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MoS₂ modified screen printed carbon electrode based flexible sensor for detection of Copper

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Abstract— Monitoring of heavy metal ions in aquatic environment can be a tedious process, especially in harsh, logistically challenging field conditions. This work demonstrates the detection of copper ions in water using a low-cost screen printed 2D molybdenum disulfide (MoS₂) nanoparticle based electrochemical sensor. To deal with the common field-testing challenges, an easily disposable, flexible, compact sized reliable sensor was fabricated using a screen-printing technique. The developed sensor shows an excellent performance with a linear range of 5 μM to 1000 μM, a low limits of detection (LOD) value of just 0.3125 μM, and high repeatability with standard deviation less than 0.5%. With this performance and attractive attributes such as flexible form factor, low-cost fabrication and disposability *etc.* the presented sensor shows a great potential for practical applications in soil and water monitoring.

Keywords— *Electrochemical; Screen printed; copper detection; Flexible sensor; SPCE.*

I. INTRODUCTION

The presence of heavy metals in water has become a major environmental and human concern, which is being addressed through suitable monitoring practices informing policies that prevent the location of chemical and ore mining companies near vulnerable water resources or directly reduce the harmful effluent from them through mediation [1, 2]. Monitoring the trace concentration of heavy metals, particularly copper (Cu), is vital as it is potentially toxic [3] and its excess intake may lead to significant health issues including diseases such as Alzheimer's, and Wilson diseases *etc* [4, 5]. The Environmental Protection Agency (EPA) recommends that the maximum permissible amount of Cu in drinking water should be 1.3 ppm (20.5 μM) [6] and to stay healthy the human body requires a Cu intake of about 1.5 to 3 mg/day [7]. Traditionally, the presence of heavy metal traces is monitored by collecting discrete water or soil samples at weekly or monthly intervals and analysing them in the laboratory. However, rivers, water bodies, and large supplies (*e.g.*, in urban settings) exhibit highly dynamic and often non-linear behaviour in both time and space, and as a result such low-frequency data collection makes it difficult to establish linkages between cause and effect and develop potential management strategies in a timely manner. Additionally, the outcomes of these 'sample collection and lab analysis' methods could vary substantially due to the time gap between sampling and analysis.

To address these challenges, various types of sensors including ion sensitive field effect transistors have been explored [8-10]. For large scale deployment, it is vital to have cost-effective sensors that can autonomously measure the

presence of heavy metals. Further, the sensor needs to be flexible, responsive, sufficiently sensitive and made from sustainable and eco-friendly materials [11]. In this regard, the screen printed based electrochemical sensors on flexible substrates are attractive [12-15] as, besides being low-cost, it is easy to deploy them for field testing under varying conditions such as flowing and turbid water at depths. Moreover, they are affected by fouling due to presence of various algae and bacteria in aquatic environments. The deterioration in the sensing performance due to fouling, demands a frequent replacement / cleaning of field sensors and the low-cost screen-printed sensors are also attractive in this regard. Considering the above benefits, herein we present a facile, disposable, and replaceable screen-printed carbon electrode (SPCE) based sensors for Cu detection. Molybdenum disulfide (MoS₂) nanomaterials were used as the sensing layer as their high electrocatalytic property with catalytic edge sites makes them sufficiently sensitive to the detection of copper ions [16]. The developed sensor shows an excellent performance with a linear range of 5 μM to 1000 μM, a low limits of detection (LOD) value of 0.3125 μM, and high repeatability with standard deviation less than 0.5%.

This paper is organised as follows: The materials and methods used for the development of sensors are explained in Section II. The results from evaluation of sensors are given in Section III and the key outcomes are explained in Section IV.

II. MATERIALS AND METHODS

A. Materials

Sodium molybdate and thiourea were purchased from Merck. Commercial conductive carbon paste ink for screen printed electrodes was purchased from Sun chemicals. Copper Chloride, Dimethylformamide (DMF), Phosphate Buffer Saline (PBS) tablets were purchased from Merck. The chemicals obtained are used without any further purification.

