UV Lithography-Assisted Fabrication of Low-Cost Copper Electrodes Modified with Gold Nanostructures for Improved Analyte Detection

Jagriti Gupta, Subhavna Juneja, and Jaydeep Bhattacharya*

ABSTRACT: An in-house UV lithography setup has been optimized to fabricate low-cost disposable electrochemical sensing Cu electrodes using a copper clad board. In view of the high oxidation probability of copper, the low-cost electrodes were modified using different gold nanostructures and a conducting polymer PEDOT:PSS to attain maximal signal output and improved shelf-life. Zero-dimensional (0D) gold nanoparticles (~40 nm) and three-dimensional (3D) gold nanoflowers (~38 nm) mixed with PEDOT:PSS were used as signal-enhancing conductors for the ultrasensitive detection of our model contaminant, methylene blue dye (MB). The bare copper electrode was sensitive to MB, linearly within the range of 4–100 μM, with a limit of detection of 3.49 μM. While for gold nanoparticle-PEDOT:PSS-modified electrode, the sensitivity of the electrode was found to increase linearly in the range of 0.01–0.1 μM, and for gold nanoflowers-PEDOT:PSS, the sensitivity achieved was 0.01–0.1 μM with the LOD as 0.0022 μM. For a PEDOT:PSS-modified Cu electrode, used as a comparative to study the contributing role of gold nanostructures towards improved sensitivity, the linearity was found to be in the range of 0.1–1.9 μM with the LOD as 0.0228 μM. A 6 times improvement in signal sensitivity for the nanoflower-PEDOT:PSS electrode compared to the nanoparticle-PEDOT:PSS-modified electrode indicates the influence of nanoparticle shape on the electrode efficiency. 3D gold nanoflowers with a large surface area-to-volume ratio and a high catalytic activity prove to be a superior choice for electrode modification.

INTRODUCTION

Conventional environmental monitoring practices based on discrete sample collection followed by extensive laboratory analysis procedures are expensive and time-consuming and have limited detection resolution. Thus, developing a real-time analysis methodology which is rapid, inexpensive, and yet capable of sensitive detection is desirable. Chemical sensors, specifically electrochemical, have been used for on-site environmental monitoring of various parameters such as organic pollutants (pesticides), biomolecules, trace elements, and pH among others. Development of an electrochemical sensing technology yet continues to grow rapidly, to meet the challenges posed by new environmental and clinical analytes. An electrochemical sensor offers selectivity, portability, opportunity for miniaturization, and limited space and power requirements.

Sensitivity of any electrochemical sensor majorly comes from a robust and efficient electrode system since the electrical signal derived from the analytical input is an outcome of the analyte–recognition interaction on the sensing electrode. Traditional electrodes such as gold, platinum, or glassy carbon are excellent conductors and highly sensitive systems yet limited owing to their high fabrication and operational cost. Conductive polymers and their composites were extensively used previously to modify and improve the electrode surfaces, finding an abundant mention in the literature. Some common examples include monomers of aniline, gallic acid, and pyrene among others. The electronic transfer efficiency, a marker of electrode output, was often found mediocre owing to the ineffective charge transfer between the electrode surface and the polymer backbone, instilling the need for improved electrodes. Progressively, Nafion-coated electrode surfaces were fabricated for improved signal transductions. Nafion coatings containing terminal sulfonic showed a promising selectivity toward biomolecules and were developed as a potential catecholamine detector with clinical significance. The high cost and nonuniversal application limited their use.

