

Co-electrodeposited rGO/MnO₂ nanohybrid for arsenite detection in water by stripping voltammetry



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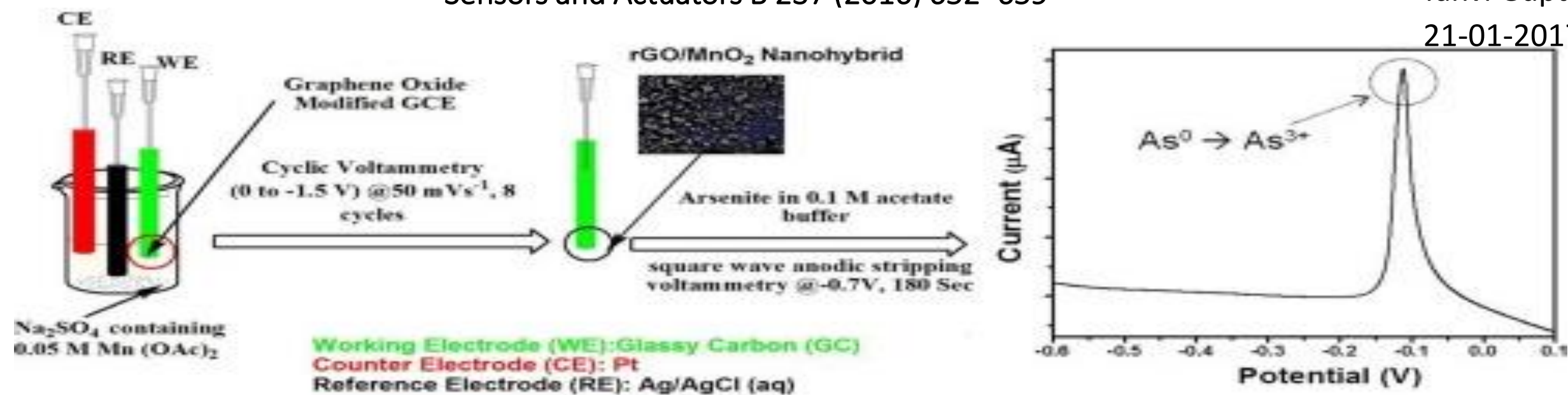
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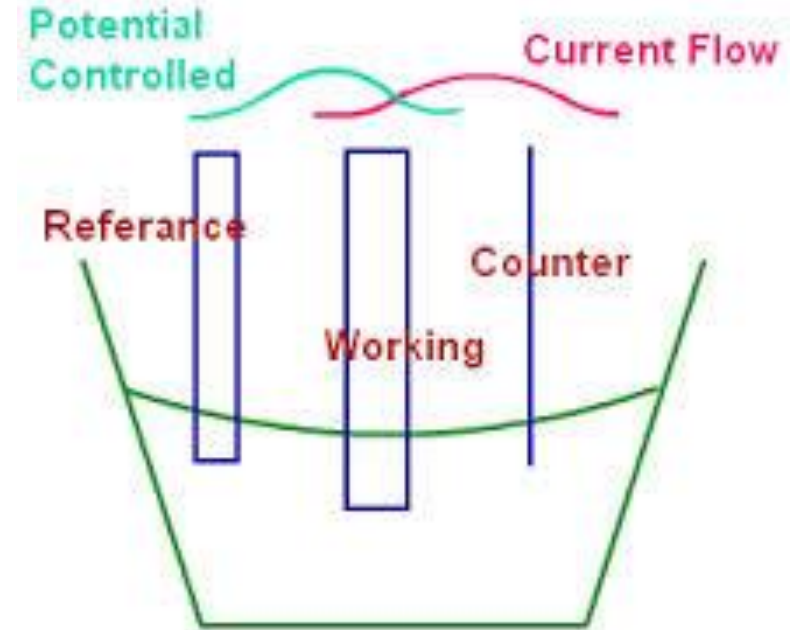
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Introduction

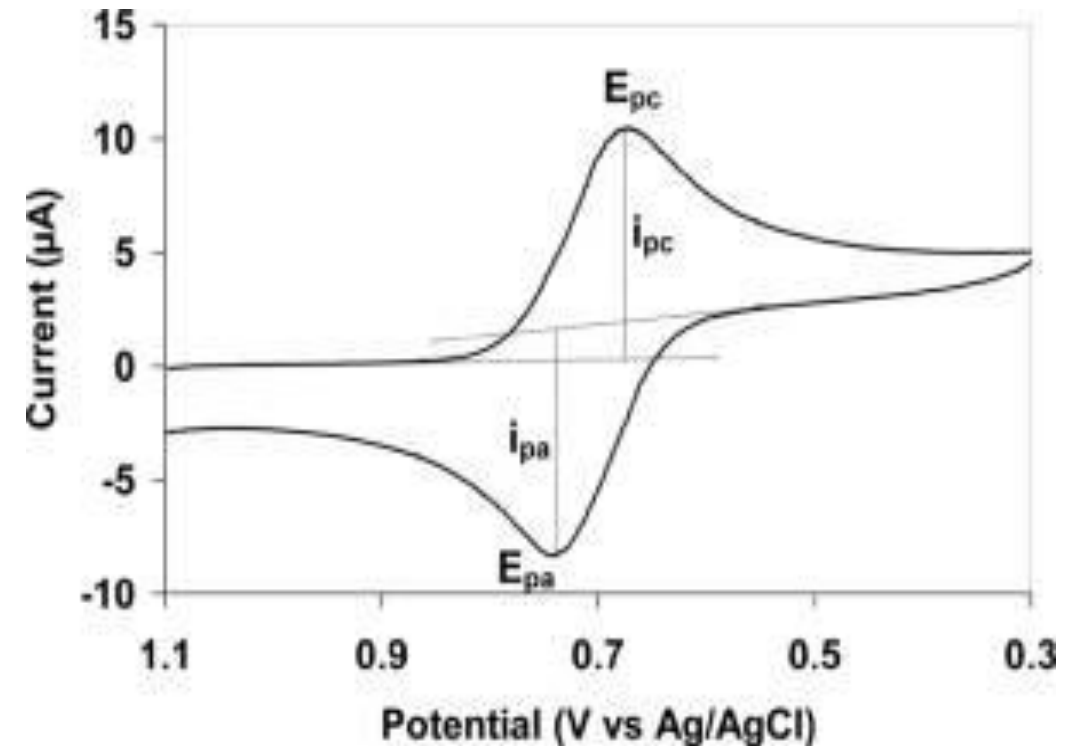
Common electroanalytical methods:

