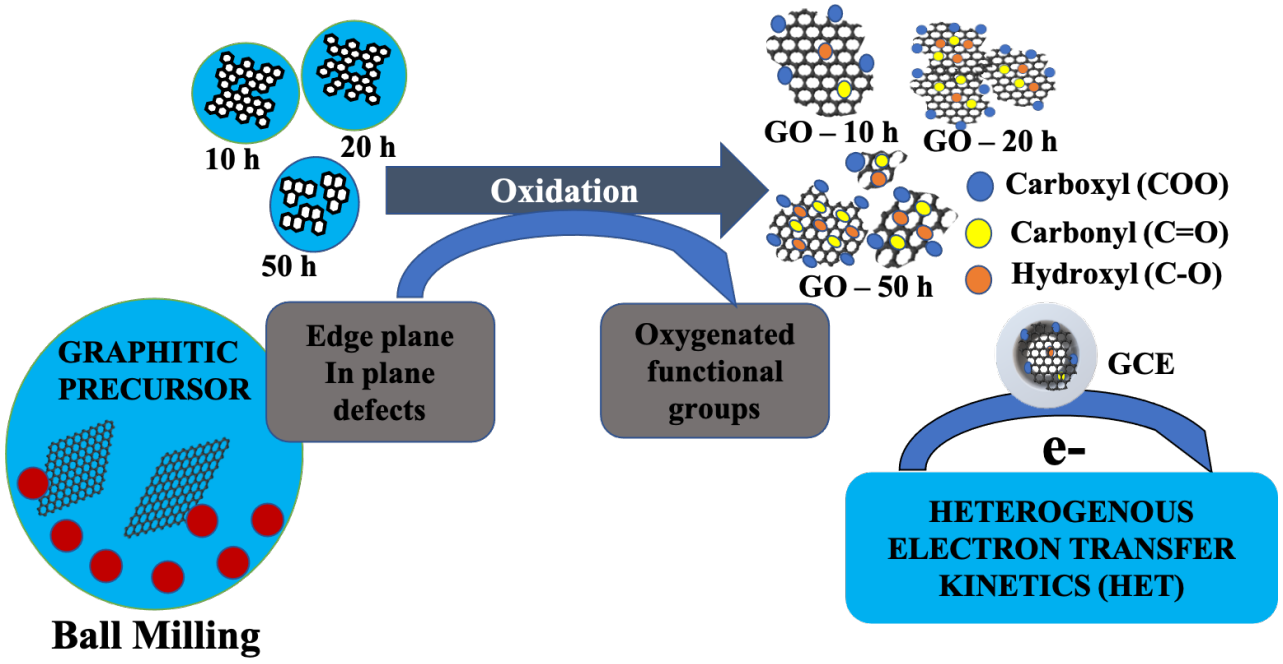
International Winter School 2021: Frontiers in Material Science

Surface engineered graphene oxide to enhance heterogeneous electron transfer kinetics