With the advent of the nanoscale technology, electrochemical sensor electrode systems saw an upgradation with reduced costs, higher sensitivities, enhanced biocompatibility, precise targeting, and multiplexing abilities. Contributed by the faster electron kinetics, improved conductivity and high surface area for enhanced redox activity made them an attractive alternative. Different classes of nanomaterials ranging from carbon-based, semiconductors, quantum dots, nanofibers,
etc. have found acceptance as electrode material base or modifier.\textsuperscript{22–24} Metal nanoparticles, one of the most widely used nanomaterials toward modified transducers, have an excellent catalytic property and a high affinity for chemical and biofunctionalization, qualifying as efficient electrochemical accessories. Graphene, the single-carbon graphitic structure, with excellent thermal stability and excellent conductivity also makes an excellent electrode material. Martin and co-workers developed graphene nanoribbons on screen-printed surfaces as a potential electrochemical sensor for uric acid determination. The developed nanoribbon electrodes were fast (100 s), sensitive (at +0.35 V), and inexpensive (disposable).\textsuperscript{25} Test systems aside, the actual use of graphene is limited by its tendency to aggregate and deficiency of electrochemically active defect sites with respect to its application toward sensing biomolecules. Supported by high isoelectric points, non-toxicity, spectrum of morphologies, and the respective physical and chemical properties make ZnO a potential suitable electrode; however, the commercial production and sensor fabrication reproducibility of ZnO prohibit its real-time use.\textsuperscript{26} Improved printing technologies and lithography attracted enough attention for the fabrication of low-cost electrodes and also functional devices using plastic or even paper as substrate. For example, Määttänen et al. generated a paper-based electrochemical chip capable of exhibiting comparable performance to a conventional electrochemical cell.\textsuperscript{27} Cellulose membranes functionalized with gold nanoparticles printed with ink-jet printers have been synthesized by immersing them in a plating solution of HAuCl\(_4\) and NH\(_2\)OH until conducting electrode structures were formed.\textsuperscript{28} A large material consumption, need of pattern stencil, and a high human expertise can be considered as its major drawbacks for widespread application. Moreover, solid substrate electrodes are often restrictive for reuse due to the gradual fouling of the electrode surface, consequently from the absorption of reaction by-products, products, or contaminants in the case of crude samples.\textsuperscript{29–31} Also, solute sensing is often subdued due to hampered electron transfer because of inappropriate electrode material, alleviating the need to design better electrode systems.

In this work, a cost-effective, disposable, ultrasensitive microelectrode array was fabricated using an in-house UV lithography setup. The copper clad board serves as the solid substrate of high conductivity and low cost. The in-house lithography setup consisted of a 311 nm UV CFL (9 W) as the illumination source for pattern transfer and some transparency sheets, which were used as the positive photoresist. The masks and patterns were generated in three simple steps, precisely (1) coating of positive photoresist, (2) exposure to UV light for pattern transfer, and (3) removal of excess unexposed region. Since Cu, our base electrode material, is prone to oxidation, coating of positive photoresist, (2) exposure to UV light for pattern transfer, and (3) removal of excess unexposed region. Since Cu, our base electrode material, is prone to oxidation. Notably, for nanoparticles, only a single narrow intense peak at 520 nm is observed, while for nanostructures, a set of two unequal broad peaks are observed. The characteristic visible-region wavelength range (520–580 nm), which indicates a successful gold nanostructure synthesis. Optical properties of the synthesized samples, both GNP and GNF, were studied using UV–vis spectroscopy. The plots are presented in Figure 1a,b. Localized surface plasmon resonance (LSPR) peaks for both gold nanoparticles and nanoflowers were clearly observed in the characteristic visible-region wavelength range (520–580 nm), which indicates a successful gold nanostructure synthesis. Notably, for nanoparticles, only a single narrow intense peak at 530 nm is observed, while for nanoflowers, a set of two unequal broad peaks are observed. The first peak, observed near 586 nm, is broader and more intense compared to the second minor peak observed in the far visible region around 742 nm. From the literature, the origins of these two peaks

![Figure 1. UV–visible spectra, TEM micrograph, and SAED pattern of gold nanoparticles (a–c) and gold nanoflowers (d–f), respectively.](https://dx.doi.org/10.1021/acsomega.9b03125)
have been related to the center and terminals of the anisotropic nanostructures, respectively.\textsuperscript{32,33}

