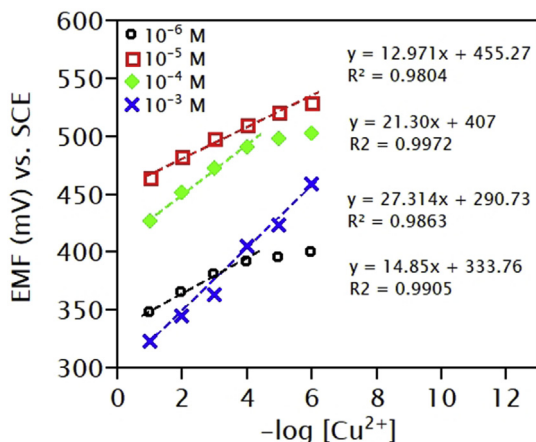
membranes are compared in Table 2. All the membranes show linearity in the cell EMF over a concentration range from 10^{-6} to 10^{-1} M. However, the Nernstian slope was greatly affected by the composition of the membrane. Only membrane 3 electrode showed the Nernstian slope of 27.31 mV per decade change in concentration of Cu(II) ion. All the other membranes did not show satisfactory slopes and, therefore, were discarded for further study. It is clear that the composition of the membrane profoundly affects the response and performance of the membrane electrode. The low Nernstian slopes in membrane electrode other than electrode 3 show the sluggish establishment of ionic equilibrium at the PVC membrane-solution interface, which is affected by the surface distribution of the CuS particles in the PVC matrix [22]. These electrodes needed a relatively longer time to give higher Nernstian slope, which is not practical in real measurements. The result shows that membrane electrode 3 can be well used for monitoring Cu(II) ion concentration as low as 64 ppb with great accuracy, which fulfills the requirement of Cu(II) sensor for environmental monitoring of Cu(II) ion in drinking water, wastewater, and any such applications which discharge low amount of Cu(II) ion. Also, this sensor showed better Nernstian response and stability compared to all solid-state CuS electrode [20] without facing any problem of membrane crack unlike in all solid-state membrane.

To further understand the response of the 3rd membrane electrode towards Cu(II) ion, the effect of the internal filling solution was studied by varying its concentration viz., 10^{-3} to 10^{-6} M Cu(II), and measuring the cell EMF in the range of 10^{-6} to 10^{-1} M external $\text{Cu}(\text{NO}_3)_2$ solutions. The internal filling solution results on cell EMF are presented in Figure 6, and slopes and linear concentration range are tabulated in Table 3.

Figure 6 and Table 3 show that the best working range (10^{-1} – 10^{-6} M Cu(II)), as well as the Nernstian slope (27.31 mV/decade Cu(II) against a theoretical Nernstian slope of 29.16 mV), is obtained for internal filling solution of 10^{-3} M Cu(II). Another internal filling solution has resulted in

Table 2. Various parameters evaluated from plots in Figure 5 for different membrane compositions.

Membrane no.	Intercept (mV)	Concentration range (M)	Slope mV/decade
1	305.67	10^{-1} – 10^{-6}	8.20
2	376.12	10^{-1} – 10^{-6}	2.92
3	290.73	10^{-1} – 10^{-6}	27.31
4	301.89	10^{-1} – 10^{-6}	9.22

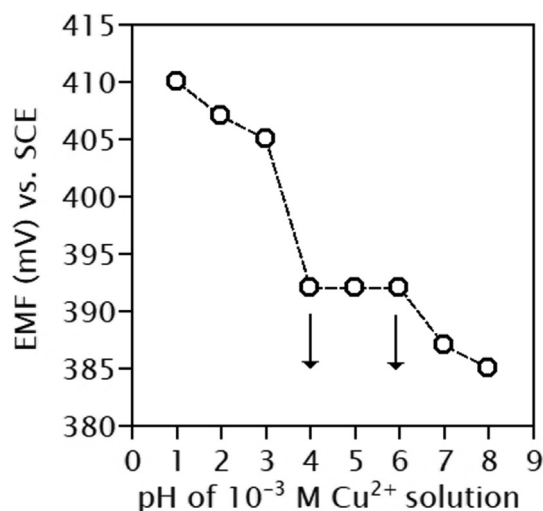
**Figure 6.** Cell EMF vs. concentration plots for 3rd membrane electrode with different internal reference solutions of $\text{Cu}(\text{NO}_3)_2$.**Table 3.** Effect of internal solution on the slope of the 3rd membrane electrode.

