



EDTA Modified PANI/GO Composite Based Detection of Hg (II) Ions

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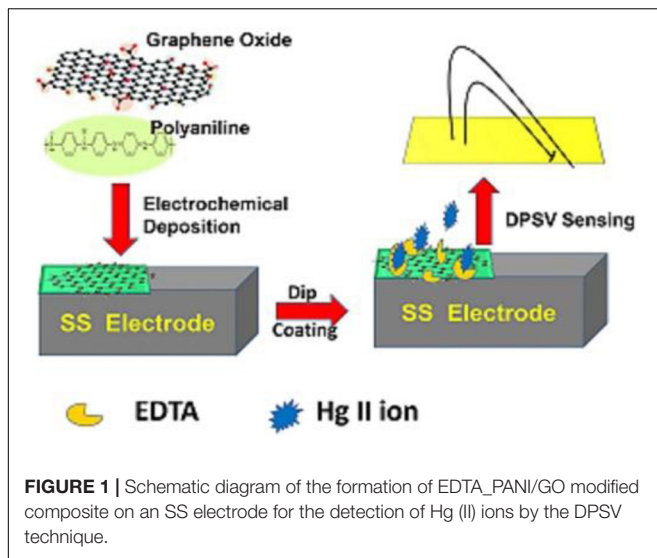
Electrochemical recognition of Hg (II) ions utilizing EDTA modified polyaniline (PANI)/Graphene Oxide (GO) composite is reported in the present communication. Graphene Oxide (GO) synthesis was carried out by a modified Hummer's method. Electrochemical characterizations, namely cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were performed before and after modification of the composite. The topographies of the PANI/GO composite and EDTA_PANI/GO electrodes were studied using AFM. Roughness parameter values were compared for confirmation of surface modification. Fourier transform infrared spectroscopy (FTIR) was utilized for the compositional analysis of PANI/GO and EDTA_PANI/GO electrodes. The EDTA_PANI/GO composite exhibits sensitivity toward Hg (II) ions when probed using the differential pulse stripping voltammetry (DPSV) technique with a lower detection limit of 2 ppb. EDTA modified SS_PANI/GO composite (PANI/GO composite deposited on a stainless-steel substrate) showed superior sensitivity in the detection of Hg (II) ions. The sensitivity was observed to extend to 1 ppb, which is smaller than the maximum contaminant level (MCL) endorsed by the Environment Protection Agency (EPA, United States).

Keywords: PANI, GO, EDTA_PANI/GO, EIS, DPSV, Hg (II) ion detection

INTRODUCTION

Heavy metals are moderately scarce in the crust of the Earth. These heavy metals are characterized by comparatively high densities and atomic numbers (Tekaya et al., 2013). Heavy metals can harm air, water, and soil quality, and in this manner, cause hazards to human wellbeing and the environment (Bánfalvi, 2011; Turdean, 2011). Among them, some metals like iron, cobalt, and zinc provide crucial nutrients or are relatively innocuous (such as ruthenium, silver, and indium) but yet can be fatal in larger amounts. Some heavy metals like cadmium, mercury, and lead are profoundly poisonous and cancer-causing above trace levels (Nagajyoti et al., 2010; Lansdown, 2013). Of these, mercury has a greater affinity to sulfur and thiol-containing molecules, resulting also in nephrotoxicity and neurotoxicity (Gumpu et al., 2015; Jan et al., 2015). For these reasons, the need arises for sensors that can acquire real-time measurements of heavy metals in water.

Electrochemical detection of heavy metal ion concentration is a versatile tool. Anodic stripping voltammetry (ASV) is the commonly used technique (Bansod et al., 2017; Deshmukh et al., 2018a).



However, ASV has weaknesses such as instability, low sensitivity, and limits to detection (Zhao et al., 2014; Patil et al., 2018).