B. Synthesis of MoS₂

For the preparation of MoS₂ nanomaterial, hydrothermal synthesis technique was followed. The precursor mixture of 4.84 g of (0.020 moles) of sodium molybdate and 6.24 g (0.080 moles) of thiourea was mixed with 60 mL of deionized water and left for stirring at 60 mins in room temperature. After stirring, the mixture was transferred into 100 mL Teflon lined stainless steel autoclave and further heated inside an oven at 220 °C for 24 hrs. Later the resultant black precipitate was collected from the autoclave and was washed multiple times with water and later with IPA, using centrifuge technique. After vigorous washing, it was left for drying at 60 °C for 12 hrs and the left out was collected as MoS₂ nanoparticles [17].

C. Sensor fabrication and modification

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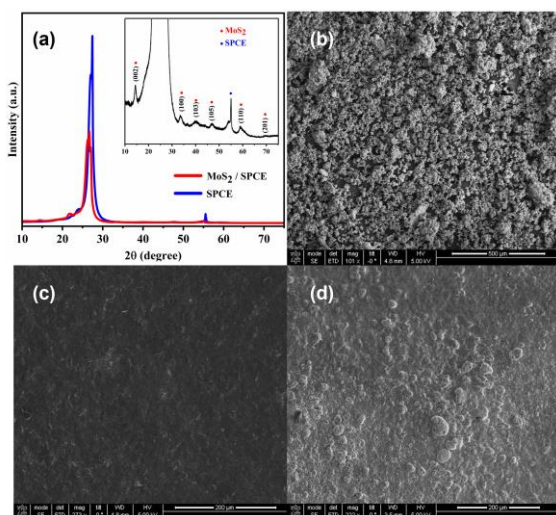


Fig. 1 (a) The XRD Pattern for MoS₂ powder and MoS₂ coated SPCE layer; SEM images of (b) MoS₂ powder, (c) SPCE, (d) MoS₂ modified SPCE.

The sensor was fabricated on a flexible polyvinyl chloride (PVC) substrate through screen printer. Screen printing was done by Screen Stencil Printer C920 from AUREL Automation. The developed screen-printed carbon electrode (SPCE) is based on three electrode configurations having a working electrode (WE, with a diameter of 10 mm), reference electrodes (RE) and counter electrode (CE). The printed electrodes were kept at 65°C for 30 minutes. To modify the WE, ~40 μL of 20 mg/mL MoS₂ solution in DMF was drop casted over the SPCE. The coated layer was cured at 65 °C for 30 minutes. The wiring is done using the same carbon ink and a dielectric ink placed on the contact points to avoid interference. After this the polyimide (PI) tape was placed, as shown in Fig. 2(a).

D. Electrochemical measurement

Cu ions detection using the developed sensor was examined using an electrochemical workstation (Metrohm Autolab (PGSTAT302N)). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) analysis were carried out for the detection of Cu ions in neutral PBS solution (0.1 M, pH 7). Here, to prepare such PBS electrolyte solution, 2 tablets of PBS were added to 500 mL of deionized (DI) water.

III. RESULTS AND DISCUSSION

A. Material characterisation

The X-ray diffraction (XRD) analysis was obtained using XRD P'Analytical X'Pert with Cu K α ($\lambda = 1.541 \text{ \AA}$) and scanning electron microscopy (SEM) analysis was carried out using FEI Nova. The peak at 14.17°, 33.45°, 39.5°, 49.17°, 58.843° and 69.434° (of red line) in the XRD patterns (Fig. 1(a)) confirm the lattice planes of hexagonal phase of 2-H MoS₂ i.e. (002), (100), (103), (105), (110), (201) respectively through ICDD card no: 37-1492 and the blue line indicates the XRD pattern for SPCE [17]. The SEM images were taken to understand the surface morphology of MoS₂ modified SPCE, unmodified SPCE, and drop casted MoS₂ over SPCE in Fig. 1 (b, c, d). The synthesized MoS₂ nanoparticle powder appeared to be a cluster of agglomerated spherical nanoparticles. The SPCE has a smooth layer of well homogenous carbon ink surface. Meanwhile, the modified SPCE has a surface of high roughness with few cracks on them. This confirms the presence of MoS₂ nanoparticle over SPCE after modification.