To confirm our UV–visible observations, the samples were characterized using TEM. As seen in Figure 1b,e, we could conclude the successful synthesis of nanospheres and nanoflowers, respectively. As observed in Figure 1b, spherical gold nanoparticles with nearly monodisperse population were formed. Their surface was found to be smooth, and the average size was calculated to be $20 \pm 4$ nm. While, for the gold nanoflower sample (Figure 1e), irregular 3D structures with small petal-like protrusions arising from the center were obtained. Each nanostructure was seen to comprise minor grooves at the terminal, giving it a flowerlike appearance. A distinct contrast difference between the structure center and tips was observed, which is ascribed to the difference of metal thickness at the core compared to termini. The average nanoflower size was estimated to be $38 \pm 5$ nm. The selected area electron diffraction pattern was generated to gather insights into the growth planes of the synthesized nanostructures. As observed in Figure 1c,f for both nanoparticles and nanoflowers, the SAED patterns comprised small bright spots, which were arranged in circular ringlike patterns, indicating the polycrystalline nature of the synthesized structures. The SAED pattern data analysis for nanoparticles indexes growth planes as [111] and [200], while for nanoflowers, the diffractions match the [111, 200, 220] and [311] planes of cubic gold.\textsuperscript{34}

**Electrode Characterization.** Photolithographically fabricated electrodes were washed with deionized water and hard-baked at 55–65 °C for half an hour. After that, the prepared electrodes were observed under a microscope to investigate their surface. As observed from the images obtained from the microscope at 10× magnification (Figure 2a–c), both the linear and curved sections of the structure patterned on the substrate were regular, homogeneous, and smooth.

**Electrochemical Impedance Spectroscopy (EIS) Measurements of the Nanostructure-Functionalized Cu Electrodes.** Impedance measurements for all of the four different electrodes, namely, bare Cu, PEDOT:PSS, GNP-PEDOT:PSS, and GNF-PEDOT:PSS, were performed. The obtained graphs for the same are presented in Figure 3. For the bare Cu electrode (Figure 3a), a nonsemicircular curve is obtained, indicating an uninhibited electron transfer but a high internal resistance. However, when the bare Cu electrode was modified with PEDOT:PSS, the nature of the curve transformed into a semicircle (Figure 3b). This characteristic semicircular curve reflects the increased input impedance by PEDOT:PSS on account of the increased resistance in electron transfer by the conductive polymer. To limit the increasing impedance value, gold nanostructures (GNP/GNF) were mixed with the polymer and drop-cast onto the electrodes. The impedance graph for the gold nanostructure-modified electrodes is presented in Figure 3c,d. The nature of the graph for the modified electrodes was yet semicircular but less steep compared to bare PEDOT:PSS, which points to the increase in the electric current flow. Among the two different nanostructures used to modify the electrode, GNF were found to show a smaller input impedance compared to GNP, indicating a lesser resistance to electron transfer in GNF.

**Effect of pH.** To study the effect of pH on the fabricated electrode, cyclic voltammetry was done in phosphate buffer with varying pH, in the presence of MB as a model electrochemical dye. We can see from Figure S1 that the anodic peak current increases with increasing pH and exhibits the maximum value at pH 9. At pH below 6, there are two H$^+$. 

![Figure 2](image1.png)

Figure 2. (a–c) Digital and high-resolution microscopy images of the electrodes as obtained from the linear and curved sections of the pattern.