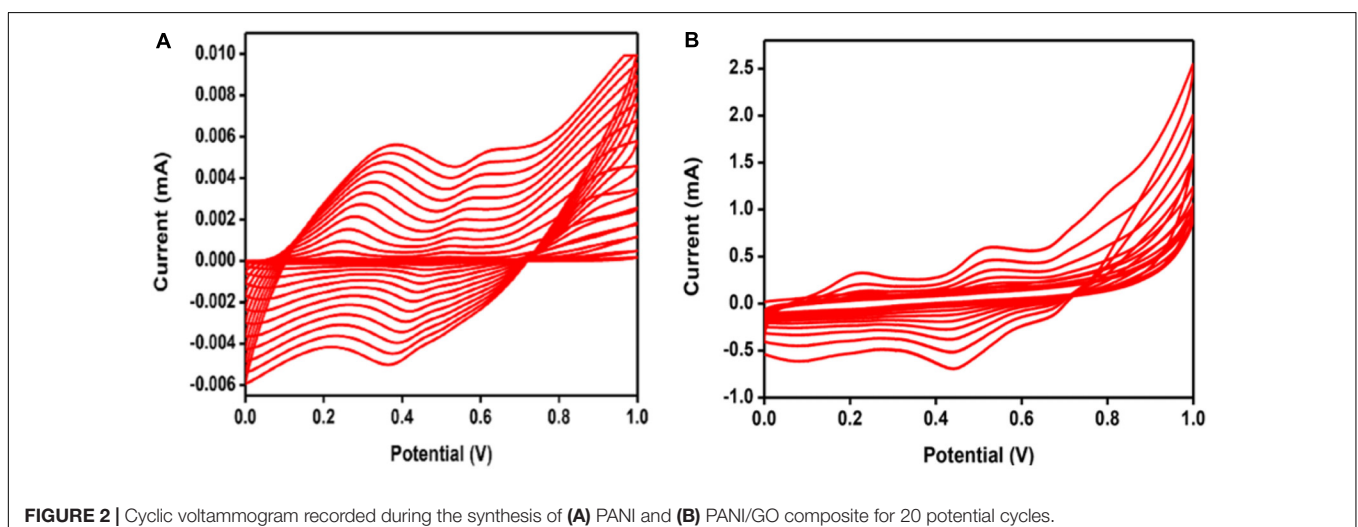
To conquer this problem, many advanced materials are being investigated, such as conducting polymers, carbon nanotubes (CNTs), graphene and its derivatives, and metal oxides (Choi et al., 2011; Oztekin et al., 2011; Strong et al., 2012; Lei et al., 2014). However, these advanced materials have certain limitations, e.g., organic conducting polymers have low selectivity, sensitivity, and a lack of environmental stability (Zhang et al., 2011; Das and Prusty, 2012). One of the shortcomings of carbon nanotubes (CNTs) is the entrapment of molecules at interstitial sites, which decreases reproducibility (Musameh et al., 2011; Herrera-Herrera et al., 2012).

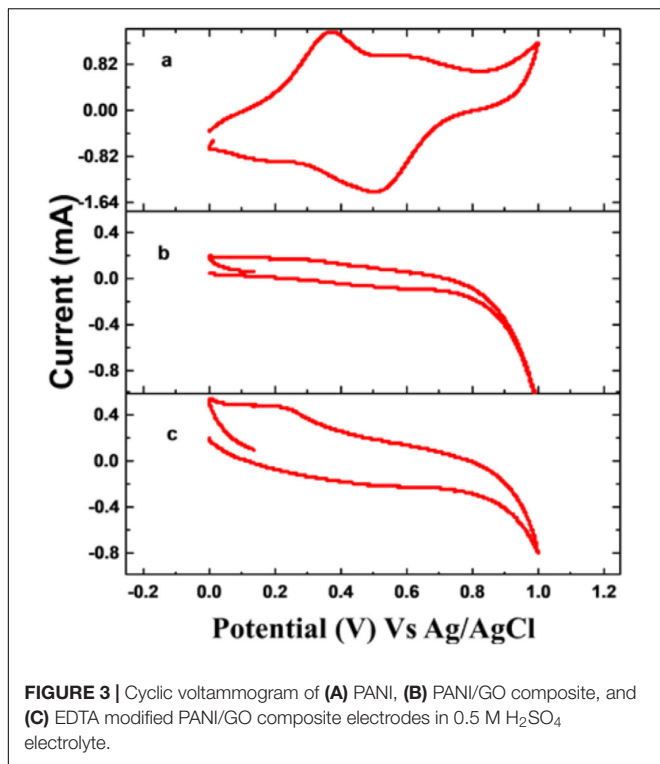
To overcome such limitations, composite or functionalized materials are employed for the effective detection of metal ion concentration (Chen et al., 2012; Deshmukh et al., 2018b). Zhou et al. (2014) have reported on conducting polymers such as polyaniline (PANI), which performs as a *p*-type

semiconductor and has demonstrated incredible potential for application because of its electrical conductivity, solubility, optical activity, easy processing, good sensitivity at room temperature, and good environmental stability. Graphene-based sensors are comparatively novel and can possibly meet the objective of quick *in situ* estimation of metals in water (Wang et al., 2010; Chang et al., 2014). It was reported that graphene has a huge hypothetical explicit surface area, high intrinsic mobility, and good electrical conductivity (Zhu et al., 2010). Graphene additionally has a honeycomb lattice with two sublattices bonded together with a σ -bond. Every carbon atom in the lattice contains a π orbital that offers ascent to a delocalized electron (Charlier et al., 2007; Roth and Carroll, 2015). Aside from these astounding properties, the remarkably low electronic clamor of graphene provides the opportunity to sensitively detect numerous analytes using graphene (Roth and Carroll, 2015).