- Cyclic voltammetry.
 - Anodic stripping voltammetry.
 - Amperometric.
 - Cathodic stripping voltammetry.
 - Chronoamperometry.
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- A standard electroanalytical biosensor has a three electrode setup: reference electrode, working electrode, and counter electrode.



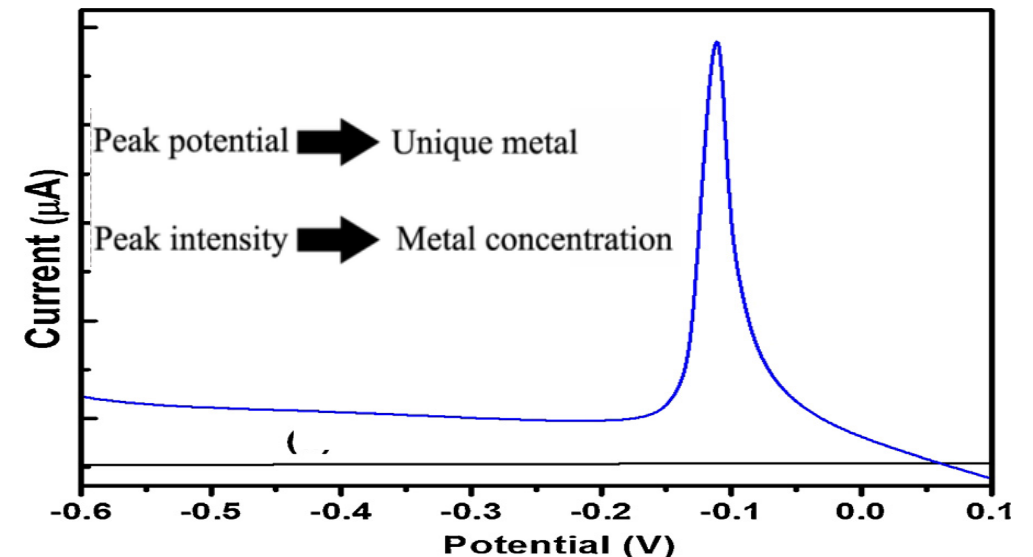
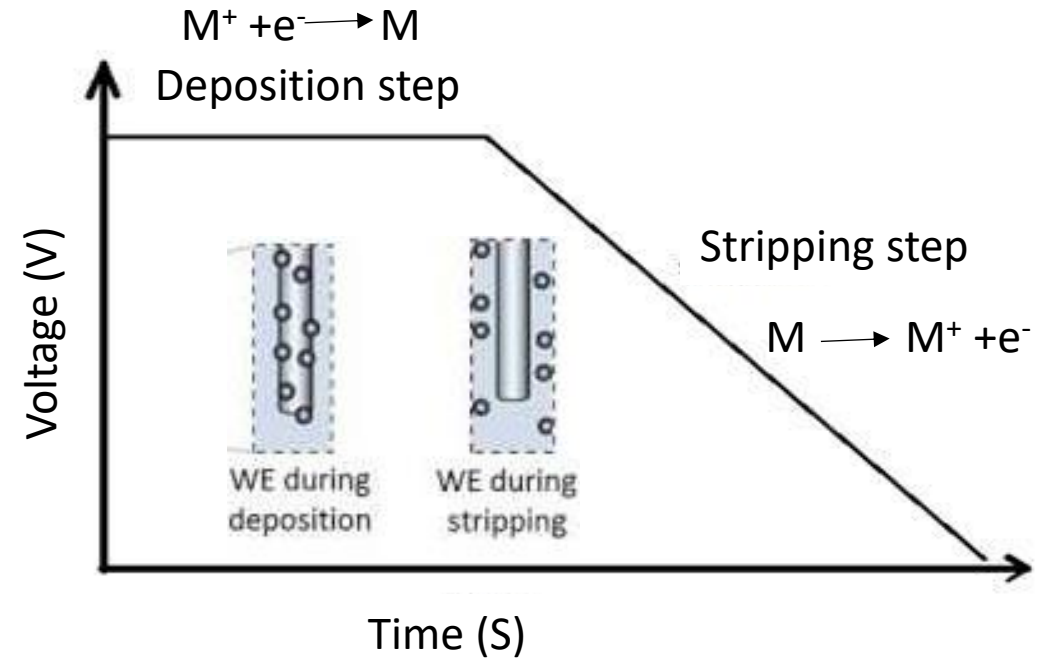
Cyclic voltammetry

- The working electrode potential is ramped linearly versus time. After the set potential is reached, the electrode's potential is ramped in the opposite direction to return to the initial potential.
- These cycles of ramps in potential may be repeated as many times as needed.
- The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution.
- The analyte has to be redox active within the potential window to be scanned.
- A negative potential sweep results in the reduction. A cathodic current is observed until a peak is reached. After the reduction potential of the analyte is reached, the cathodic current will decrease as the concentration of reducible analyte is depleted.
- The direction of potential sweep is reversed. The reduced analyte will start to be re-oxidized, giving rise to a current of reverse polarity (anodic current).