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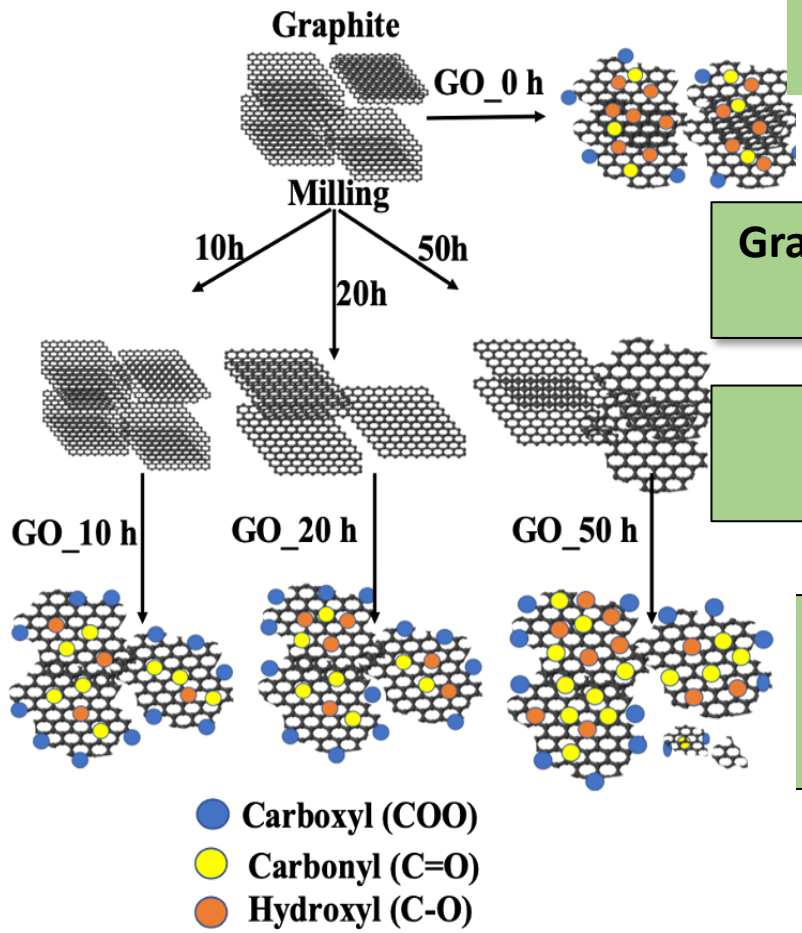
Introduction:

- **Electrochemical sensor:** The sensing ability of an electrode material depends on the heterogenous electron transfer (HET) kinetics and surface interaction with the analyte.
- Mechanical milling of graphitic sheets at different time intervals leads to the creation of edge plane defect, vacancies and interplane sp^3 bonds.
- Upon chemical oxidation, these defect sites are the preferred ones for the anchoring of the oxygen-containing functional groups such as carboxyl, carbonyl and hydroxyl groups .
- The edge/basal plane sites with oxygenated functional groups on graphene oxide (GO) act as heterogenous catalytic sites for electrochemical reactions.

Experimental Section:



Graphite powder was ball milled for 10 h, 20 h and 50 h

Chemical Exfoliation – Tour's method

The produced GO samples are GO-0 h, GO-10 h, GO-20 h and GO-50 h .

- The as-produced GO samples showed a variation in aromatic to non-aromatic carbon content (sp^3/sp^2 ratio), functional group constitution and defects.
- The effect of these parameters on the electrochemical behaviour was investigated using the electrochemical redox probe potassium ferricyanide [$K_4Fe(CN)_6$] and also towards the enzyme less detection ability for hydrogen peroxide (H_2O_2).

Material Characterization:

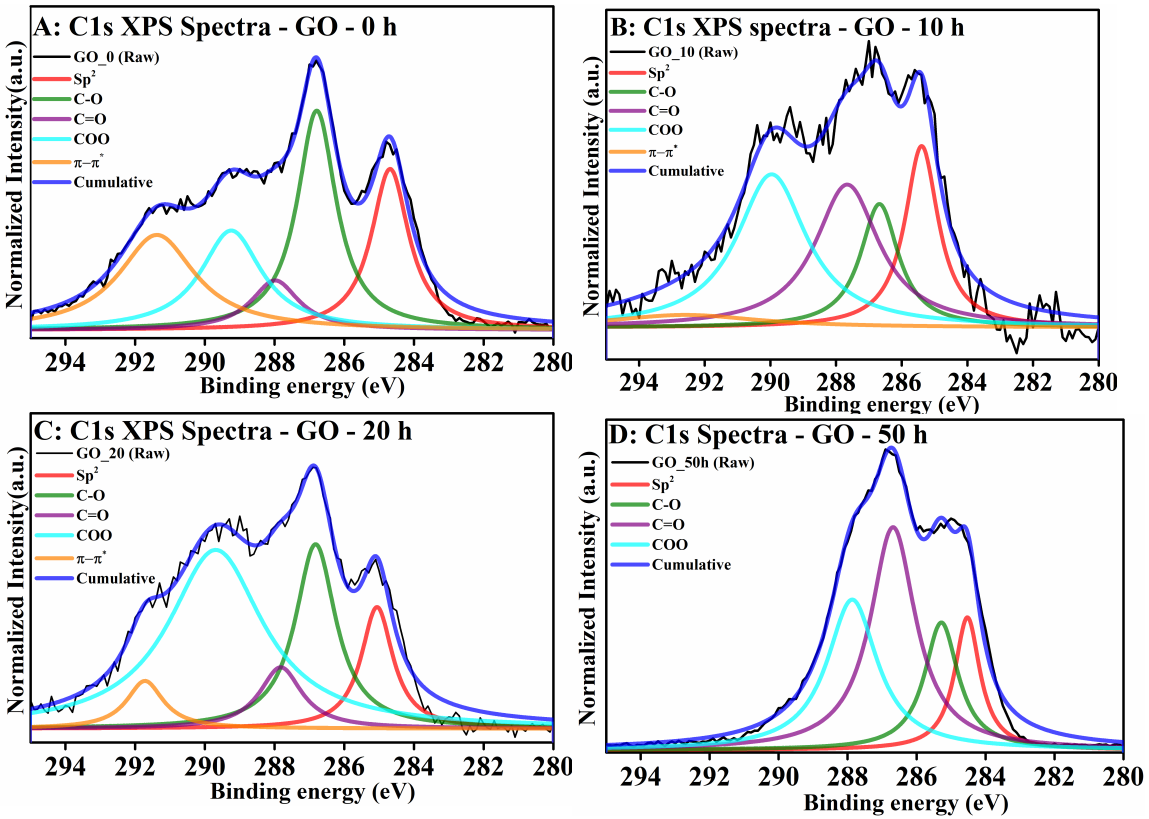


Fig. 1:
XPS spectra for GO series –
A: GO-0 h, B: GO-10 h, C: GO-20 h, D: GO-50 h.

