Supplementary Information

Sulfhydryl Functionalization of MXenes; Enables Selective Sensing of Mercury Ions

Dani George[1], Chandan Hunsur Ravikumar*[1], Jomy Jose Philip[1], R. Geetha Balakrishna[1]*

[1]Centre for Nano and Material Science, Jain Global Campus, Jain (Deemed-to-be) University, Jakkasandra Post, Ramanagara Dist. 562112

Corresponding Authors: br.geetha@jainuniversity.ac.in and hr.chandan@jainuniversity.ac.in

This PDF Includes:

Figure S1: EDAX Elemental Mapping

Figure S2: UV Absorption Spectra of MXene and MXene-GSH

Figure S3: XPS Spectra of C *1s* of MXene GSH

Figure S4: Pre-deposition time analysis of MXene-GSH with Hg^{2+} ions.

1. Materials and Methods

1.1 Chemicals

All the chemicals used were of analytical grade and were used without further purification. Titanium Aluminium Carbide (Ti_3AlC_2, ≥90%, ≤100 μm) MAX phase and Hydrogen Fluoride (HF, 48%) were purchased from Sigma Aldrich Company. L-Glutathione Reduced (GSH, 99.5%) was purchased from SRL Chemicals. Mercury (II) Chloride ($HgCl_2$, 99%), Copper (II)Chloride ($CuCl_2$), Iron (II) Chloride tetrahydrate ($FeCl_2$. $4H_2O$), Lead (II) Chloride ($PbCl_2$), Nickel (II) Chloride ($NiCl_2$), Sodium Chloride (NaCl), Pottasium Chloride, Silver Nitrate, di-Potassium hydrogen phosphate (K_2HPO_4, 98%), Potassium hydrogen phosphate (KH_2PO_4, 98%) was purchased from Merck Millipore. Potassium ferrocyanide [$K_4[Fe(CN)_6]$, 99%], Potassium Ferricyanide[$K_3[Fe(CN)_6]$, 99%] were purchased from Qualigens Fine Chemicals. Potassium Chloride (KCl, 99.5%) was purchased from Fischer Scientific. Distilled water was used for preparing composites and solutions.

1.2 Characterisation Techniques

The characterization studies were performed to analyse the physicochemical properties of the prepared samples. A UV-Visible spectrophotometer (SHIMADZU UV-1800) was used to measure the absorption spectra of synthesized MXene-GSH composite. Bruker ALPHA eco-ATR-IR was utilised to obtain the IR spectra owing to the presence of different function groups in the composites. Confocal Raman Microscopy (Horiba Scientific Xplora plus V1.2 Multiline) was also used to confirm the bonding present in the composite. A field emission scanning electron microscope JEOL (JSM-7000F, Singapore) equipped with energy-dispersive X-ray (EDX) spectroscopy was used for the determination of the morphological features of synthesized composites. The crystalline nature of the synthesized product was analysed by powder X-ray diffraction (XRD) (Rigaku X-ray diffraction, Japan) using a Cu Kα radiation source at a scan rate of 2-degree min^{-1}. XRD patterns of the synthesized materials were analysed in the range of 2θ from 10 to 80°. Surface chemical composition of MXene-GSH were studied using X-ray photoelectron Spectroscopy (XPS, PHI-500 versa probe II, FEI Inc. USA). All the electrochemical measurements were performed using a CHI660D potentiostat (CH Instrument, Austin, USA) in a standard three-electrode set-up (CHI brand).

1.3 Synthesis Methodology

1.3.1MXene Synthesis

Required amount of Ti_3AlC_2 MAX phase was weighed and transferred slowly to a Teflon vessel containing 48% HF and kept upon magnetic stirrer for 36h. The obtained precipitate was then washed with deaerated distilled water till the pH was neutralised and kept for vacuum drying at 80℃ for overnight. Thus, the product formed is MXene which was further characterised by various characterisation techniques.