Anodic stripping voltammetry

- It is a voltammetric method for quantitative determination of specific ionic species.
- The analyte of interest is electroplated on the working electrode at lower potential during a deposition step (reduction).
- The working electrode is raised to a higher potential (anodic), and stripping (oxidizing) the analyte.
- The oxidation of analyte is registered as a peak in the current signal at the potential at which the species begins to be oxidized.
- Selective oxidation of each metal phase species occurs during an anodic potential sweep.
- The stripping step can be either linear, staircase, squarewave, or pulse.

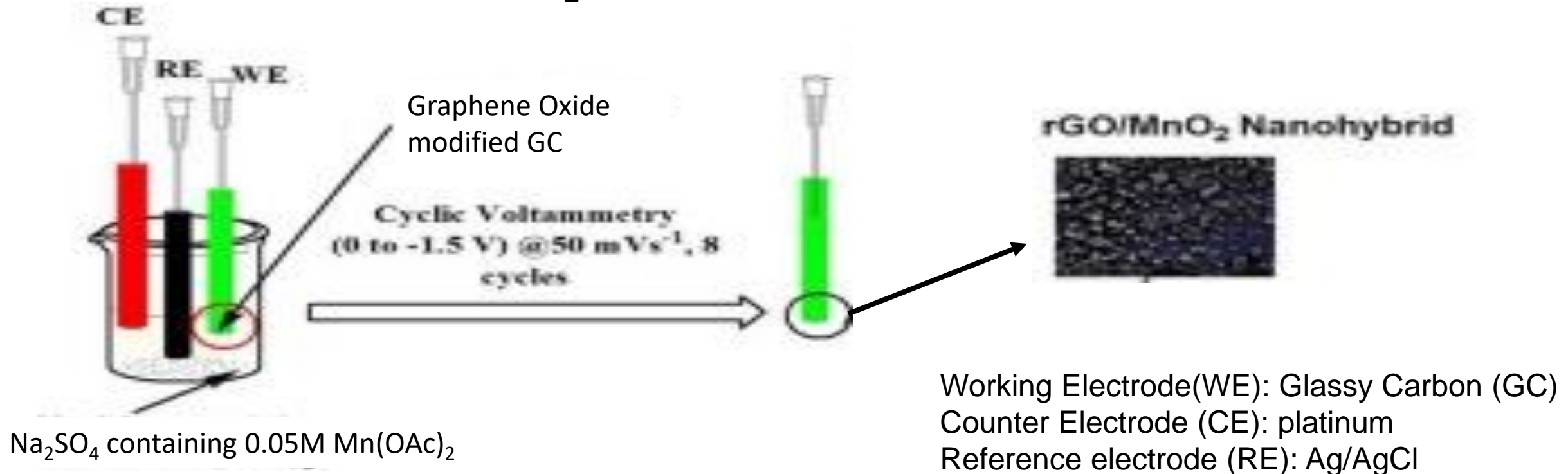


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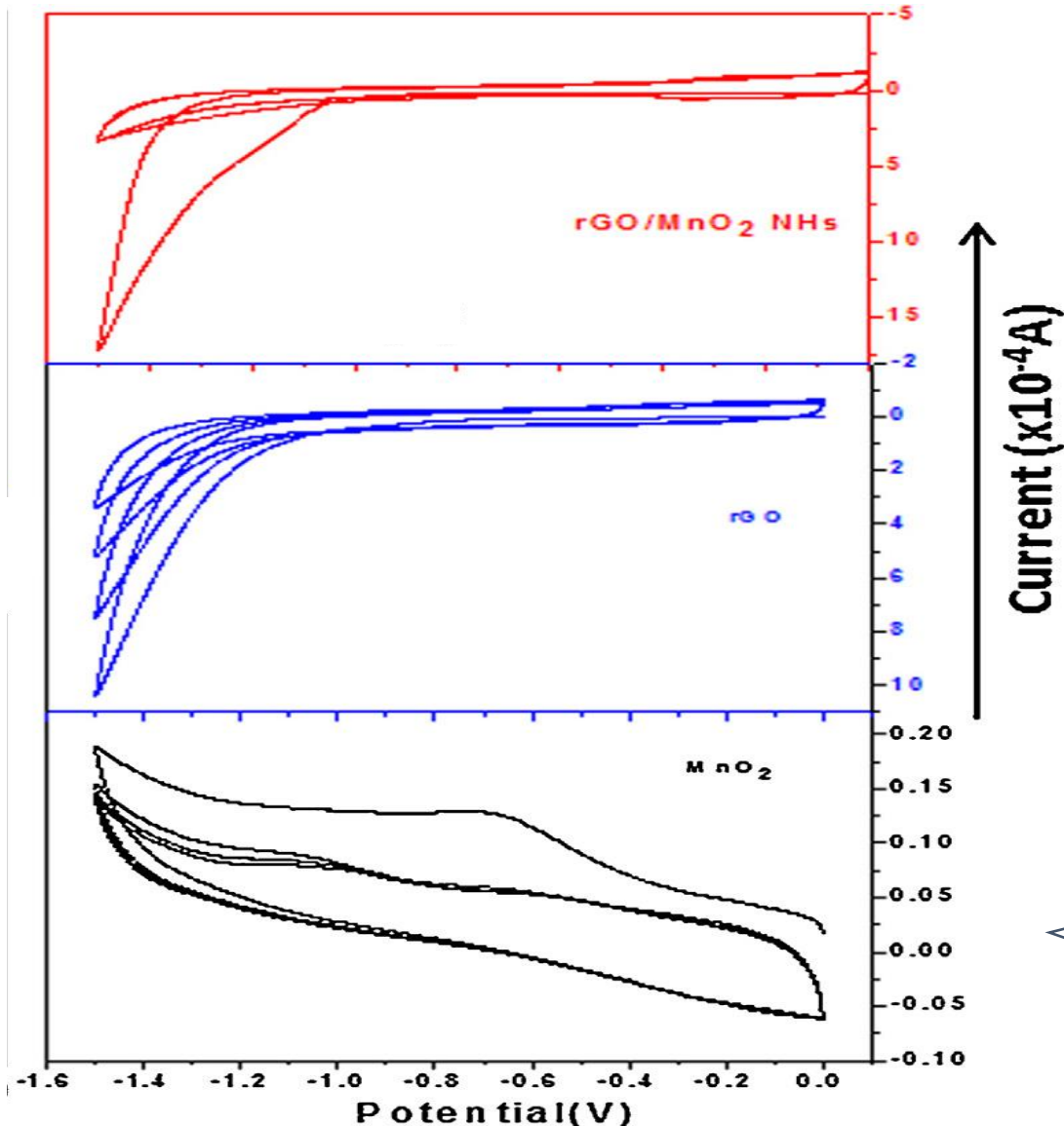
rGO/ MnO₂ for arsenite detection