Internal (Cu(II)) (M)	Slope (mV)	Linearity in external (Cu(II)) (M)
10^{-3}	27.31	10^{-1} – 10^{-6}
10^{-4}	21.30	10^{-1} – 10^{-4}
10^{-5}	12.97	10^{-1} – 10^{-6}
10^{-6}	14.85	10^{-1} – 10^{-4}

poor Nernstian slope and working concentration range. The role of internal filling solution is to charge up the outer surface of the membrane and helps attain the ionic equilibria as fast as possible. At higher concentration of internal filling, the outer surface of the membrane is highly charged up so that fast ionic equilibrium is established and therefore a higher Nernstian slope is obtained. However, when the concentration of internal filling solution is decreased (from 10^{-4} M to 10^{-6} M), the outer surface of the membrane has low charge build up and therefore it could not maintain ionic equilibrium quickly. This also results in decrease in linearity in the outer $\text{Cu}(\text{II})$ ion solution (to 10^{-4} M) due probably to disturbance in the ionic flux at the outer surface. Therefore, the best membrane composition and internal filling solution were finally obtained to study the membrane electrode response towards $\text{Cu}(\text{II})$ further.

3.4. Effect of pH

The pH effect of the test solution on the EMF response of the 3rd CuS -PVC membrane was studied in the pH range of 1–8, as shown in Figure 7. $\text{Cu}(\text{II})$ ion concentration of 1.0×10^{-3} M was used as both external and internal solution to study the pH effect on the cell EMF. The cell EMF remained independent of pH in the range 4–6. In the acidic solution below pH 4, effected by adding 2 M HNO_3 dropwise, the cell EMF increases drastically due to the adsorption of H^+ ions. On the other hand, as the pH shifted to higher values than 6 the cell EMF decreases due to the adsorption of OH^- ions on the membrane surface. The results show that the cell EMF responded to H^+ and OH^- concentrations at low and high pH, respectively, and therefore for application of this membrane

**Figure 7.** Effects of pH on the EMF of the 3rd membrane electrode immersed in 10^{-3} M external $\text{Cu}(\text{II})$ solution containing the same internal solution concentration.

electrode for the measurement of $\text{Cu}(\text{II})$ ion, a pH range of 4–6 should be maintained. The pH response of solid-state Cu -ISE has been reported to be almost similar [37].

3.5. Potentiometric titration

The analytical utility of the membrane electrode has been established using it as an indicator electrode in the potentiometric titration of $\text{Cu}(\text{II})$ with a standard solution of EDTA as titrant. 30 mL of 1×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ was titrated against 1×10^{-2} M standard EDTA solution, and the titration curve is shown in Figure 8. As the EDTA solution was added to the $\text{Cu}(\text{II})$ solution, the EDTA- Cu complex was formed and resulted in a gradual decrease in cell EMF value due to the decrease in $\text{Cu}(\text{II})$ concentration. Unlike in other potentiometric titration, a sharp breakpoint was not found that could indicate a precise estimation of $\text{Cu}(\text{II})$. But, from a certain point, the cell EMF increased gradually. Therefore, at the intersection of two regions of EMF change, the endpoint was located at 3.2 mL of EDTA solution (Figure 8), which was about 107% of the theoretical values and within the experimental error. The concentration of $\text{Cu}(\text{NO}_3)_2$ solution was calculated using a well-known formula, as