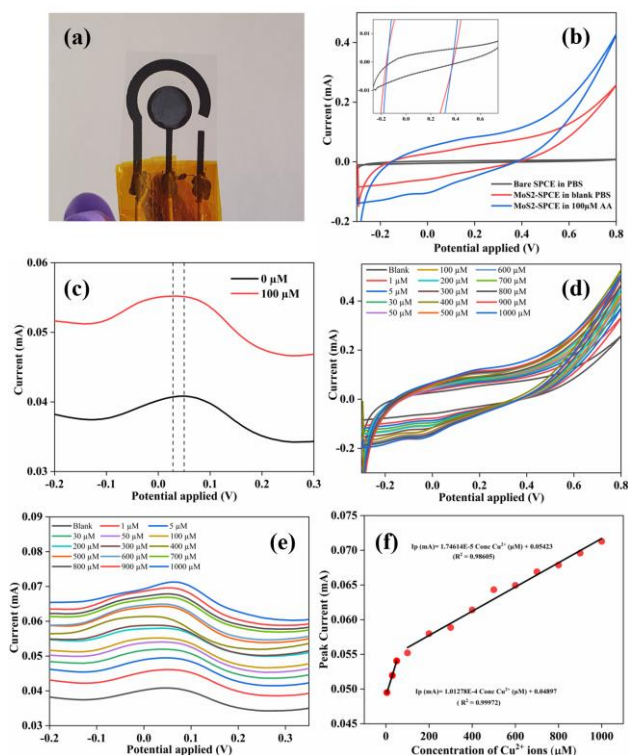


Fig. 2 (a) The image of fabricated sensor. (b) CV curves for bare SPCE, MoS₂/SPCE in absence and presence of 100 μM of Cu ions in 0.1 M PBS solution. (c) DPV profile for MoS₂/SPCE in absence and presence of 100 μM of Cu ions in 0.1M PBS. (d, e) CV and DPV curves for varying concentration of Cu from 1 to 1000 μM in electrolyte (f) Concentration of Cu analyte vs oxidation peak current (IP).

B. Electrochemical detection of Cu ions using MoS₂ modified SPCE

The detection of Cu ions in water was carried out by electrochemical method via CV and DPV analysis. The CV responses, in Fig. 2(b), was obtained at the scan rate of 50 mV/s, over the potential window of -0.3 V to 0.8 V in the 0.1 M PBS (7 pH) electrolyte solution. The black and red line represents the cyclic responses of the unmodified SPCE and MoS₂ modified SPCE sensor in the absence of analyte in blank PBS solution. With the modification of SPCE, it was observed that the shape of the cyclic voltammogram response were altered, and the overall current level increased from 6 μA to 0.2 mA at peak. The blue line in Fig. 2(b) indicates the cyclic response of the same modified SPCE but in the presence of 100 μM of Cu ions at similar scan rate and potential window. Here, due the presence of Cu analyte in the PBS solution, the oxidation and reduction peaks were observed at 0.2 V and -0.01 V correspondingly. These peaks reflect an occurrence of reversible redox reaction. Fig. 2(c) displays the DPV profile for the MoS₂ modified SPCE in the presence and absence of 100 μM Cu ions in the PBS electrolyte solution. In respect to the addition of Cu analyte, there was a negative peak shift in the anodic current from 0.05 V to 0.028 V.

C. Concentration study

For the concentration study, the quantity of Cu ions in PBS electrolyte was varied from 1 μM to 1000 μM and then their CV and DPV responses are discussed. In Fig. 2(d), Cyclic voltammograms for the potential window of -0.3 V to 0.8 V in respect to varying concentration of Cu ions (1 μM to 1000 μM) in 0.1 M PBS electrolyte is displayed at 50 mV/s scan speed. Due to the presence of Cu analyte, there is a negative shift observed in both oxidation and reduction peaks of the

