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Circular sensing of nitrate levels in water with flexible screen-printed sensors on biodegradable cellulose substrate

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Abstract— Inorganic nitrate (NO_3^-) is ubiquitous in the environment and has become a center of attention in industrial and agricultural sectors, but it is regarded as a major contaminant in water and soil. In this work, we present a flexible, cost-effective amperometric sensor that is screen-printed on a biodegradable cellulose substrate. The sensor's working electrode was functionalized with Cu nanoclusters, followed by the application of a solid-state ion-selective membrane (ISM), enabling continuous monitoring of nitrate levels in the water. The optimized electrodeposition of Cu nanoclusters served as a metal catalyst to reduce nitrate ions, while the optimized ISM cocktail selectively detected nitrate ions. The sensor showed a wide linear detection range from 1 ppm (16 μM) to 100 ppm (1.6 mM) with a high sensitivity of 687 nA/ppm. Selectivity tests conducted with common interfering substances (Na^+, Cl^-, SO_4^-, HCO_3^-, and NO_2^-) showed minimal impact on nitrate sensing. The mechanical durability of the sensor was also assessed using a customizable bending setup. Additionally, Fourier transform infrared spectroscopy (FTIR) results demonstrated the gradual degradation of the cellulose substrate into the soil, highlighting the attainment of sustainable and circular sensing capabilities.

Index Terms—Biodegradable sensor, Nitrate sensor, Solid-state sensor, Sustainable and circular electronics.

I. INTRODUCTION

Over the past decade, water and soil contamination has become a major concern all over the world due to the excessive use of nitrogen-based fertilizers [1], [2]. Nitrate, a prominent contaminant, contributes to eutrophication, a natural phenomenon where algal bloom occurs causing hypoxia to animal life in water bodies [3]. Moreover, high levels of nitrate in drinking water can cause various acute conditions, including liver diseases, Parkinson's disease, and blue-baby syndrome [4], [5]. Therefore, there is a need for rapid and cost-effective monitoring of nitrate levels in both soil and water. Conventional methods of nitrate analysis are expensive, time-consuming, and often require trained personnel. In this context, electrochemical sensors have gained much attention due to their cost-effectiveness, high sensitivity, and rapid response [6]. Recent research studies have explored different metal catalysts, such as copper (Cu), gold (Au), and silver (Ag), for nitrate reduction, eliminating the need for complex biorecognition elements such as enzymes [7], [8]. Cu, with its high conductivity (5.8×10^7 S/m), has demonstrated superior performance as an electro-reduced catalyst for detecting nitrate ions compared to other metal catalysts [9]. Additionally, Cu can be easily electrodeposited on the sensor surface using cyclic voltammetry or chronoamperometry, allowing for convenient adjustment of deposition time and current density [10]. In addition to Cu catalysts, researchers have utilized ion-selective membranes (ISMs) on modified electrode surfaces to selectively detect nitrate ions, [11], [12]. However, a common challenge with ISM sensors is the gradual formation of a thin water layer between the metal electrode and the ISM, hindering fast electron transfer. To overcome this issue, Ali et al. [13] introduced a hydrophobic composite consisting of poly(3-octylthiophene-2,5-diyl) (POT) and molybdenum disulfide (MoS_2). This composite, drop-casted prior to applying the ISM, effectively served as a solid-state ion-to-electron transition layer, thereby preventing the formation of a water layer in potentiometric nitrate sensors.

In addition to the fabrication process of electrochemical sensors, the choice of substrate or platform is equally significant to consider. Large-scale implementation of conventional silicon-based sensors is not suitable due to the accumulation of electronic waste left behind. Hence, there is a need to develop sensors/energy devices entirely from biodegradable components as they will have a lower environmental footprint while monitoring molecular dynamics in the environment. With the increasing focus on sustainable practices and the utilization of recyclable and biodegradable materials, various approaches have been reported for fabricating sensors and their platforms [14]–[16]. These approaches aim to achieve biodegradability or complete dissolution of the sensor platform by exploring diverse materials such as hydrogel, soft polymers, and plant-derived substances. Among these options, cellulose-based materials have garnered significant attention due to their distinct advantages, including biodegradability, flexibility, screen-printability, and cost-effectiveness [17]. Abidi et al. [18] developed flexible and transparent cellulose bioplastic films from low-quality cotton fiber through a series of sequential procedures involving dissolution, regeneration, plasticization, and hot-pressing. Indeed, the biodegradability of this film specifically in soil makes it an ideal substrate for sensor fabrication.