It was as well reported that Graphene Oxides (GO) have layered, oxygenated graphene sheets that contain oxygen functional groups, for example, epoxides, carboxyls, hydroxyls, and alcohols, on their basal planes and edges. These groups in GO can be utilized as decent sites for surface alteration. As indicated by chemical examination, the carbon to oxygen ratio is 3:1 (Stankovich et al., 2006). GO can be reduced to nearly graphene by various chemical reduction methods; however, some promising applications of GO have recently been reported (Gilje et al., 2007; McAllister et al., 2007; Rao et al., 2009; Chen et al., 2012).

In recent years, compositing or modification of polyaniline (PANI) with carbon-based materials has received much attention. The properties of GO, such as its flat structure, charge transfer ability, incorporation of hydrophilic functional groups, and good dispersion ability in aqueous media, lead to more sites at which PANI can become attached (Dreyer et al., 2010; Vadivel et al., 2016). Also, the interaction of PANI with GO is by Π - Π stacking, electrostatic interaction, and hydrogen bonding (Wang et al., 2010). The Π - Π interaction will support faster signal processing and enhancement of the sensitivity of the sensor. Moreover, in coordination chemistry, EDTA falls within the





aminopolycarboxylic acid family of ligands. Typically, EDTA ties to a metal cation through its two amines and four carboxylates. A significant number of the subsequent coordination compounds bear octahedral geometry. This octahedral geometrical structure assists with attaching the metal ion and furthermore expands the level of cross-linking inside the PANI film (Zagal et al., 1996). This implies that a composite of PANI/GO modified by EDTA will have better discrimination toward Hg (II) ion. The differential pulse stripping voltammetry (DPSV) technique is utilized for the identification of heavy metal ions.

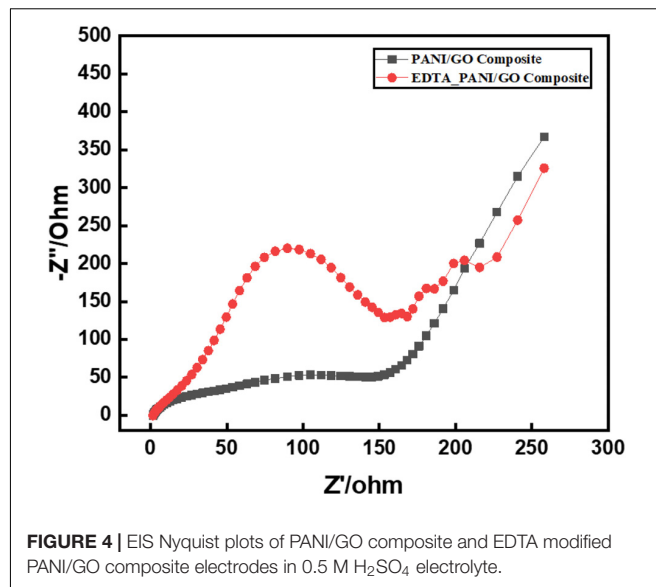
In the present investigation, we have amalgamated a composite of polyaniline (PANI) and graphene oxide (GO), which was then modified by ethylenediaminetetraacetic acid (EDTA) for the detection of mercury ions (Hg II) using DPSV.

Over the most recent couple of years, the greater part of the information revealed shows the simultaneous identification of different heavy metal ions, which reflects the issue of selectivity (Gumpu et al., 2017; Ullah et al., 2018; Yi et al., 2019). In the present investigation, this problem is substantially resolved. Moreover, the present investigation also achieves the detection of Hg (II) ions beneath the MCL level, i.e., up to 1 ppb, with a quantifiable yield current.

MATERIALS AND METHODS

Materials

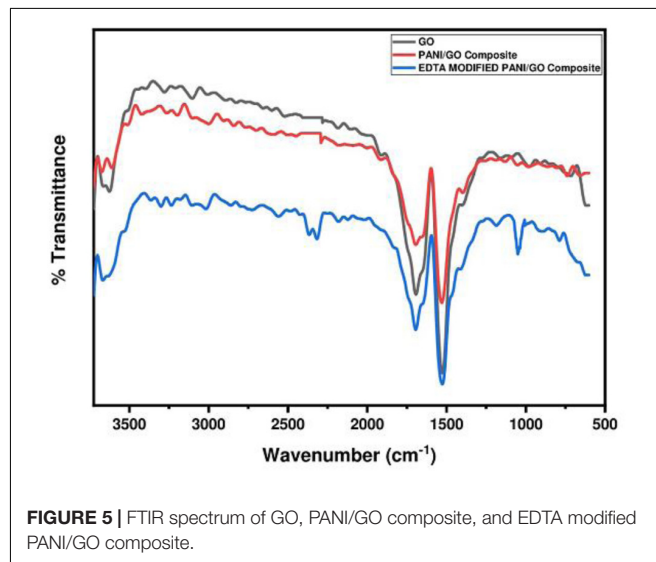
Aniline of reagent grade, sulfuric acid, and ethylenediaminetetraacetic acid (EDTA) were bought from Fluka (Germany), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide

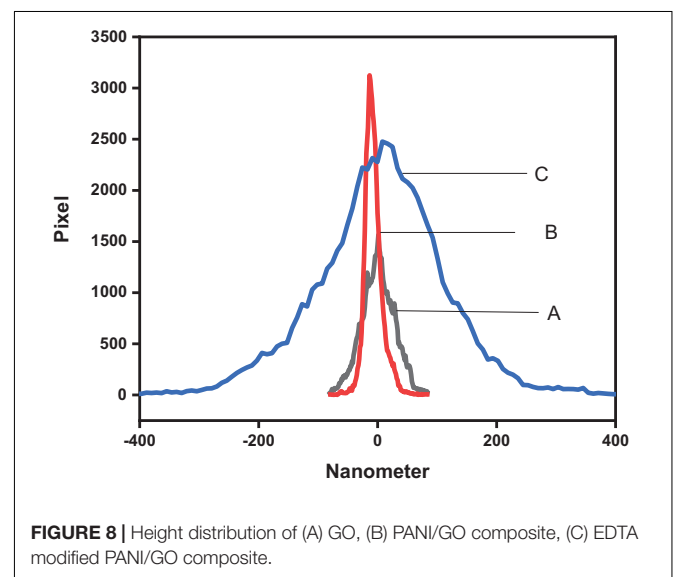
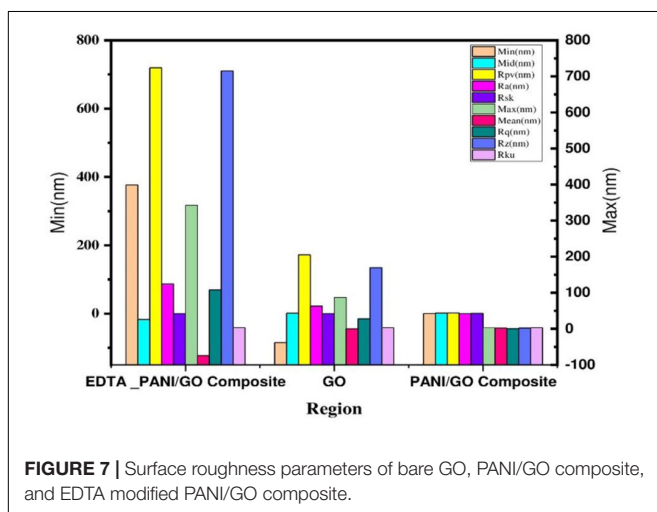
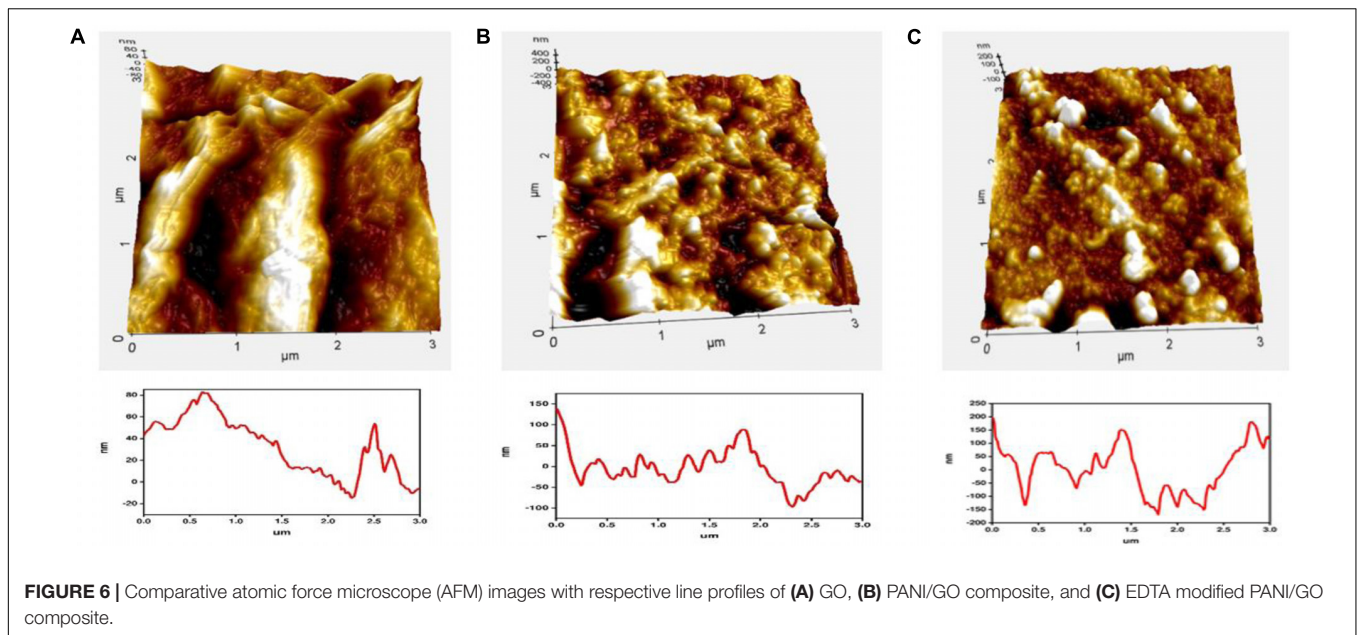