- Manganese oxide materials have been reported for removal and detection of arsenic in water due to its stability and excellent adsorption capability towards arsenic.
- Graphene and its associates provide conductive platform for electrochemical biosensing due to their easy fabrication, low cost, large surface-to-volume ratio & high conductivity at room temperature.

Fabrication of rGO/MnO₂ nanohybrid (NH) electrodes



Characterization of rGO/MnO₂ electrode

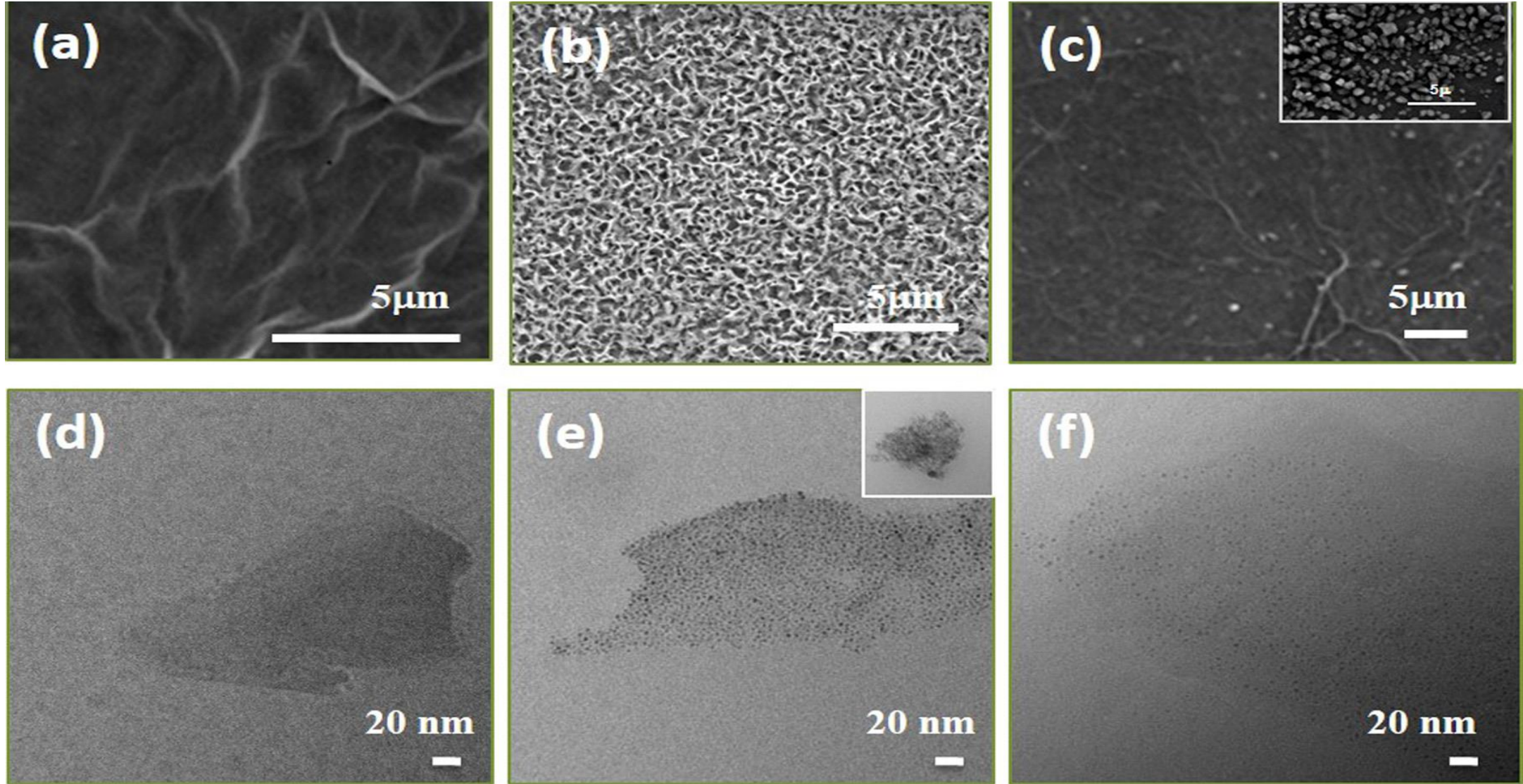


- A large cathodic peak at -1.5 V in the first cycle
- Reduction of the hydrophilic functional groups (OH, COOH) of the GO.
- Disappearance of reduction peak, indicates the catalytic role of manganese in the electrochemical synthesis

The appearance of oxidation and reduction peaks at -0.7 and -1.1 V, respectively confirms the synthesis of MnO₂/GC.