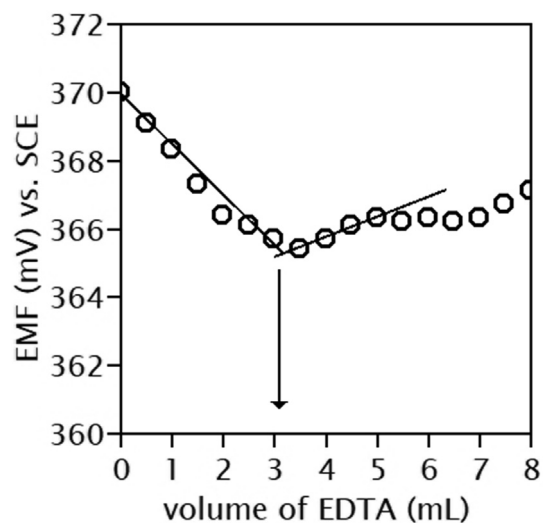
**Figure 8.** Potentiometric titration of 30 mL of 1×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ solution vs. 1×10^{-2} M EDTA solution using 3rd electrode.

Table 4. Calculation of concentration of $\text{Cu}(\text{NO}_3)_2$ solution using $V_1M_1 = V_2M_2$.

Volume of $\text{Cu}(\text{NO}_3)_2$ (mL)	Concentration of EDTA (M)	Volume of EDTA consumed (mL)	Estimated Concentration of $\text{Cu}(\text{NO}_3)_2$ (M)
30.0	1×10^{-2}	3.2	1.06×10^{-3}

shown in Table 4. The increase of cell EMF after endpoint indicates that the membrane electrode also responds to the EDTA. The result shows that the CuS-PVC membrane electrode could be successfully used for the potentiometric determination of Cu(II) ions with an EDTA solution as a titrant.

3.6. Response time

The practical time required for the Cu-sensor membrane to reach a potential of equilibrium value after a rapid change in the concentration of Cu(II) ions brought about by the standard addition method to effect a 10-fold difference in concentration was measured. The cell EMF vs. time plot is shown in Figure 9. As seen in the figure, the cell EMF reaches its equilibrium value in about 25–30 seconds in most cases, except at low concentration. In 10^{-6} M Cu(II) ion concentration, the electrode was not allowed to remain in the test solution for too long a period as this leads to deterioration of the membrane. The estimated response time of the membrane electrode suggests it could monitor the Cu(II) ion concentration inflow system such as sewage and drainage from industry.

3.7. Potentiometric selectivity

Selectivity studies were carried out by the potential match method. Ions like Pb^{2+} and Ag^+ showed little interference at concentration $<10^{-2}$

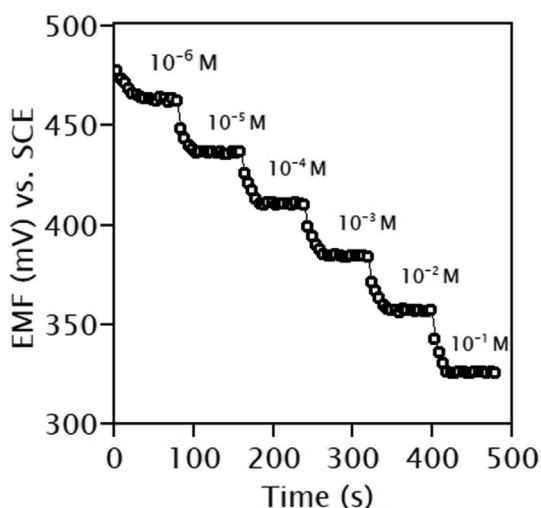


Figure 9. Change of cell EMF with drastic change of concentration of 1×10^{-2} ion by standard addition method giving the response of the membrane electrode.

Table 5. Effect of different ions on the response of the CuS-PVC membrane electrode.