![Figure 3](image2.png)

Figure 3. Nyquist plot for EIS measurement at modified electrode: (a) bare Cu electrode, (b) Cu/PEDOT:PSS-modified electrode, (c) Cu/GNP-PEDOT:PSS-modified electrode, and (d) Cu/GNF-PEDOT:PSS-modified electrode in 0.1 M PBS (pH 7) with 0.01 M KCl.
ions involved in the electrode reaction,\textsuperscript{35} due to which several peaks were observed in response to MB and high oxidation of Cu electrode at acidic pH increased the complexity of electrochemical reaction and decreased the sensitivity. Within pH 6−9, a prominent single anodic and cathodic peak corresponds to the involvement of single proton and two electrons in the reversible oxidation reduction process, similarly to that reported by several authors.\textsuperscript{35−37} Some others also reported phosphate buffer with alkaline pH as the best electrolyte for estimation of MB.\textsuperscript{36,38} A change in the position of anodic and cathodic peak potential with increasing pH was also observed, and the shifting of the anodic peak potential toward the less positive potential determines that the oxidation of MB is easy at alkaline pH. A systematic shift of the reduction peak potential with change in pH suggested the involvement of proton during electron transfer.\textsuperscript{39} The shift in the anodic peak potential with pH follows the regression equation as $E_{pa} = 0.08078 - 0.03499 \text{pH}$ with the correlation coefficient ($R^2 = 0.99917$).

Figure 4. (a) Differential pulse voltammogram at different concentrations of MB with bare Cu electrode. (b) Peak current vs concentration with bare Cu electrode. (c) Differential pulse voltammogram of MB at PEDOT:PSS-coated Cu electrode in 0.1 M PBS + 0.01 M KCl. (d) Peak current vs concentration with PEDOT:PSS-coated Cu electrode.

Figure 5. (a) Differential pulse voltammogram of MB at GNF-PEDOT:PSS composite-modified Cu electrode in 0.1 M PBS + 0.01 M KCl. (b) Peak current vs concentration with GNF-PEDOT:PSS composite-modified Cu electrode. (c) Differential pulse voltammogram of MB at GNP-PEDOT:PSS composite-modified Cu electrode in 0.1 M PBS + 0.01 M KCl. (d) Peak current vs concentration with GNP-PEDOT:PSS composite-modified Cu electrode.
The addition of the MB, it was not in the linear range. However, we proceed our further work at pH 7 ± 0.4.

Effect of Scan Rate. The effect of scan rate was investigated by varying the scan rate in the range of 0.01−0.05 V/s (Figure S2a), and it was found that with increasing scan rate, the current is increased because at higher scan rate, the diffusion layer gets decreased. The oxidation peak current when plotted against the square root of scan rate in the presence of 100 μM MB (Figure S2b) shows a linear increase with correlation coefficient (R² = 0.994). From the result, it can be deduced that the reaction is quasi-reversible and involves freely diffusing redox species.

Effect of Mode. Figure S3 demonstrates the comparison in modes for MB detection by a modified electrode using cyclic voltammetry (CV), differential pulse voltammetry (DPV), and linear sweep voltammetry (LSV) in the presence of 100μM MB in 0.1 M PBS + 0.01 M KCl. The peak currents obtained in response to 100 μM MB were 4.43, 9.54, and 28.649 μA for CV, LSV, and DPV, respectively. An exquisite performance of the modified electrode for MB sensing was found by DPV, with enhanced current response and peak-to-peak separation with minimum background current. Although DPV is a more sensitive method than CV, CV plays a key role in understanding and deducing the kinetics of the electrochemical reaction of MB.

Electrochemical Performance of Developed Sensor in Terms of Quantitative Analysis of MB by DPV. DPV was used as an analytical tool to measure the sensitivity of fabricated sensors. It has benefits over the CV because of its higher sensitivity and peak-to-peak separation due to the relatively short pulse time and differential nature.