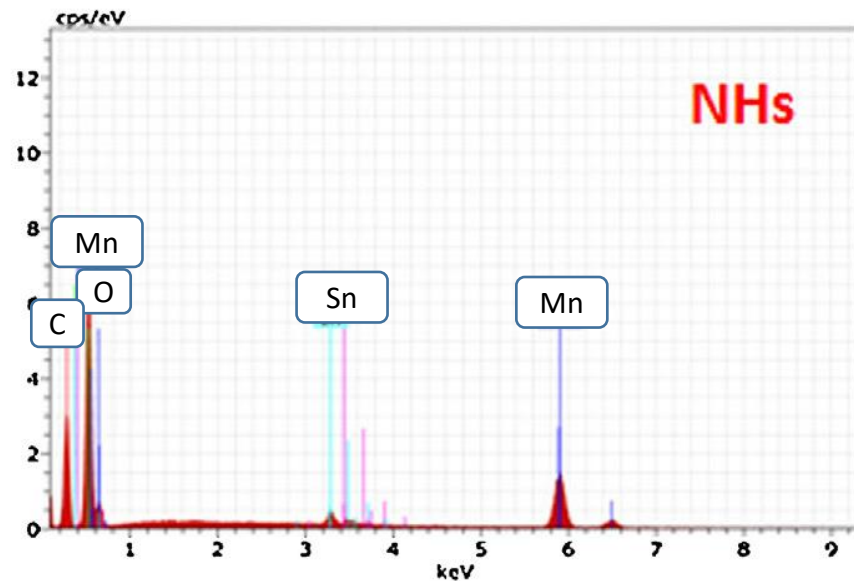
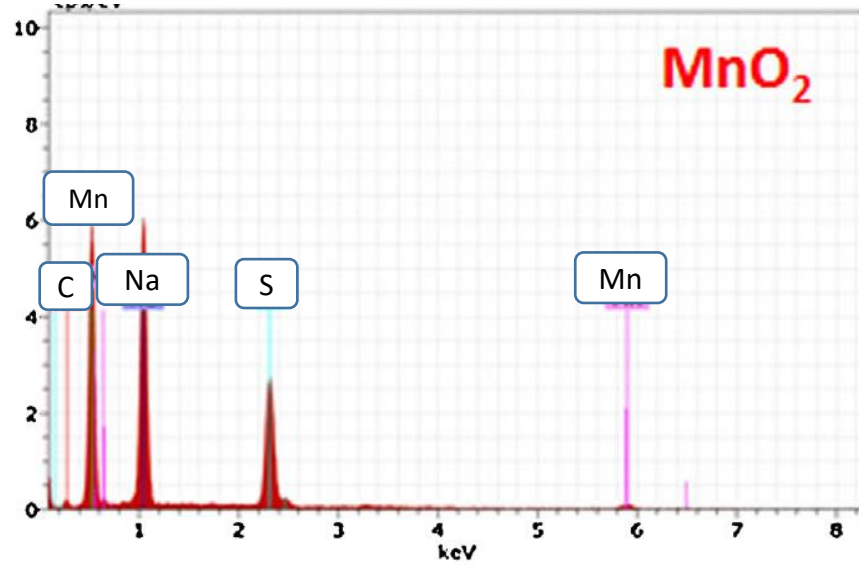
Cyclic voltammogram for the synthesis of rGO/MnO₂NHs/GC, rGO/GC and MnO₂/GC electrodes in 0.1 mol/LNa₂SO₄aqueous solution (Scan rate: 50 mVs⁻¹).

SEM & TEM

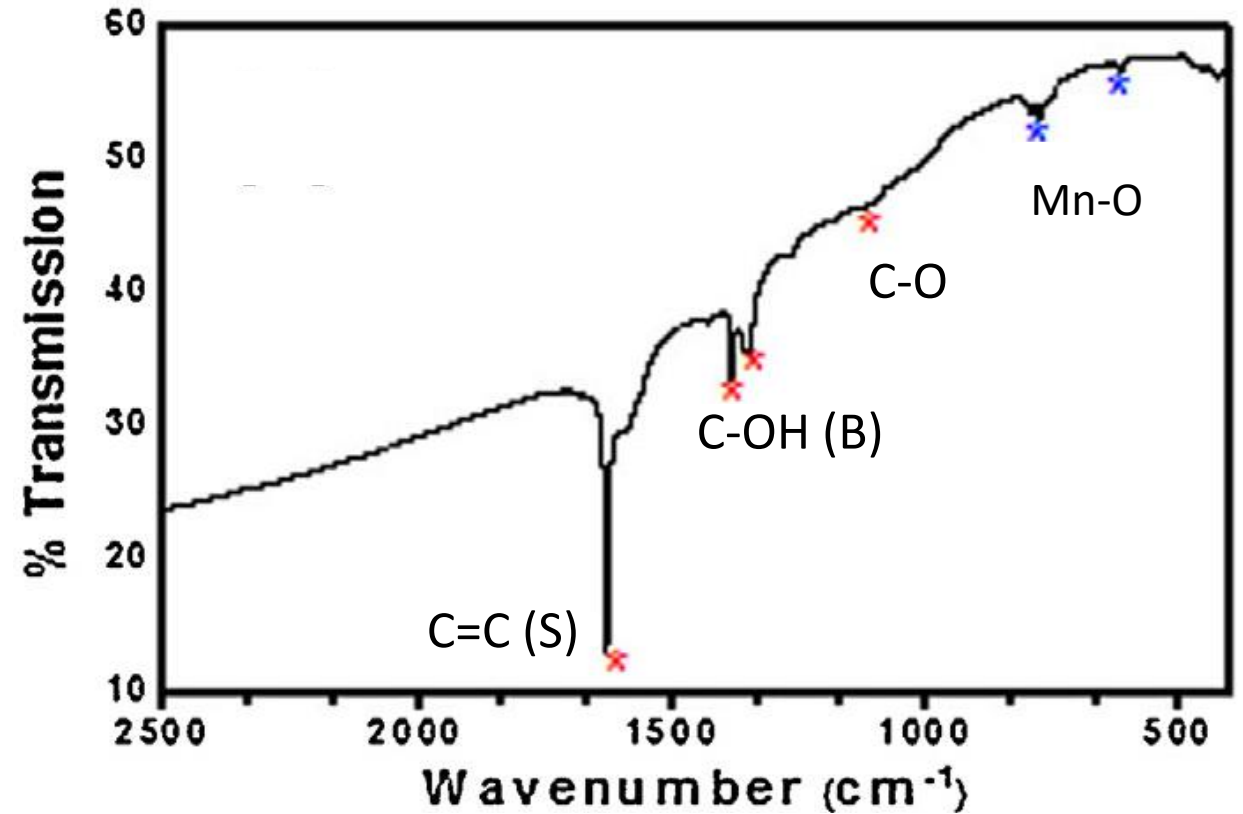


Microscopy analysis of rGO/GC, MnO₂/GC and NHs/GC electrodes: (a-c) SEM images and (d-e) TEM micrographs (c inset: at $\times 17,000$)