modified sensor. For the varying analyte concentration, the oxidation peak occurs between 0.15 V to 0.2 V and the reduction peak occurs between -0.04 V to 0.03 V. For DPV profile, the scans are taken at a step potential of 0.005 V, modulation time of 0.25s and modulation amplitude of 0.25 V; for concentration of Cu ions from 1 μM to 1000 μM in the PBS electrolyte. The scans are illustrated in Fig. 2(e). Here, a minor negative shift occurs between 0.06 V to 0.001 V for the presence of Cu ions and the overall current value increases gradually in a linear manner. It is depicted in the Fig. 2(f), where the peak current is plotted against the concentration of Cu ions. For the Cu ions concentration between 5 μM to 50 μM , there is a sharp rise in the increasing peak current, which can be expressed as:

$$I_p \text{ (mA)} = 1.01278E - 4 * \text{Conc. Cu } (\mu\text{M}) + 0.04897$$

$$(R^2 = 0.99972) \quad \text{Eq. 1}$$

The sharp initial rise of peak current for low concentration of Cu ions is due to the availability of plentiful electrocatalytic edge sites on the surface of MoS₂, which allows easy accessibility for diffusion of the analyte species i.e., Cu²⁺ ions. But for the concentration between 100 μM and 1000 μM , the linear regression equation can be expressed as:

$$I_p \text{ (mA)} = 1.74614E - 5 * \text{Conc. Cu } (\mu\text{M}) + 0.05423$$

$$(R^2 = 0.98605) \quad \text{Eq. 2}$$

The second linear increase in the peak current for the higher concentration between 100 μM to 1000 μM can be explained as follows: the oxidation process of Cu to cupric ions (Cu²⁺), the Cu²⁺ gets diffused onto the surface of MoS₂ catalytic sites and this results in the limited accessibility for diffusion due to the blockage of the sensitive surface at higher concentration. This is because of the preoccupying of deposited Cu²⁺ ions over the MoS₂ surface after diffusion of certain threshold concentration of oxidation (100 μM in this case). Then the reduction reaction reduces the deposited Cupric ions to Cu ions which also clears the deposition over sensitive layer. The slope value for each concentration range was close to 0.5 and R-Squared (R²) value of >0.985. Thus, exhibiting a diffusion-based sensing process. The sensor shows linear sensitivity throughout the 1 μM – 1000 μM . The limit of detection (LOD) was found to be 3.125 μM and limit of quantification (LOQ) was estimated to be 9.47 μM .

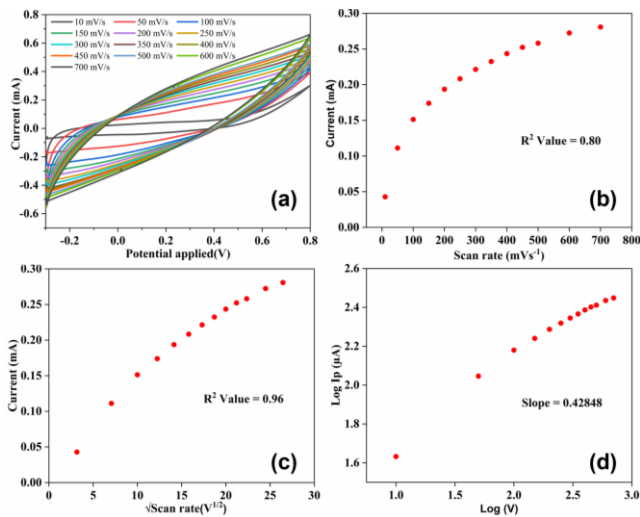


Fig. 3 (a) CV response curves for MoS₂/SPCE in 100 μM of Cu²⁺ ions in PBS with different scan rate of 10 to 700 mV/s; (b) I_p versus Scan rate; (c) I_p versus $\sqrt{\text{scan rate}}$; (d) log of I_p versus Log of Scan rate

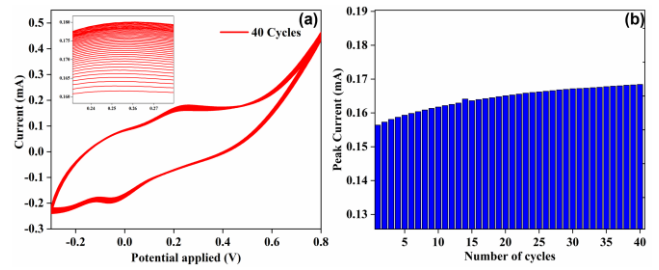


Fig. 4 (a) CV response of MoS₂/SPCE in 100M of Cu²⁺ ions in PBS for 40 cycles at 50 mV/s; (b) Bar graph for 40 CV cycles with their oxidation peak current response.