First, the measurement was performed with the bare Cu electrode (Figure 4a) over the concentration range of 1−100 μM, and it was found that the reduction peak current was linear in the range of 4−100 μM with regression coefficient R² = 0.9917 (Figure 4b) and limit of detection (LOD) = 3.49 μM. When the Cu electrode was modified with PEDOT:PSS, sensitivity was increased and the linear range was obtained from 0.1 to 1.9 μM (Figure 4c) with regression coefficient R² = 0.9991 (Figure 4d) having an LOD of 0.0228 μM. Further, the DPV was performed with GNF-PEDOT:PSS-modified electrode in the concentration range of 0.001−0.1 μM (Figure 5a). Although some reduction current was obtained with 0.001 μM addition of the MB, it was not in the linear range. The linear range was obtained between 0.01 and 0.1 μM with regression coefficient R² = 0.99877 (Figure 5b) and an LOD of 0.0022 μM. To distinguish the role of nanostructure over the presence of nanomaterial, GNP-PEDOT:PSS modification was also performed and the result of DPV toward MB was evaluated in the range of 0.001−0.1 μM (Figure 5c). The linear range of reduction peak current was obtained between 0.01 and 0.1 μM with regression coefficient R² = 0.9959 (Figure 5d) and an LOD of 0.0052 μM. The peak current values reported above from DPV are blank-corrected for best linear fit and to deduce the true value of intercept in the regression equation. The LOD was calculated by the formula (3 × δ/slope), where δ represents the standard deviation and the slope was inferred from linear regression equation.

Both the nanomaterial fabricated sensors were following the extreme linearity in the range of 0.01−0.1 μM, but the LOD value for the GNF-PEDOT:PSS-modified electrode is very low, i.e., 0.0022 μM, which is 2.36 times lower than that of the GNP-PEDOT:PSS-modified electrode; moreover, the ratio of the slope in between these two nanostructure-modified sensors was 6.54 (Figure 6) and reduction current obtained is also more in the case of GNF-PEDOT:PSS-modified electrode. This might be due to the presence of petals in GNF, which increases the surface area to the utmost level and increases the catalytic property and therefore drives faster the electron transfer kinetics. (After interpreting all of these data, we are inferring that the proposed sensor fabricated with GNF-PEDOT:PSS is highly sensitive toward MB.)

Reproducibility, Reusability Test of Nanostructure-Modified Photolithographically Fabricated Electrode. The reusability test was performed in 0.1 M PBS with 0.01 M KCl in the presence of 10 μM MB for reproducibility of the fabricated sensor (Figure 7), and DPV of the proposed sensor was recorded after a good wash and sonication for 2 min. Five repetitive scans with washing of the modified electrode were recorded, and after analyzing the data, a relative standard deviation of 0.65% was found. Study revealed that PEDOT:PSS stabilized the GNF/GNP very successfully over the electrode surface and increased the conductivity as well. After analyzing all of these results, it was found that our proposed sensors show a quite high performance in the sense of economic ability, sensitivity, and multiusability over the already reported sensors for MB (Table 1).

[Table 1]

**CONCLUSIONS**

A highly efficient yet simple and cost-effective method based on photolithography (UV-assisted) for the fabrication of disposable electrochemical sensing electrodes has been...
Table 1. Comparison of Results for Methods Already Reported for Quantification of MB

| method                        | working range (μM) | LOD (μM) | references |
|-------------------------------|--------------------|----------|------------|
| UV−vis spectrophotometry     | 0.31−28.5          |          | 51         |
| UV−vis spectrophotometry     | 0.63−21.9          | 0.19     | 52         |
| cyclic voltammetry           | 0.2−10             |          |            |
| cyclic voltammetry           | 1−14               | 0.4      |            |
| potentiometry                | 1−3000             | 0.765    |            |
| differential pulse voltammetry | 0.01−1.1          | 0.0039   |            |
| differential pulse voltammetry | 0.01−0.1          | 0.0022   | this method (GNF-PEDOT:PSS) |
| differential pulse voltammetry | 0.01−0.1          | 0.0052   | this method (GNF-PEDOT:PSS) |

EXPERIMENTAL SECTION

Materials. The copper clad board (CCB) was purchased from a regular vendor in the local market. Hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O), ferric chloride, and PEDOT:PSS (1%) were procured from Sigma-Aldrich, while sodium hydroxide, trisodium citrate, l-ascorbic acid, dipotassium hydrogen phosphate, potassium dihydrogen phosphate, and potassium chloride were purchased from Fischer Scientific. Our model contaminant methylene blue (MB) was bought from SRL India Pvt. Ltd. Absolute ethanol was procured from Merck. A positive photoresist was obtained from Shipley Company s1800. All of the chemicals were of analytical grade and used as obtained. All of the aqueous solution was prepared in Milli-Q water, unless mentioned otherwise.