1.4 Electrode Fabrication

The sensor characteristics of MXene-GSH Samples are investigated in phosphate buffer solution (PBS) using a conventional three-electrode system. Normally Ag/AgCl (1M KCl) and platinum wire are used as reference electrodes and counter electrodes respectively. GCE (Glassy Carbon Electrode) has been chosen as working electrode because of its chemical inertness, robust nature, low background current, and thermal stability. GCE shows consistency in performance, and affords easy modification and restoration. In addition, its ready availability and relatively inexpensiveness over other electrodes make GCE special for sensing studies. An alumina slurry with three distinct particle sizes 1, 0.3, and 0.05 µm is used to polish a glassy carbon electrode (GCE, 3 mm in diameter) before being thoroughly rinsed with distilled water and dried. MXene-GSH (10 mg) is dissolved in 1 ml of an isopropanol-water solution (7:3 v/v) to create ink. The resulting slurry is dropcast onto the GCE surface and allowed to dry at room temperature before being used as an electrode.
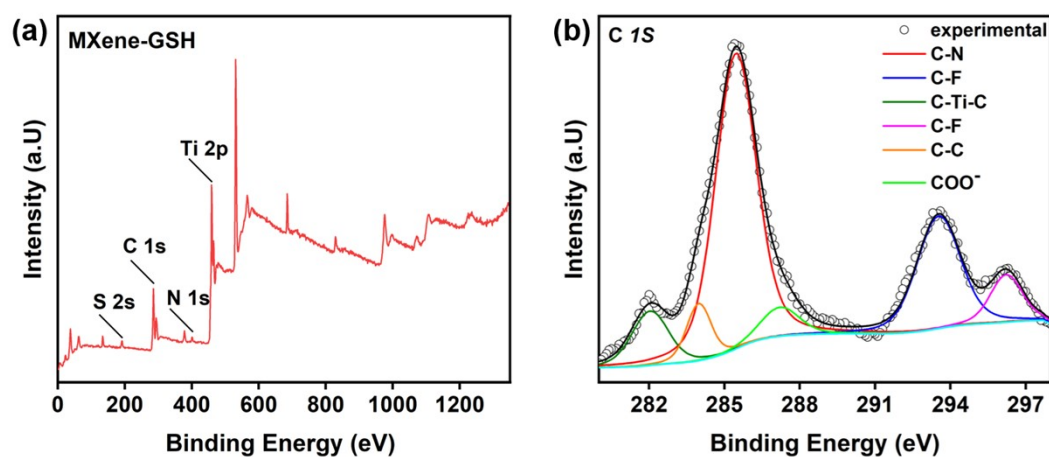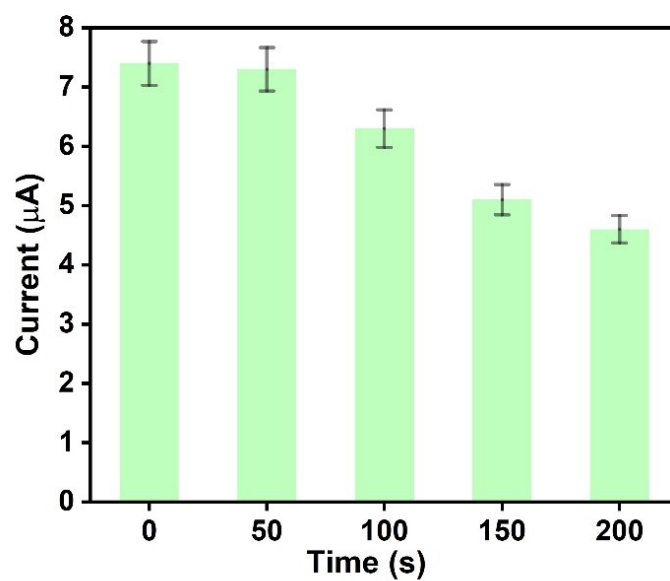
2. Result and Discussion
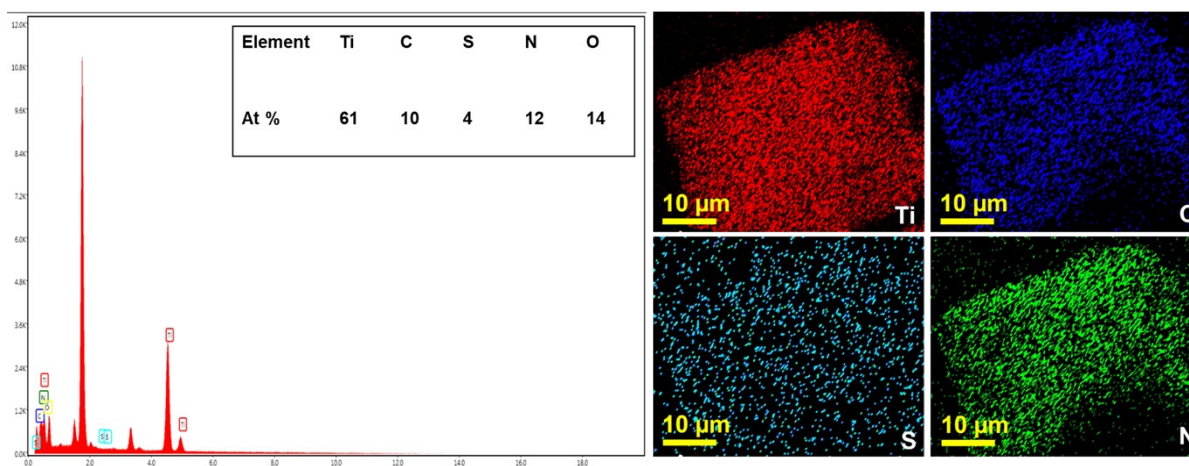
Figure S1:EDS spectra and elemental mapping analysis of MXene-GSH
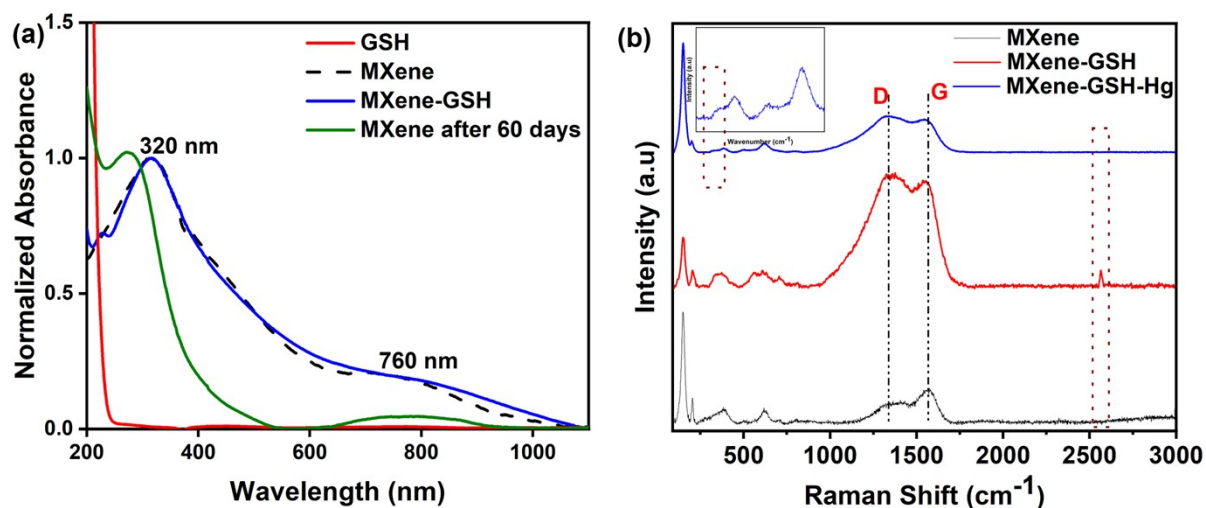
Figure S2. (a) UV absorption spectra for the probes and (b) Raman Spectra for MXene, MXene-GSH, and MXene-GSH with Hg

Figure S3: (a) Survey spectra and (b) high resolution spectra of C *1s* of MXene-GSH

Figure S4. Analysis of Pre-deposition time for MXene-GSH (1:1) with Hg^{2+}