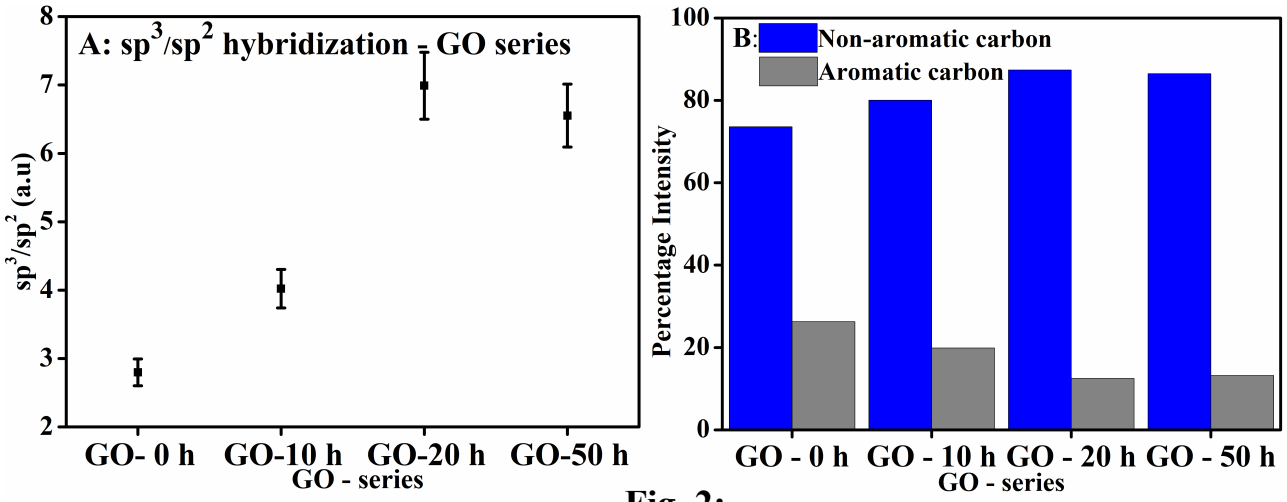


Fig. 2:
(A) Variation in the sp^3/sp^2 hybridization among the GO series;
(B) Representing relative intensities of aromatic and non-aromatic carbon content through the GO series

Discussion:

- **Fig.1:** An increase in the percentage of oxygen- containing functional groups along the GO series (increasing milling time) indicates different degree of oxidation.
- **Fig.2A:** The sp^3/sp^2 ratio was found to increase linearly along the GO series indicating an increase in the sp^3 hybridized carbon domains which agrees with the effect of graphitic precursor milling duration.
- **Fig.2B:** The linear increase in the non-aromatic carbon content indicating the accumulation of more oxygen functional groups.