EDAX Spectra

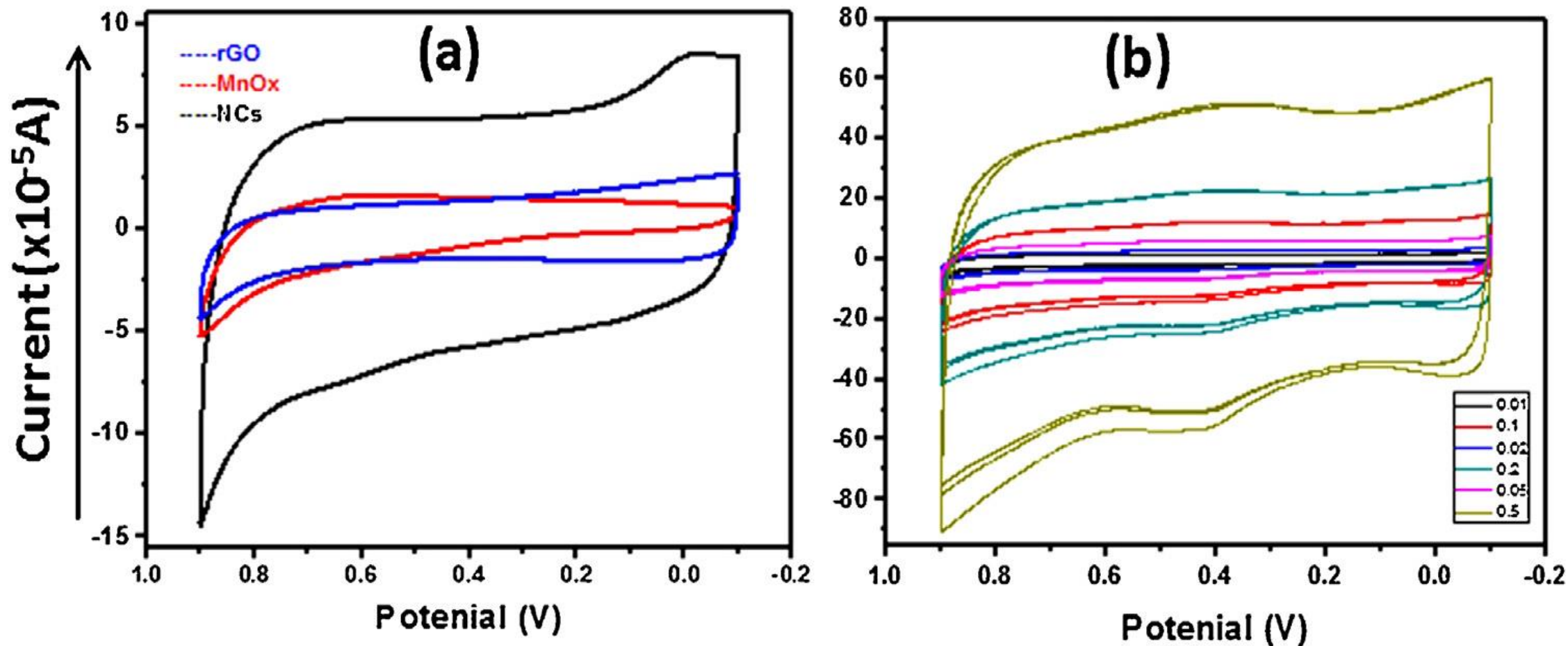


FTIR Spectra of NHs



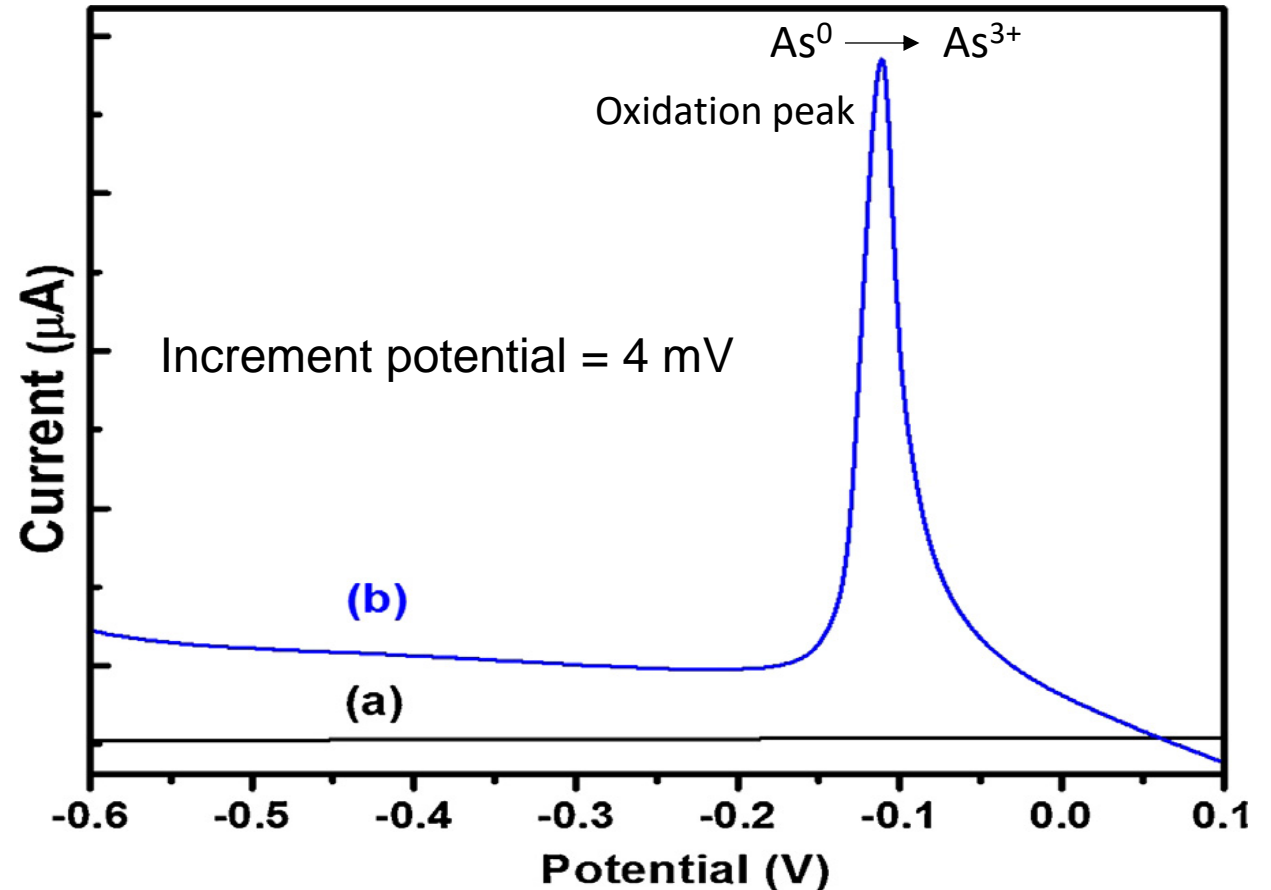
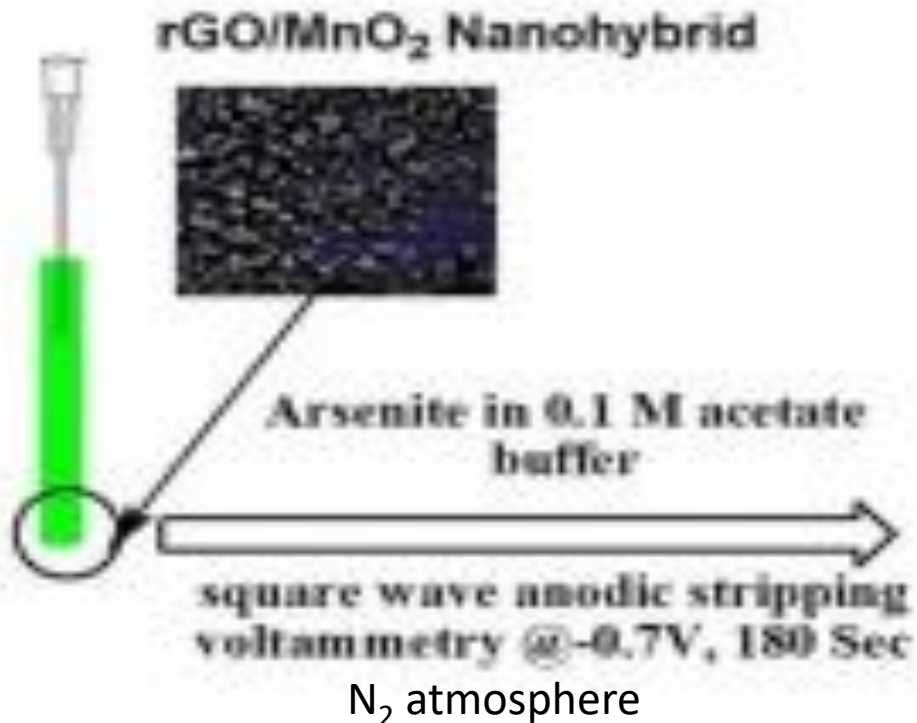
Cyclic voltammetry

- NHs electrodes exhibited a broader and larger current density.