Here, we report a novel way of integrating a nitrate sensor into a green and circular electronics platform using cellulose films. The uniqueness of the sensor lies in the combination of Cu electrodeposition and ISM drop casting processes, along with the

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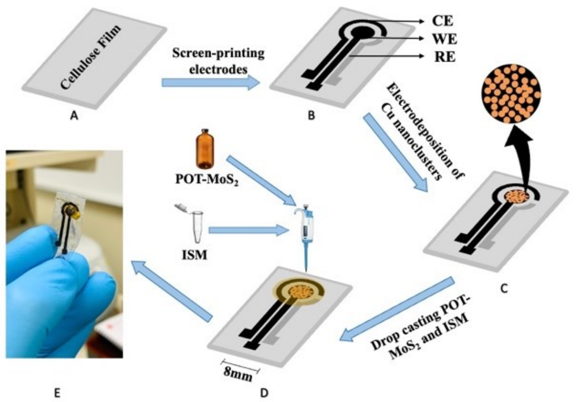

Fig. 1: Schematic illustration of the fabrication process of nitrate sensor: (A) Cellulose film, (B) Screen-printed electrodes, (C) Electrodeposition of Cu nanoclusters, (D) Drop-casting POT-MoS_2 and ISM, (E) Optical image of the sensor realized on cellulose substrate.

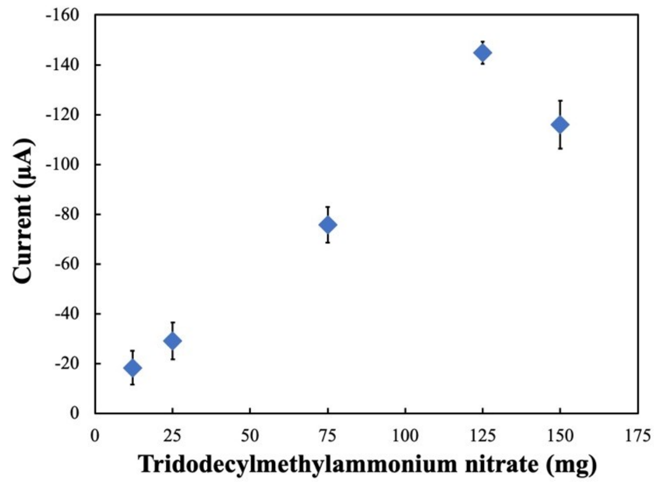

Fig. 2: The reduction peak current of the nitrate sensor was measured using cyclic voltammetry at 100 ppm of NO_3^- concentration. TDMAN concentrations were varied during the preparation of the ISM cocktail.

measurement of nitrate reduction current using amperometry. The ISM layer selectively permits only nitrate ions, while Cu aids in the reduction of nitrate to nitrite. Although potentiometry has been predominantly employed in ISM-coated sensors due to its ease of use, we propose the use of amperometry, which offers advantages such as wider detection range, higher selectivity, and the prevention of potential drift caused by leaching of the reference electrode. These features enable the stable detection of nitrate ions at much lower concentrations. Finally, the cellulose substrate was naturally degraded into the soil after use, leaving no electronic waste.