D. Accumulation study

For the accumulation study, the influence of scan rate for the concentration of 100 μM Cu ions in PBS solution was studied, as shown in Fig. 3(a). Here, the scan rate for the CV scans was varied from 10 to 700 mV/s and corresponding oxidation peaks were recorded. Fig. 3(b and c) depicts the plot of oxidation peak current (I_p) against the scan rate and square root of the scan rate. The R-squared value of the anodic peak currents for different scan rate was found to be 0.80. The anodic peak currents did not vary linearly with the scan rate. Hence the mechanism was found not an absorption-controlled process. The R-squared value for the anodic peak against square root of scan rate was found to be 0.96 and this shows that there is a linear dependence of observed peak current against square root of scan rate. Thus, the observed mechanism was diffusion-controlled process. To confirm the diffusion-controlled process, the logarithm of anodic peak current of CV scans were plotted against different scan rate, as displayed in Fig. 3 (d). Here, the slope value for log of I_p against log of scan rate was found to be 0.43, which is close to the ideal diffusion-controlled process i.e., 0.5 as per the kinetic theory for the electrode reaction [18]. Here, the optimized scan speed was 50 mV/s.

E. Repeatability

For the repeatability study, a continuous cyclic voltammogram for 40 cycles was carried out for 100 μM Cu ions concentration in PBS electrolyte solution at scan speed of 50 mV/s, as illustrated in Fig. 4(a). Due to the preconditioning for modified SPCE, the peak current for both oxidation and reduction gradually increased initially and saturated later. The Fig. 4(b) displays a bar graph showing the oxidation peak current of each cycle. The standard deviation for collective 40 cycle is 0.00334 mA.

IV. CONCLUSION

In summary, the low-cost, easily disposable MoS₂ SPCE based electrochemical sensor presented in this work is an attractive alternative for detection of Cu ions. The sensor shows a low LOD value of 3.125 μM , and high linear detection range of 1 μM to 1000 μM and covers the range expected in natural water ways. The repeatability studies for the presented sensor show a standard deviation of less than 0.5%. Due to its quick response and potentially lesser energy requirements, this highly sensitive sensor can be further explored with an integrated readout apparatus for real time field testing. Also, an adaptation of presented sensor on either paper or other biodegradable substrate will lead to nontoxic eco-friendly disposable sensor, though relative performance over its lifespan will need careful assessment.