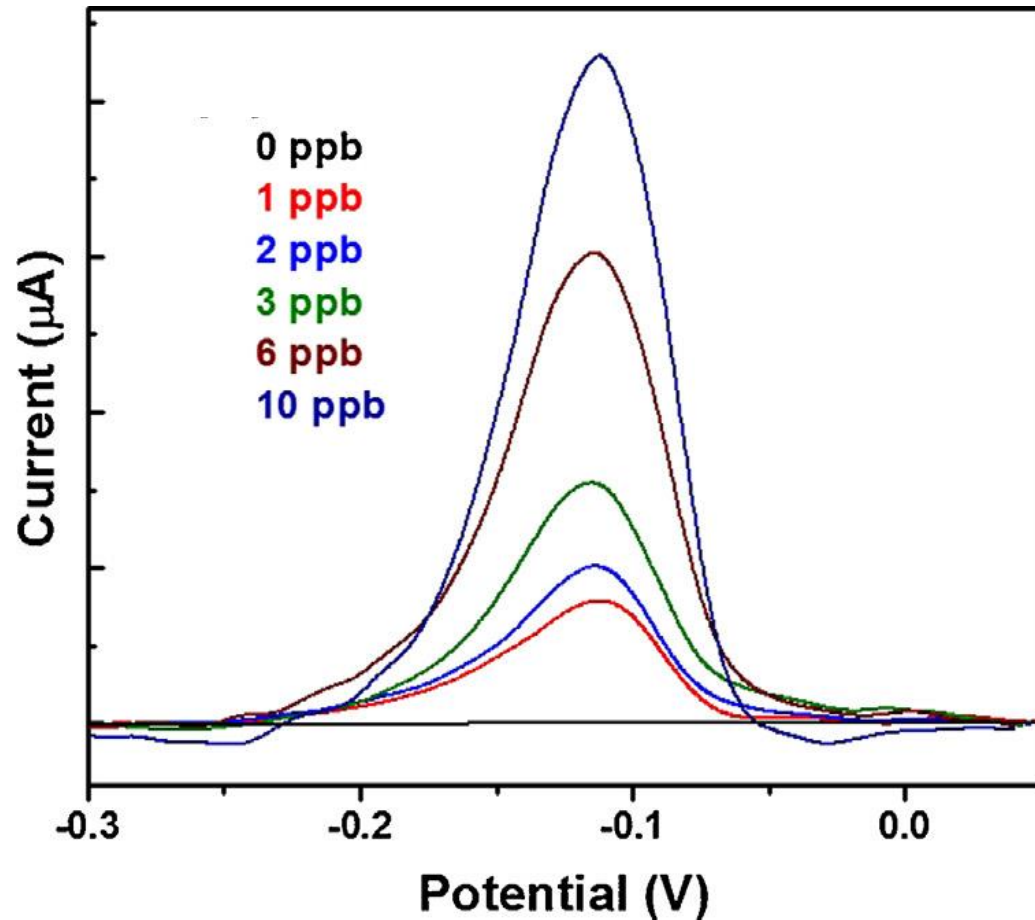
(a) Cyclic voltammogram of NHs/GC, MnO₂/GC and rGO/GC electrodes in 1 mol/L Na₂SO₄ electrolyte 50 mV/s scan rate
(b) effect of scan rate (10–500 mV/S) on NHs/GC electrodes (increased current density with increased scan rates)