Interfering Ions	Selectivity coefficient
Co^{2+}	3.5×10^{-3}
Ni^{2+}	7.0×10^{-3}
Cd^{2+}	3.0×10^{-3}
K^+	2.5×10^{-3}
NH_4^+	5.0×10^{-3}
Na^+	4.6×10^{-3}

M. Table 5 shows that the selectivity coefficient values are less than 1.0, which indicates that these ions could not affect the response of the CuS-PVC membrane for Cu(II) ions in the concentration range over which it showed linearity. The selectivity coefficient values are minimal, so the membrane can be used to determine Cu(II) ions with the same accuracy.

4. Conclusion

This study shows that a Cu(II) ion-selective electrode has been successfully fabricated using CuS particles trapped in a PVC matrix. Formation of CuS particles are confirmed by the XRD pattern showing an average crystalite size of 13.2 nm. The FTIR spectrum shows the presence of Cu-S stretching peaks around 669 and 478 cm^{-1} . The surface image by SEM indicates the granular but irregular distribution of particle size. The membrane electrode prepared with 0.4 g CuS, 0.5 g PVC with 1 ml AP shows the best response towards Cu(II) ion in the concentration range of 10^{-1} M to 10^{-6} M (64 ppb) with a Nernstian slope of 27.31 mV in the pH range 4–6. The membrane electrode performs well as an indicator electrode in the potentiometric titration of Cu(II) with EDTA solution. The prepared Cu-PVC electrochemical sensor is portable, inexpensive, and shows good response time. However, it cannot be used for more than 3 months.

Declarations

Author contribution statement

Dipak Kumar Gupta, Shova Neupane: Analyzed and interpreted the data; Wrote the paper.

Harish Chand Yadav, Vivek Subedi: Performed the experiments.

Sanjay Singh, Ram Jeewan Yadav, Anju Kumari Das, Brahamdeo Yadav, Krishna Badan Nakarmi, Nabin Karki: Contributed reagents, materials, analysis tools or data.

Amar Prasad Yadav: Conceived and designed the experiments; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