(EDC) was acquired from Sigma Aldrich (Germany). The phosphate buffer solution (PBS) used was of pH 7. Graphene powder (~60 mesh size) was procured from Molychem (Mumbai, India), and potassium permanganate was from Kemphasol (India). An acetate buffer solution was set up by regulating 0.1 M sodium acetate (Aldrich) to the desired pH, 4.1. All the progressions were carried out in aqueous media using deionized water (DI).

Preparation of PANI/GO Composite

Graphene Oxide was produced from graphite powder using the Modified Hummer's Method (Shahriary and Athawale, 2014). Separately, PANI/GO composite was synthesized by an electrochemical method. First, 50 mL of aqueous 0.25 M aniline and 0.5 M H₂SO₄ suspension were mixed and maintained for



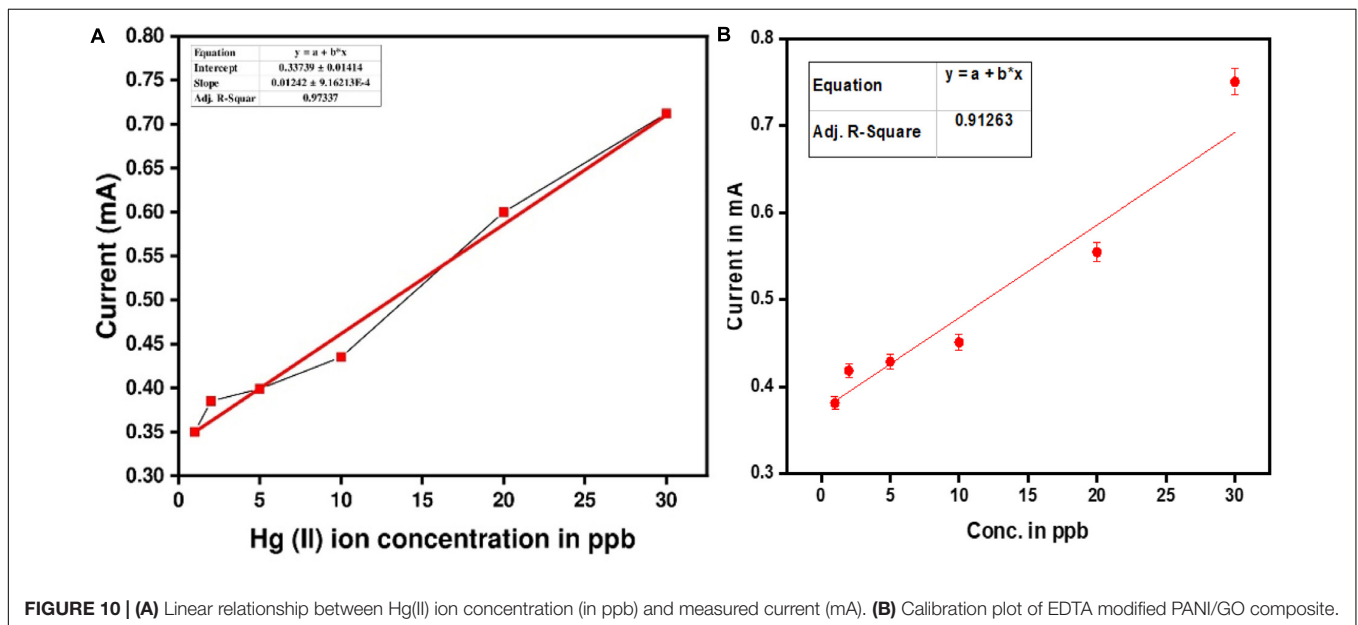
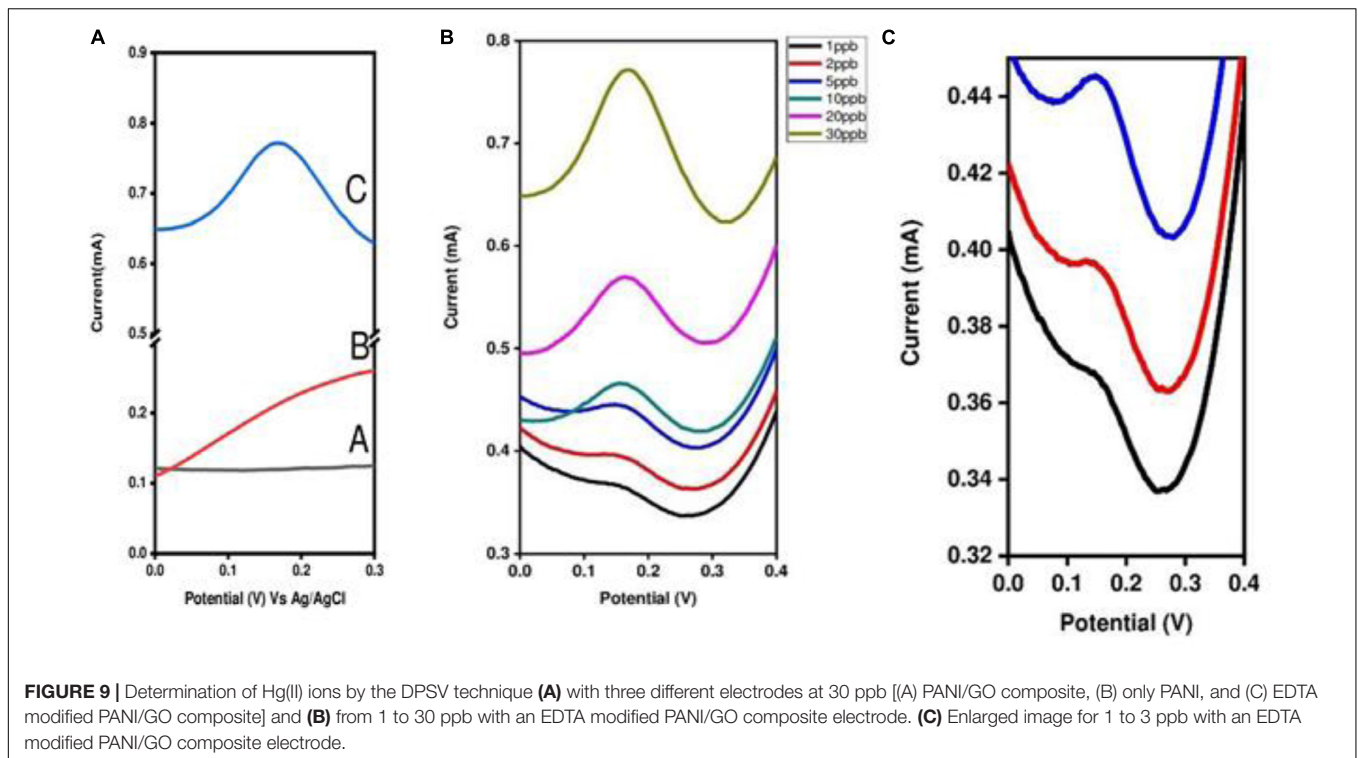


20 min, stirring. Then, 10 ml of GO in the ratio 0.1 mg/ml was mixed with the above electrolyte solution. The mixture was kept for 20 min, stirring, followed by 20 min sonication. The electrochemical synthesis of PANI/GO composite was carried out by the cyclic voltammetry method inside the potential scope of 0 to +1 V at a scan rate of 0.1 V/s for 20 cycles, with a stainless steel (SS) electrode as the working electrode, platinum as the counter electrode, and Ag/AgCl as the reference electrode. It was performed on a CHI 660C electrochemical workstation. After applying the voltage for 20 cycles, a blackish green-colored coating was observed on the working electrode. The deposited film was washed with deionized water to evacuate the concentration of electrolyte at the substrate surface, and the electrode was afterward dried at room temperature. A schematic of the synthesis of PANI/GO composite and the subsequent

modification of the composite through the EDTA chelating ligand is represented in **Figure 1**.