II. MATERIALS AND METHODS

A. Sensor fabrication

Fig. 1 shows the step-by-step fabrication process of the nitrate sensor. Different steps were applied for the preparation of cellulose substrate, as outlined in Abidi et al. [19]. The process started with dissolving cotton fibers in dimethylacetamide-LiCl solution for fiber dissolution followed by molding for regeneration. Later plasticization was done using optimized glycerol concentration and the process finished with hot-pressing which made the surface of the cellulose smooth and transparent. The assembly of the standard three-electrode sensor started by cleaning the cellulose film with isopropyl alcohol, acetone, and deionized (DI) water (Fig. 1A). Subsequently, plasma cleaning (PIE Scientific, USA) was performed in ambient air for 10 min. The three-electrode patterns were designed using AutoCAD Fusion 360 and transferred onto vinyl plotter paper using a vinyl cutter (USCutter, USA). Afterward, the design was screen printed on the cellulose substrate using a mesh (80T) (Fig. 1B). Carbon ink (Kayaku C-2500) was applied to fabricate the counter and working electrodes, while silver/silver chloride ink (MKCR-4482) was used for the reference electrode. After ink application, the electrodes were annealed in an oven at 120 °C for 15 min. The optimized Cu electrodeposition was performed on the working electrode (Fig. 1C) by running cyclic voltammetry (CV) in 0.1 M $CuSO_4.5H_2O/H_2SO_4$ (pH=2.0) solution at room temperature, in the potential range from –1.0 to 0 V and at a scan rate of 0.1 Vs^{-1} according to the method outlined in [20]. Following the Cu deposition, 5 µL of POT-MoS_2 was drop-casted on the working areas of the three electrodes and kept at 65 °C for 1 hour. Afterward, 10 µL of ISM cocktail solution was drop-casted onto the entire area coated with POT-MoS_2 and kept at 4 °C in the refrigerator for 24 hours (Fig. 1D). The final three electrode-based sensors had a dimension of 22 × 8 mm^2 (Fig. 1E).

B. Electrochemical and mechanical measurements

The morphological characterization of the cellulose films was evaluated by a diamond attenuated total reflection (ATR)-Fourier Transform Infrared Spectroscopy (FTIR) instrument (Thermo Fisher Scientific, MA, USA). FTIR analysis was employed to investigate the chemical bonding and assess the successful degradation of the cellulose film. Spectra were recorded in the absorbance mode within the range of 600–3500 cm^{-1}. All electrochemical experiments were performed at room temperature using a handheld potentiostat (PalmSen, Netherlands). To gain insights into the reduction reaction of nitrate to nitrite, cyclic voltammetry (CV) was performed in the potential range from -1 to 1 V at a scan rate of 0.05 Vs^{-1} for different concentrations of nitrate (1 ppm to 100 ppm). Furthermore, a customized bending setup was employed to assess the mechanical stability of the sensor.

III. RESULTS AND DISCUSSION

A. Electrochemical characterization

To prepare the ISM cocktail solution, tridodecylmethylammonium nitrate (TDMAN) was used as the nitrate ionophore. Consequently, it was crucial to optimize the concentration of TDMAN. Five different concentrations of TDMAN were individually used to prepare separate ISM cocktails. The sensors were prepared using these ISM concentrations and subjected to cyclic voltammetry measurements with a nitrate concentration of 100 ppm. As depicted in Fig. 2, the highest nitrate reduction was observed with 125 mg of TDMAN, after which the reduction rate started to decline, indicating saturation of the sensor. Based on this outcome, 125 mg of TDMAN was selected for the preparation of the ISM cocktail.

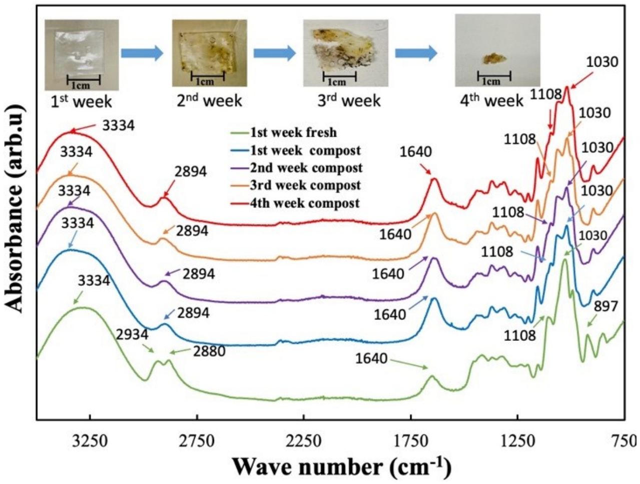

Fig. 3. FTIR spectra were collected weekly to analyze the cellulose film's degradation within the compost soil. The Inset image visually depicts the actual degradation of the cellulose film.