- [1] X.-H. Zhao, Q.-J. Ma, X.-B. Zhang, B. Huang, Q. Jiang, J. Zhang, G.-L. Shen, R.-Q. Yu, A highly selective fluorescent sensor for Cu^{2+} based on a covalently immobilized naphthalimide derivative, *Anal. Sci.* 26 (2010) 585–590.
- [2] M.R. Shishehbore, N. Nasirizadeh, A.H. Shabani, M. Tabatabaee, Spectrophotometric determination of trace copper after preconcentration with 1,5-diphenylcarbazone on microcrystalline naphthalene, *Can. J. Anal. Sci. Spectrosc.* 50 (2005) 130–134.
- [3] A.K. Singh, S. Mehtab, A.K. Jain, Selective electrochemical sensor for copper (II) ion based on chelating ionophores, *Anal. Chim. Acta* 575 (2006) 25–31.
- [4] M. Tutulea-Anastasiu, D. Wilson, M. del Valle, C. Schreiner, I. Cretescu, A solid-contact ion selective electrode for copper(II) using a succinimide derivative as ionophore, *Sensors* 13 (2013) 4367–4377.
- [5] D.A. Skoog, F.J. Holler, J.J. Leary, T.A. Nieman, *Principles of Instrumental Analysis*, Saunders College Pub., 1998.
- [6] I. Isa, M.I. Saidin, M. Ahmad, N. Hashim, S.A. Ghani, S.M. Si, Development of new copper(II) ion-selective poly(vinyl chloride) membrane electrode based on 2,6-diacetylpyridine- (1R)-(-)-fenchone diazine ligand, *Int. J. Electrochem. Sci.* 8 (2013) 11.
- [7] I. Ibrahim, H.N. Lim, O.K. Abou-Zied, N.M. Huang, P. Estrela, A. Pandikumar, Cadmium sulfide nanoparticles decorated with Au quantum dots as ultrasensitive photoelectrochemical sensor for selective detection of copper(II) ions, *J. Phys. Chem. C* 120 (2016) 22202–22214.
- [8] A.P. Yadav, R.R. Pradhananga, Preparation and characterization of silver sulphide/ silver iodide ion selective electrodes for the determination of I^- , S_2^{2-} , and Ag^+ ions, *Nepal Chem. Soc.* 15 (1996) 9–15.
- [9] K.B. Nakarmi, A.P. Yadav, Effect of precipitating media on the response behaviour of Ni(II) ion-selective electrode, *Int. J. Chem. Stud.* 6 (2018) 1436–1440.
- [10] J. Bobacka, A. Ivaska, A. Lewenstam, Potentiometric ion sensors, *Rev. Chem.* 108 (2008) 329–351.
- [11] S. Hassan, E. Elnemma, A. Mohamed, Novel potentiometric copper (II) selective membrane sensors based on cyclic tetrapeptide derivatives as neutral ionophores, *Talanta* 66 (2005) 1034–1041.
- [12] A. Jain, V. Gupta, L. Singh, J. Raisoni, Chelating ionophore based membrane sensors for copper(II) ions, *Talanta* 66 (2005) 1355–1361.
- [13] R.K. Mahajan, P. Sood, Novel copper(II)-Selective electrode based on 2,2': 5',2''-terthiophene in PVC matrix, *Int. J. Electrochem. Sci.* 2 (2007) 17.
- [14] V. Gupta, Preparation of ethambutol–copper(II) complex and fabrication of PVC based membrane potentiometric sensor for copper, *Talanta* 60 (2003) 149–160.
- [15] A.S. Panggabean, Hardianti, S.P. Pasaribu, Ion selective electrode-copper(II) based on EDTA as ionophores in poly(vinyl chloride) matrix, *Asian J. Chem.* 29 (2017) 362–366.
- [16] L.P. Singh, J.M. Bhatnagar, Copper(II) selective electrochemical sensor based on Schiff Base complexes, *Talanta* 64 (2004) 313–319.
- [17] M.R. Ganjali, A. Ghafarloo, F. Faridbod, P. Norouzi, Copper-selective PVC membrane sensor, *Int. J. Electrochem. Sci.* 7 (2012) 11.
- [18] E. Bakker, P. Bühlmann, E. Pretsch, Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics, *Chem. Rev.* 97 (1997) 3083–3132.
- [19] M. Bralic, M. Buzuk, M. Baljac, S. Brinic, Potentiometric studies on chemically and electronically prepared sulphide active materials for determination of copper (II), *Int. J. Electrochem. Sci.* 9 (9) (2014) 4854–4865.
- [20] K.B. Nakarmi, A.P. Yadav, Preparation of Cu(II) sensor prepared by simple co-precipitation method, *Nep. Chem. Soc.* 34 (2016) 81–87.
- [21] A. Craggs, G.J. Moody, J.D.R. Thomas, PVC matrix membrane ion-selective electrodes, *J. Chem. Educ.* 51 (8) (1974) 541.