Modification of SS_PANI/GO Composite

The SS_PANI/GO composite electrode (PANI/GO composite synthesized on a stainless steel substrate) was modified by EDTA chelation by a dip-coating method because, after polymerization of a conducting polymer, it is easy to attach another active group covalently. For modification, an EDTA suspension was set up in a 0.2 M phosphate buffer solution (PBS) at pH 7.2, having 0.1 M EDC as a triggering operator and 0.01 M EDTA. The SS PANI/GO electrode was inundated in the readied solution of EDTA and left for 12 h under non-stop stirring at room temperature. This resulted in the formation of covalent bonding

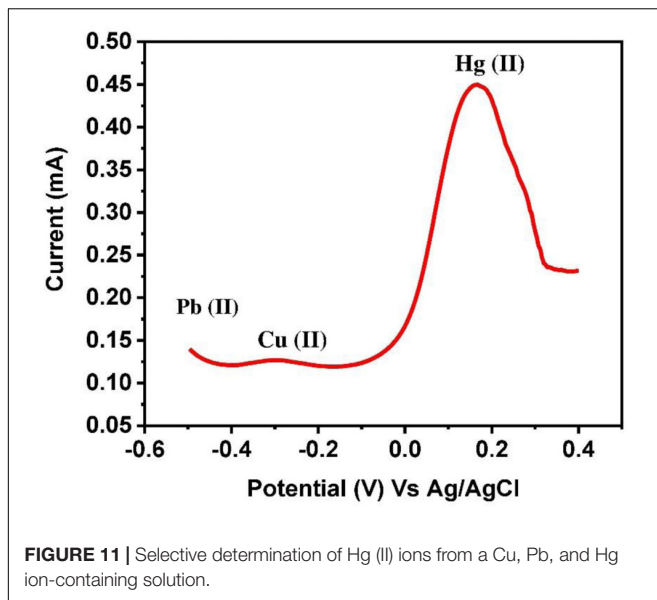


of COOH⁻ with the NH₂ group of the composite. The electrodes were subsequently cautiously washed with deionized water to expel the gently bound molecules.

Electrochemical Detection of Mercury [Hg (II)] Ions

Electrochemical detection of mercury ions was carried out by differential pulse stripping voltammetry (DPSV) employing

a three-terminal arrangement at room temperature. The SS_PANI/GO/EDTA electrode filled in as the working electrode (1 cm²) and Ag/AgCl and platinum as the reference and counter electrodes, respectively. The modified electrode was drenched in acetate buffer solution of pH 4.1 with different concentrations of Hg (II) ion and kept under continuous stirring for 2 min at 600 rpm for accumulation. This 120 s was the deposition time for Hg (II) ions. Since EDTA has the capacity of multidentate ligands to make a complex with many metal ions at various pH



values, the pH for Hg (II) ions has been optimized as 4.1, achieved via the acetate buffer solution. After completing accumulation, DPSV scan was applied in the potential range of 0.0 to 0.4 V to oxidize mercury ions from the electrode surface.

RESULTS AND DISCUSSION

Electrochemical Synthesis of PANI/GO Composite

Electrochemical synthesis of PANI/GO composite was performed by cyclic voltammetry, as portrayed in **Figure 1**, between the range 0 to +1 V for 20 cycles on the SS electrode at a 0.1 V/s scan rate. **Figure 2** illustrates the relative cyclic voltammogram recorded during the amalgamation of PANI and PANI/GO composite film. During the synthesis of PANI, a greenish-colored film was observed to form, while for, the composite, a blackish green-colored film formed.

During synthesis, increase in the current in the PANI/GO composite as compared to PANI is clearly exhibited in **Figure 2B**, which relates to the development of composite film on the SS electrode. The conductivity of the film increments by expanding the applied potential, which affirms the formation of PANI/GO composite.

Electrochemical Characterization

Figure 3 represents the electrochemical behavior of PANI, PANI/GO Composite, and EDTA modified PANI/GO Composite in 0.5 M H₂SO₄ solution. The oxidation and reduction peaks of PANI are easily observed, and PANI/GO composite exhibits lower oxidation potential compared to PANI and EDTA modified PANI/GO composite. The PANI/GO composite exhibits an increase in oxidation potential after modification by EDTA due to the electrostatic interaction present on the surfaces of the electrodes.

The PANI/GO composite and EDTA modified PANI/GO electrodes were characterized by EIS in the frequency range of 1 to 1000 Hz in 0.5 M H₂SO₄, which is a functioning strategy for evaluation of procedures occurring at electrode surfaces. **Figure 4** shows the EIS Nyquist plots of the PANI/GO composite and EDTA modified PANI/GO composite electrodes. The EIS for EDTA modified PANI/GO composite electrodes indicates a moderately large semi-circular province, which exhibits a large interfacial electron transfer resistance between the redox probe and the modified PANI/GO composite electrode. The PANI/GO electrodes show lower interfacial electron resistance in the Nyquist plot, which indicates that the structure of the PANI/GO composite electrode stimulates electron transfer, which demonstrates the superb electrochemical action of the PANI/GO composite electrode.