Gold Nanostructures Synthesis. Gold nanostructures with spherical and flowerlike morphologies were obtained using the chemical reduction method. The synthesis protocol was optimized by our group previously.54 Briefly, for gold nanoflower (GNF) synthesis, 10 mM HAuCl₄ was added to 70 mL of 19.8 mM ice-cold l-ascorbic acid under a high stirring rate (1000 rpm). The reaction mixture almost instantaneously turns faint blue, indicating the formation of anisotropic nanoparticles. For spherical particles (GNP), 50 mL of a 2.5 mM aqueous solution of sodium citrate was heated to bring it to boiling temperature. Once bubbles begin to form, 1 mL of HAuCl₄ was added to the above reaction mixture and left undisturbed to react for the next 10 min. The color of the reaction mixture changes from colorless to wine red, which indicates reaction completion. The nanoparticle colloidal solution was cooled down to room temperature prior to storage. The samples were appropriately labeled and stored at 4 °C until further use.

Fabrication of Microelectrode Array (MEA) by In-House Photolithography Setup. The copper clad board was washed sequentially with a mild soap and Milli-Q water. To minimize any chance of artifacts, the cleaned board was rinsed thoroughly with absolute alcohol and air-dried in a hot-air oven for 10 min at 60 °C prior to use. Upon complete drying, the CCB was coated with the positive photoresist (30 μL) using the Arduino microcontroller-driven spin coater comprising a stepper motor. The coated copper clad slide was soft-baked at 90 °C on a hot plate for 90 s (Figure 8). Using Microsoft Paint, the desired mask pattern was designed and then printed on transparency sheets, as shown in Figure 9a. Following the mask patterning, the mask was exposed to a 9 W 311 nm UV illuminating source to allow its transfer onto the CCB. UV light helps in breaking the cross-link on the photoresist, allowing the shifting of pattern on the board. The pattern-carrying slides were then washed with 4 and 5% NaOH solution simultaneously for a few seconds to fix the patterns onto the board. Since the photoresist is positive, under UV exposure, chemical bonds in the photoresist lack stability, leading to their disintegration. The patterns can be seen clearly in the mask-covered area for subsequent processing (Figure 9b). To retain the pattern onto the board, wet etching was performed using 30% FeCl₃. Complete removal of the
photoresist was done in absolute ethanol to get the desired electrode patterns (Figure 9c).

Modifications of the Electrodes with Gold Nanostructures. The fabricated MEAs were cleaned with distilled water followed by ultrasonic cleaning in ethanol for 10 min. After drying the electrodes at room temperature, 1 μL of the nanostructure-PEDOT:PSS colloidal solution (1:1) was drop-cast on the electrodes and allowed to dry in a hot-air oven at 70 °C for 5 min. The drop-casting step was repeated twice. The scanning electron micrograph images of bare and modified Cu electrodes are shown in Figure 9e–g.