B. Morphological characterization

The biodegradability of the cellulose film was evaluated using FTIR on a weekly basis for a month. Three samples were placed in different types of soil: natural soil, compost wet soil, and compost dry soil. The sample from compost wet soil showed gradual degradation every week, as depicted in Fig. 3. The FTIR spectra revealed specific absorbance peaks at 3334 and 1640 cm^{-1}, which were assigned to the OH stretching vibrations, indicating the presence of native cellulose, as described in [21], [22]. On the other hand, IR bands at 2934 and 2880 cm^{-1} originated from glycerol, which was used during the processing of the cellulose film [18]. These peaks disappeared as degradation started, and a new band at 2894 cm^{-1} emerged due to the CH stretching vibration of cellulose polysaccharides, as shown in [23]. Furthermore, as reported in [24], the complete disappearance of the band at 897 cm^{-1} and the gradual fading of the band at 1108 cm^{-1} provided evidence of cellulose degradation.

C. Sensor performance

The sensor performance was evaluated with different concentrations (0, 1, 10, 25, 50, and 100 ppm) of nitrate in DI water with a neutral pH, without the use of any strong electrolyte. These concentrations were tested using CV to assess the sensor's response. The reduction peak current appeared at -0.8 V when the ISM layer selectively allowed only nitrate ions, and the Cu nanoclusters on the working electrode facilitated the reduction of NO_3^- ions to NO_2^-. The calibration curve (shown in Fig. 4) was constructed based on the average reduction peak current of 3 sensors for each concentration, with the error bar indicating the standard deviation. The calibration curve exhibited a linear detection range (R^2 = 99.1%) and a high sensitivity of (687 nA/ppm) compared to the sensors reported in the literature [25]–[27]. In addition, our sensor could detect nitrate levels down to 1 ppm. To evaluate the sensor's selectivity, common interferents (Na^+, Cl^-, SO_4^-, HCO_3^-, and NO_2^-) were tested individually at a fixed concentration of 50 ppm. The reduction peak current for each interferent was compared to that of nitrate at the same concentration. As shown in Fig. 5, the sensor response was minimally affected by the presence of different interferents.

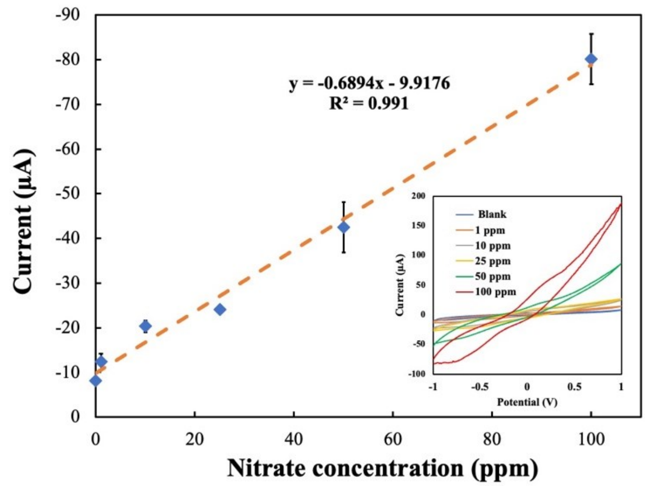

Fig. 4. Calibration plot of the nitrate sensor. The reduction peak current was obtained from the average values. The error bars represent standard deviation for 3 repeated measurements. Inset shows the cyclic voltammograms at different concentrations of nitrate.