FTIR Analysis

The PANI/GO composite and EDTA modified PANI/GO composite were further characterized by FTIR spectroscopy, as depicted in **Figure 5**. Peaks at 1690 cm⁻¹ and 1510 cm⁻¹ in every spectrum confirm the presence of C = O and C-O functional groups. C = N stretching is clearly observed at 1120 cm⁻¹ in the EDTA modified PANI/GO composite. This stretching indicates strong interaction with the EDTA ligand. The peak perceived at 2340 cm⁻¹ relates to the (isocyanate group) N = C = O asymmetric vibrations.

Surface Morphologies of GO, PANI/GO Composite, and EDTA Modified PANI/GO

The surface morphologies of the prepared samples were studied with an atomic force microscope (AFM). **Figure 6** represents the surface morphology of (A) bare GO, (B) PANI/GO composite, and (C) EDTA modified PANI/GO composite, which plainly reveals the transformations in surface morphology. The plot in **Figure 7** distinguishes the roughness parameters of graphene oxide drop-casted on a glass substrate, PANI/GO composite synthesized by the electrochemical method, and PANI/GO composite modified with EDTA by dip coating.

Figure 8 shows the height distribution of (A) GO, (B) PANI/GO composite, and (C) EDTA modified PANI/GO composite. **Figure 8** evidently shows that there is an increasing distribution height from bare graphene oxide to PANI/GO composite to EDTA modified PANI/GO composite.

COMPARATIVE AND SELECTIVE DETERMINATION OF HG(II) IONS BY THE DPSV METHOD

The best method for the determination of mercury ions was elaborated on in section “Electrochemical Detection of Mercury [Hg (II)] Ions,” Determination was performed by the differential pulse stripping voltammetry technique (DPSV) with EDTA modified PANI/GO composite on an SS electrode. The modified SS electrode was immersed in a mercury ion solution and, by following the methodology mentioned in

section “Electrochemical Detection of Mercury [Hg (II)] Ions,” measurement was carried out. **Figure 9A**, represents the comparative detection of Hg (II) ions at 30 ppb with three different electrodes, that is, (A) PANI/GO composite, (B) only PANI, and (C) EDTA modified PANI/GO composite. From this, it can be easily concluded that EDTA modified PANI/GO composite is more sensitive than the PANI and PANI/GO composite electrode. Thereafter, the determination of Hg (II) ions with the EDTA modified PANI/GO composite electrode was performed at different concentrations down to as low as 1 ppb (**Figure 9B**). As the concentration increases, the measured value of the current also increases linearly, as depicted in **Figure 10A**. An estimation of the determination and linearity of the device has been made by way of the calibration plot in **Figure 10B**. The gadget revealed a linearity factor $R^2 = 0.91283$ for room temperature estimation. The sensitivity of the SS_EDTA modified PANI/GO composite was 12.42 mA/ppb, and the limit of detection (LOD) was 0.612 ppb.

The limit of detection was determined by utilizing the equation,

$$\text{LOD} = 3.3 \times (\text{Standard deviation of the regression line/Slope})$$

Selective determination was carried out from the solution containing Cu, Pb, and Hg ions. For selectivity, the potential (vs. Ag/AgCl) was applied from -0.6 to 0.4 V. The sharp apex is observed at 0.2 V, which clearly indicates the presence of Hg (II) ions (**Figure 11**). It can be concluded that the EDTA modified PANI/GO composite electrode is selective to Hg (II) ions only.

CONCLUSION

An EDTA modified PANI/GO composite on stainless steel (SS) electrode for use in the detection of Hg (II) ions was synthesized and characterized effectively. Electron transfer resistance between the redox probe and EDTA modified PANI/GO composite or PANI/GO composite was clearly observed. Modification by

the EDTA chelating ligand increases the affinity of PANI/GO composite toward Hg (II) ions. An EDTA modified PANI/GO electrode shows excellent response to Hg (II) ions from 30 to 1 ppb, which is well below MCL (2 ppb). A successful and linear determination of Hg (II) was performed by differential pulse stripping voltammetry (DPSV) down to 1 ppb.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

MM and MS conceived of the presented idea and developed the theory. MM performed the experiments and computations. HP and GB encouraged the investigation and verified the analytical methods. NI, PS, TA-G, and SS assisted with CV, FTIR, and EIS measurements. All authors discussed the outcomes and added to inscribe the final manuscript. MS contributed to the final version of the manuscript and supervised the project.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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