Electrochemical Measurements. For CV measurements, the voltammograms were taken in a potential range of −1 to +1 V (vs Ag/AgCl); after that, a potential window was chosen between −0.5 and 0.3 V, with a step potential of 2.4 mV and a scan rate of 30 mV/s. All parameters were optimized for the best response. For impedance measurement, the frequency was chosen between 100 KHz and 0.01 Hz along with the number of frequencies as 50, amplitude as 0.01 V, and applied potential as 0.2 V/s. For differential pulse voltammetry, the potential was kept between −0.45 and 0.2 V, with step potential as 0.005 V, modulation amplitude as 0.025 V, modulation time as 0.05 s, modulation interval as 0.5 s, and scan rate as 0.01 V/s. For the measurement of MB, DPV was performed with the bare Cu electrode, the PEDOT:PSS-coated Cu electrode, and the GNF/GNP-PEDOT:PSS composite-modified as working electrode in 10 mL of 0.1 M PBS (pH 7.0) in 0.01 M KCl.

Characterization and Instrumentation. Optical characteristics of the synthesized gold nanostructures were studied using a Lambda 25 UV–visible absorption spectrophotometer. The nanostructure morphology and crystalline planes were analyzed using transmission electron micrographs, and selected area diffraction (SAED) patterns were obtained on a JEOL 2100F TEM operated at a voltage of 200 kV. Electrochemical measurements, i.e., differential pulse voltammetry and impedance, were performed using the PGSTAT 204 electrochemical workstation (75 W 50/60 Hz made in the Netherlands) with a conventional three-electrode system connected with a system with NOVA 1.11 software. Cu MEA fabricated by photolithography were used as the working electrode, a platinum sheet (5 mm × 5 mm) was used as the counter electrode, and an Ag/AgCl electrode purchased from BASi was used as the reference electrode. The electrochemical impedance measurement was performed in 0.01 M KCl, and cyclic voltammetry and differential pulse voltammetry were performed in 0.1 M phosphate buffer solution (pH 7.0) with 0.01 M KCl.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03125.

Cyclic voltamogram by modified Cu electrode at 100 μM MB at different pH values at 30 mV/s, enlarged oxidation peak of MB, anodic peak current vs pH, and anodic potential vs pH; effect of scan rate on peak current solution composition 0.1 M PBS + 0.01 M KCl + 100 μM MB by modified Cu electrode and peak current vs (scan rate)1/2; comparison in modes for MB detection by modified electrode using cyclic voltammetry (CV), differential pulse voltammetry (DPV), and linear sweep voltammetry (LSV) in the presence of 100 μM MB in 0.1 M PBS + 0.01 M KCl; enlarged differential pulse voltammogram of MB at bare Cu electrode in 0.1 M PBS + 0.01 M KCl; enlarged differential pulse voltammogram of MB at bare Cu electrode in 0.1 M PBS + 0.01 M KCl; enlarged differential pulse voltammogram of MB at bare Cu electrode in 0.1 M PBS + 0.01 M KCl; enlarged differential pulse voltammogram of MB at bare Cu electrode in 0.1 M PBS + 0.01 M KCl; images of bare Cu electrode, PEDOT:PSS-coated electrode, PEDOT:PSS-coated electrode after several cycles of CV, and Cu electrode after removal of
PEDOT:PSS; and XRD of bare Cu electrode, Cu electrode after few cycles of CV, PEDOT:PSS-coated Cu electrode after few cycles of CV, and PEDOT:PSS (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Jaydeep Bhattacharya — Nanobiotechnology Lab, School of Biotechnology, Jawaharlal Nehru University, New Delhi 110067, India; orcid.org/0000-0001-7268-0867; Email: jaydpb@gmail.com, jaydeep@jnu.ac.in

**Authors**

Jagriti Gupta — Nanobiotechnology Lab, School of Biotechnology, Jawaharlal Nehru University, New Delhi 110067, India

Subhavna Juneja — Nanobiotechnology Lab, School of Biotechnology, Jawaharlal Nehru University, New Delhi 110067, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03125

**Notes**

The authors declare no competing financial interest.

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CCB, copper clad board; MB, methylene blue; GNF, gold nanoflower; GNP, gold nanoparticles; MEA, microelectrode array; PEDOT:PSS, poly(3,4-ethylendioxythiophene) poly-styrene sulfonate

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