- [22] A. Cantalapietra, M.J. Gismera, J.R. Procopio, M.T. Sevilla, Electrochemical sensor based on polystyrene sulfonate–carbon nanopowders composite for Cu (II) determination, *Talanta* 139 (2015) 111–116.
- [23] S. Wang, Y. Wang, L. Zhou, J. Li, S. Wang, H. Liu, Fabrication of an effective electrochemical platform based on graphene and AuNPs for high sensitive detection of trace Cu^{2+} , *Electrochim. Acta* 132 (2014) 7–14.
- [24] P.A. Ajibade, N.L. Botha, Synthesis and structural studies of copper sulfide nanocrystals, *Results Phys.* 6 (2016) 581–589.
- [25] C.-H. Lai, M.-Y. Lu, L.-J. Chen, Metal sulfide nanostructures: synthesis, properties and applications in energy conversion and storage, *J. Mater. Chem.* 22 (2012) 19–30.
- [26] L. Wang, Synthetic methods of CuS nanoparticles and their applications for imaging and cancer therapy, *RSC Adv.* 6 (2016) 82596–82615.
- [27] F.A. Sabah, N.M. Ahmed, Z. Hassan, H.S. Rasheed, High performance CuS p-type thin film as a hydrogen gas sensor, *Sens. Actuators Phys.* 249 (2016) 68–76.
- [28] B. Pejaji, M. Reddivari, T.R.R. Kotte, Phase controllable synthesis of CuS nanoparticles by chemical co-precipitation method: effect of copper precursors on the properties of CuS, *Mater. Chem. Phys.* 239 (2020) 122030.
- [29] C. Nethravathi, R.N. R, J.T. Rajamathi, M. Rajamathi, Microwave-assisted synthesis of porous aggregates of CuS nanoparticles for sunlight photocatalysis, *ACS Omega* 4 (2019) 4825–4831.
- [30] L. Qian, J. Mao, X. Tian, H. Yuan, D. Xiao, In situ synthesis of CuS nanotubes on Cu electrode for sensitive nonenzymatic glucose sensor, *Sens. Actuator. B Chem.* 176 (2013) 952–959.
- [31] D.M. da Silva Freitas, P.L.B. Araujo, E.S. Araujo, K.A. da S. Aquino, Effect of copper sulfide nanoparticles in poly(vinyl chloride) exposed to gamma irradiation, *J. Inorg. Organomet. Polym. Mater.* 27 (2017) 1546–1555.
- [32] O.Gh. Abdullah, S.A. Saleem, Effect of copper sulfide nanoparticles on the optical and electrical behavior of poly(vinyl alcohol) films, *J. Electron. Mater.* 45 (2016) 5910–5920.
- [33] M. Kumar, A. Chandra, In situ production of CuS particles in polymer electrolyte matrix for mixed ion+electron conduction, *Ionics* 16 (2010) 849–853.
- [34] H.B. Oli, R. Timilsina, A.P., Yadav, Fabrication and characterization of phthalic acid sensor for the detection of Lead (III) ion, *Nep. Chem. Soc.* 37 (2017) 90–94.
- [35] K. Krishnamoorthy, G.K. Veerasubramani, S. Radhakrishnan, S.J. Kim, Preparation of copper sulfide nanoparticles by sonochemical method and study on their electrochemical properties, *J. Nanosci. Nanotechnol.* 15 (2015) 4409–4413.
- [36] Y. Huang, H. Xiao, S. Chen, C. Wang, Preparation and characterization of CuS hollow spheres, *Ceram. Int.* 35 (2009) 905–907.
- [37] F. Li, W. Bi, T. Kong, Q. Qin, Optical, photocatalytic properties of novel CuS nanoplate-based architectures synthesised by a solvothermal route, *Cryst. Res. Technol.* 44 (2009) 729–735.
- [38] K. Karthikeyan, N. Poornaprakash, N. Selvakumar, K. Jeyasubramanian, Thermal properties and morphology of MgO-PVA nanocomposite film, *J. Nanostruct. Polym. Nanocompos.* 5 (2009) 83–88.
- [39] Niralil.S. Tank, K.D. Parikh, M.J. Joshi, Synthesis and Characterization of Copper Sulphide (CuS) Nano Particles, in: Gujarat, India, 2017, 040018.
- [40] A.A. Taha, S.M.H. AL-Jawad, A.M. Redha, Preparation and characterization of nanostructure CuS for biological activity, *Mod. Phys. Lett. B* 33 (2019) 1950374.
- [41] S. Roy, J.-W. Rhim, L. Jaiswal, Bioactive agar-based functional composite film incorporated with copper sulfide nanoparticles, *Food Hydrocolloids* 93 (2019) 156–166.