D. Mechanical stability

To investigate the mechanical durability of the sensor, a bending test was conducted using a custom-designed setup, shown in Fig. 6. The sensors were subjected to tensile bending, reaching a radius of 5 mm for up to 500 bending cycles. Three separate sensors were evaluated at the same concentration of nitrate, and the reduction peak currents were measured before and after 250 and 500 bending cycles. The generation of reduction peak current after bending indicates the functionality of the sensor. However, the presence of higher error bars suggests the occurrence of mechanical deformation, likely caused by nano-cracks in the electrode surface.

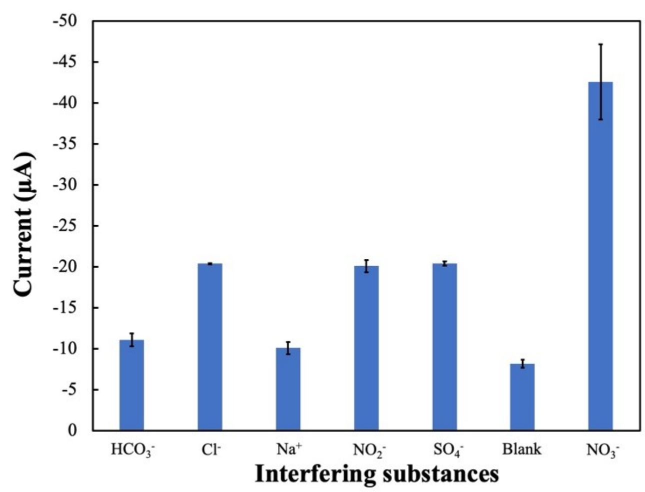

Fig. 5. Selectivity test of nitrate sensor. The average reduction peak current, along with the corresponding error bars, was obtained from CV measurements.

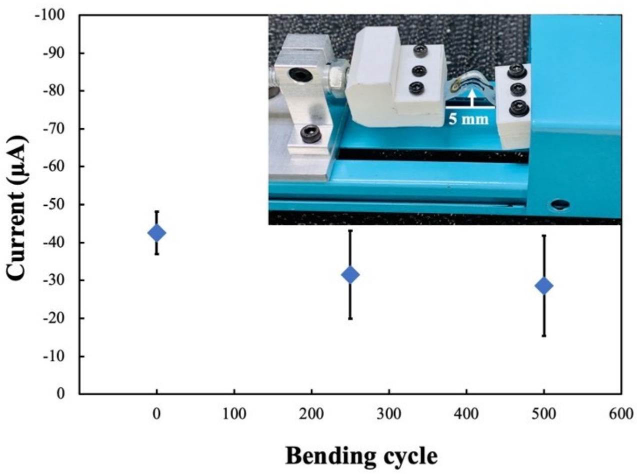

Fig. 6. Mechanical stability test by subjecting the nitrate sensor to bending. Inset shows optical image of the sensor mounted on the custom-designed bending setup and bent to a tensile radius of 5 mm.

IV. CONCLUSION

This work presents a novel circular approach to nitrate detection using a biodegradable, cost-effective, and easy-to-fabricate sensor. The nitrate sensor was fabricated on a cellulose substrate derived from cotton fibers. The sensor was coated with Cu nanoclusters followed by a solid-state ISM cocktail. The nitrate ionophore tridodecylmethylammonium nitrate (TDMAN) of the ISM cocktail was optimized to achieve high sensitivity (687 nA/ppm) and selectivity. The sensor successfully evinced the electro-reduction of nitrate ions in water, with a wide linear detection range of 1 ppm to 100 ppm. The common interferents (Na^+, Cl^-, SO_4^-, HCO_3^-, and NO_2^-) showed very negligible effects toward nitrate detection. Furthermore, the biodegradability test conducted on the cellulose films revealed dissolution of the cellulose platform over a month, ensuring zero waste generation from the sensors and promoting ecological benefits. Further research will focus on evaluating the sensor's reproducibility, testing with lake water samples, and validating its performance using analytical techniques such as high-performance liquid chromatography.

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