References

- [1] W. Pu, J. Sun, F. Zhang, X. Wen, W. Liu, and C. Huang, "Effects of copper mining on heavy metal contamination in a rice agrosystem in the Xiaojiang River Basin, southwest China," *Acta Geochimica*, vol. 38, no. 5, pp. 753-773, 2019/10/01 2019.
- [2] L. Manjakkal *et al.*, "Connected Sensors, Innovative Sensor Deployment, and Intelligent Data Analysis for Online Water Quality Monitoring," *IEEE Internet of Things Journal*, vol. 8, no. 18, pp. 13805-13824, 2021.
- [3] E. Bernalte *et al.*, "Rapid and on-site simultaneous electrochemical detection of copper, lead and mercury in the Amazon river," *Sensors and Actuators B: Chemical*, vol. 307, p. 127620, 2020/03/15/ 2020.
- [4] I. Kaur, M. Sharma, S. Kaur, and A. Kaur, "Ultra-sensitive electrochemical sensors based on self-assembled chelating dithiol on gold electrode for trace level detection of copper(II) ions," *Sensors and Actuators B: Chemical*, vol. 312, p. 127935, 2020/06/01/ 2020.
- [5] E. Y. Frag, M. E. B. Mohamed, and E. M. Fahim, "Application of carbon sensors for potentiometric determination of copper(II) in water and biological fluids of Wilson disease patients. Studying the surface reaction using SEM, EDX, IR and DFT," *Biosensors and Bioelectronics*, vol. 118, pp. 122-128, 2018/10/30/ 2018.
- [6] T. Wen, F. Qu, N. B. Li, and H. Q. Luo, "A facile, sensitive, and rapid spectrophotometric method for copper(II) ion detection in aqueous media using polyethyleneimine," *Arabian Journal of Chemistry*, vol. 10, pp. S1680-S1685, 2017/05/01/ 2017.
- [7] T. Zeinali, F. Salmani, and K. Naseri, "Dietary Intake of Cadmium, Chromium, Copper, Nickel, and Lead through the Consumption of Meat, Liver, and Kidney and Assessment of Human Health Risk in Birjand, Southeast of Iran," *Biological Trace Element Research*, vol. 191, no. 2, pp. 338-347, 2019/10/01 2019.
- [8] M. Shojaei Baghini, A. Vilouras, M. Douthwaite, P. Georgiou, and R. Dahiya, "Ultra-thin ISFET-based sensing systems," *Electrochemical Science Advances*, <https://doi.org/10.1002/elsa.202100202> vol. n/a, no. n/a, p. e2100202, 2021/12/16 2021.
- [9] M. S. Baghini, A. Vilouras, and R. Dahiya, "Ultra-Thin Chips with ISFET Array for Continuous Monitoring of Body Fluids pH," *IEEE Transactions on Biomedical Circuits and Systems*, 2022.
- [10] A. Vilouras, A. Christou, L. Manjakkal, and R. Dahiya, "Ultrathin ion-sensitive field-effect transistor chips with bending-induced performance enhancement," *ACS applied electronic materials*, vol. 2, no. 8, pp. 2601-2610, 2020.
- [11] E. S. Hosseini, S. Dervin, P. Ganguly, and R. Dahiya, "Biodegradable Materials for Sustainable Health Monitoring Devices," *ACS Applied Bio Materials*, vol. 4, no. 1, pp. 163-194, 2021/01/18 2021.
- [12] S. Khan, W. Dang, L. Lorenzelli, and R. Dahiya, "Flexible Pressure Sensors Based on Screen-Printed P(VDF-TrFE) and P(VDF-TrFE)/MWCNTs," *IEEE Transactions on Semiconductor Manufacturing*, vol. 28, no. 4, pp. 486-493, 2015.
- [13] S. Khan, L. Lorenzelli, and R. S. Dahiya, "Technologies for Printing Sensors and Electronics Over Large Flexible Substrates: A Review," *IEEE Sensors Journal*, vol. 15, no. 6, pp. 3164-3185, 2015.
- [14] S. Dervin, P. Ganguly, and R. S. Dahiya, "Disposable Electrochemical Sensor Using Graphene Oxide–Chitosan Modified Carbon-Based Electrodes for the Detection of Tyrosine," *IEEE Sensors Journal*, vol. 21, no. 23, pp. 26226-26233, 2021.
- [15] X. Dai, S. Wu, and S. Li, "Progress on electrochemical sensors for the determination of heavy metal ions from contaminated water," *Journal of the Chinese Advanced Materials Society*, vol. 6, no. 2, pp. 91-111, 2018/04/03 2018.
- [16] X. Liu, Y. Yao, Y. Ying, and J. Ping, "Recent advances in nanomaterial-enabled screen-printed electrochemical sensors for heavy metal detection," *TrAC Trends in Analytical Chemistry*, vol. 115, pp. 187-202, 2019/06/01/ 2019.
- [17] S. B. Saseendran, A. S. Asha, and M. K. Jayaraj, "Hydrothermal synthesis of MoS₂ for supercapacitive application," *AIP Conference Proceedings*, vol. 2244, no. 1, p. 070034, 2020/06/26 2020.
- [18] A. Ejaz and R. Dahiya, "Influence of Solvent Molecular Geometry on the Growth of Nanostructures," *Journal of Colloid and Interface Science*, vol. 570, 03/03 2020.