Electrochemical analysis of rGO/MnO₂NHs/GCE towards arsenite



SWASV of NHs/GC electrode towards (a) 0 ppb and (b) 40 ppb arsenic in acetate buffer (pH = 5).

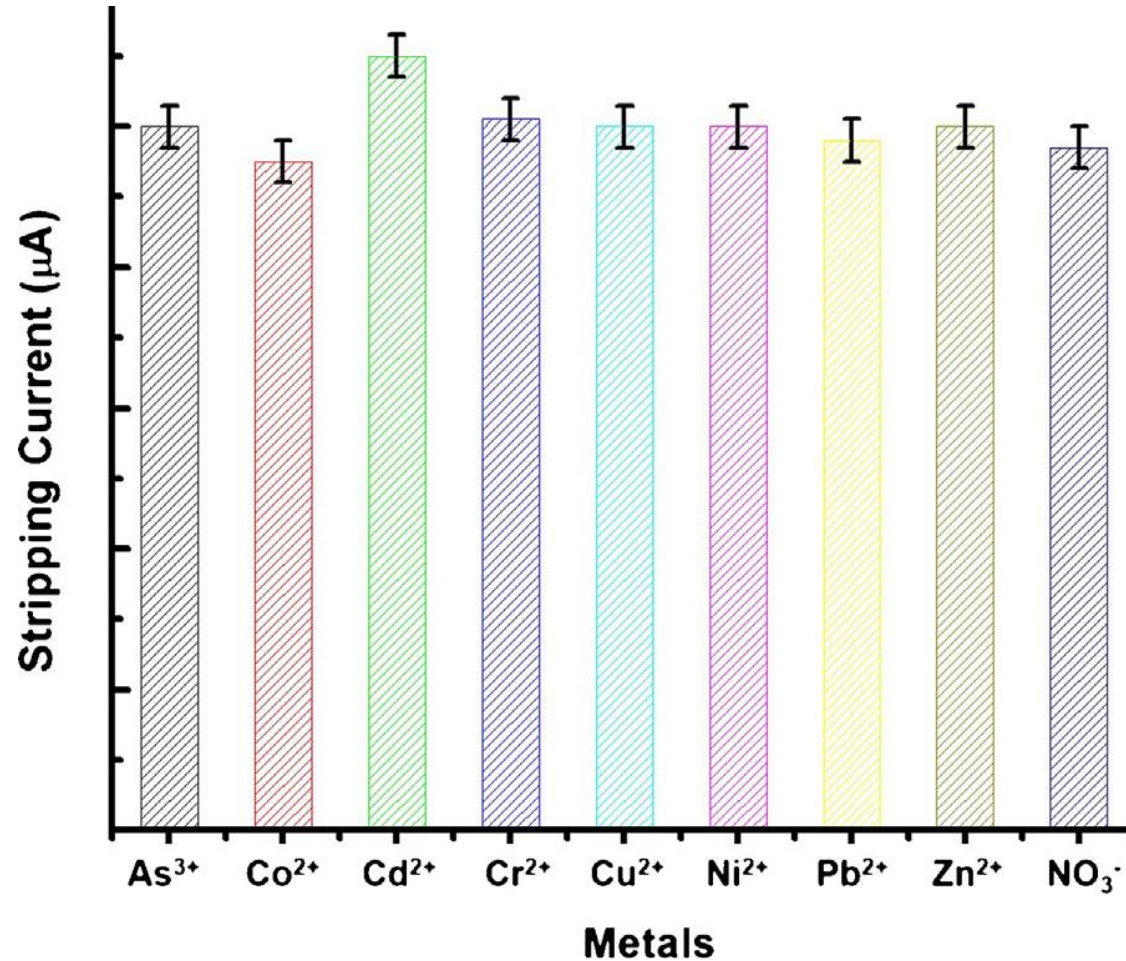
Anodic Stripping Voltammetry



- Theoretical detection limit: 0.05ppb

SWASV response of NHs/GC electrode towards As (III) in 1–10 ppb concentration range

Interference study



Effect of interfering cations and anions on arsenite (40 ppb) stripping peak current.

- Cd: slight increase in peak current
- Can be removed by chelating agents like EDTA before water analysis.

Conclusion

- Noble metal free electrode for arsenite detection in water.
- The reported material exhibits sensitivity of 0.176 $\mu\text{A/ppb}$ and LOD of 0.05 ppb.
- High selectivity towards arsenite and insulation towards common interferants commonly present in water at 10 fold concentrations.
- Cost effective material for arsenite determination in water.

Future directions

- Fabrication of such highly selective and cost effective electrodes for arsenite sensing

Thank You!!