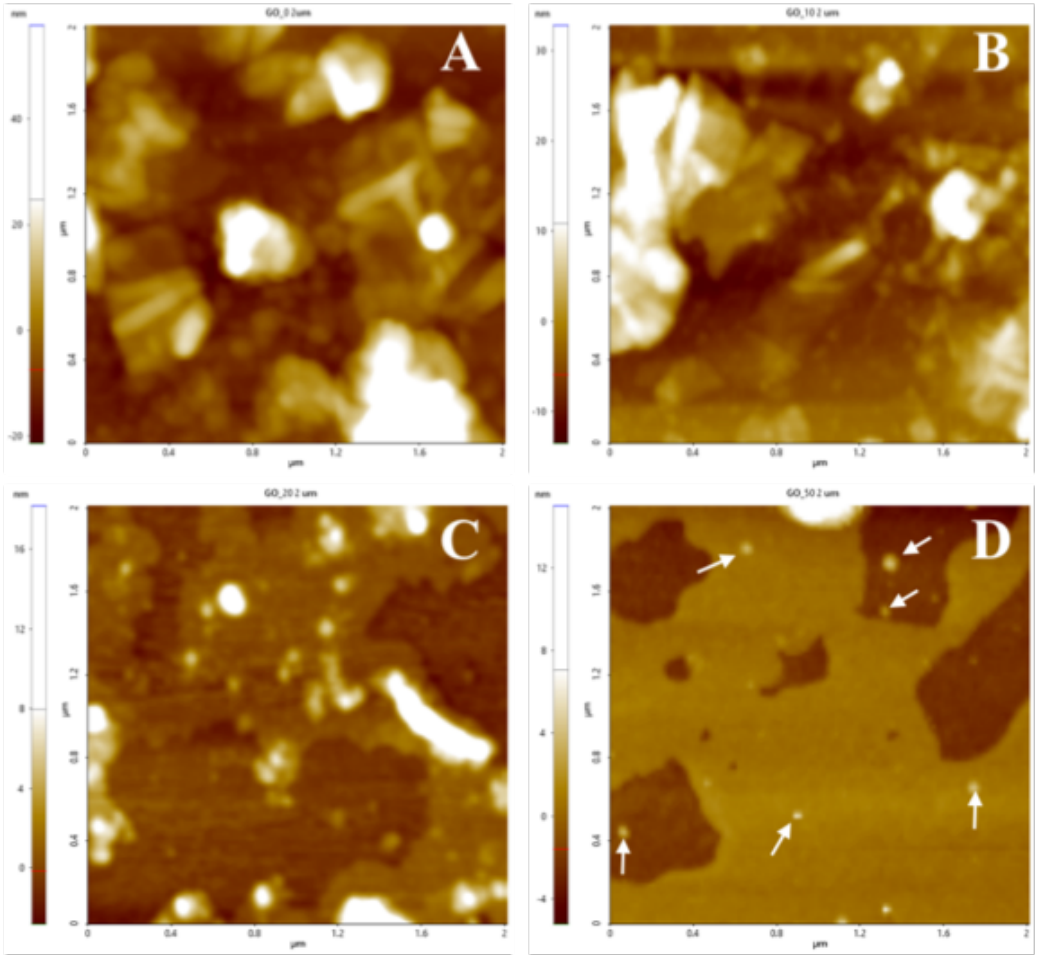


Fig. 3:
AFM images of GO series
A: GO-0h, B: GO-10h, C: GO-20h & D: GO-50h.

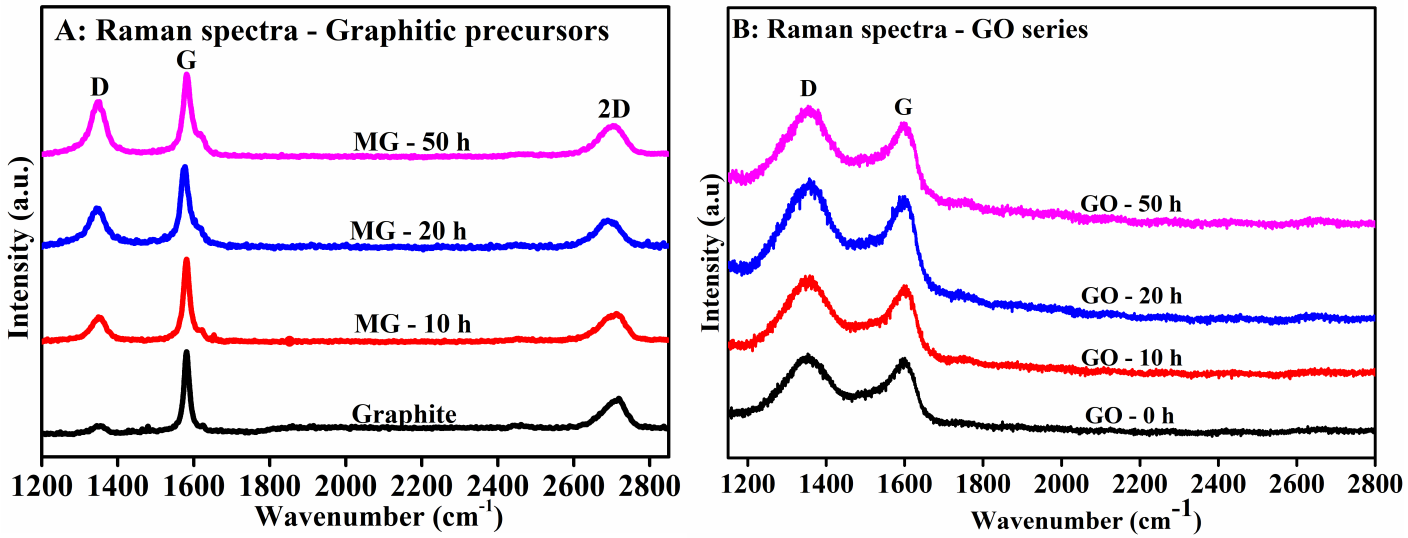


Fig. 4: Raman spectra
(A) milled graphitic precursors at different time interval
(B) Graphene oxide produced from milled graphitic precursors.

GO series	I_D/I_G	Oxidation degree	sp^3/sp^2 ratio	Average thickness of GO sheets (nm)
GO-0 h	1.04	64.7	0.20	28.6
GO-10 h	1.08	80	0.28	26.1
GO-20 h	1.09	87.7	0.49	2.1
GO-50 h	1.1	86.8	0.46	3.1

Table 1: Structural variation parameters through GO series.

Electrochemical Characterization:

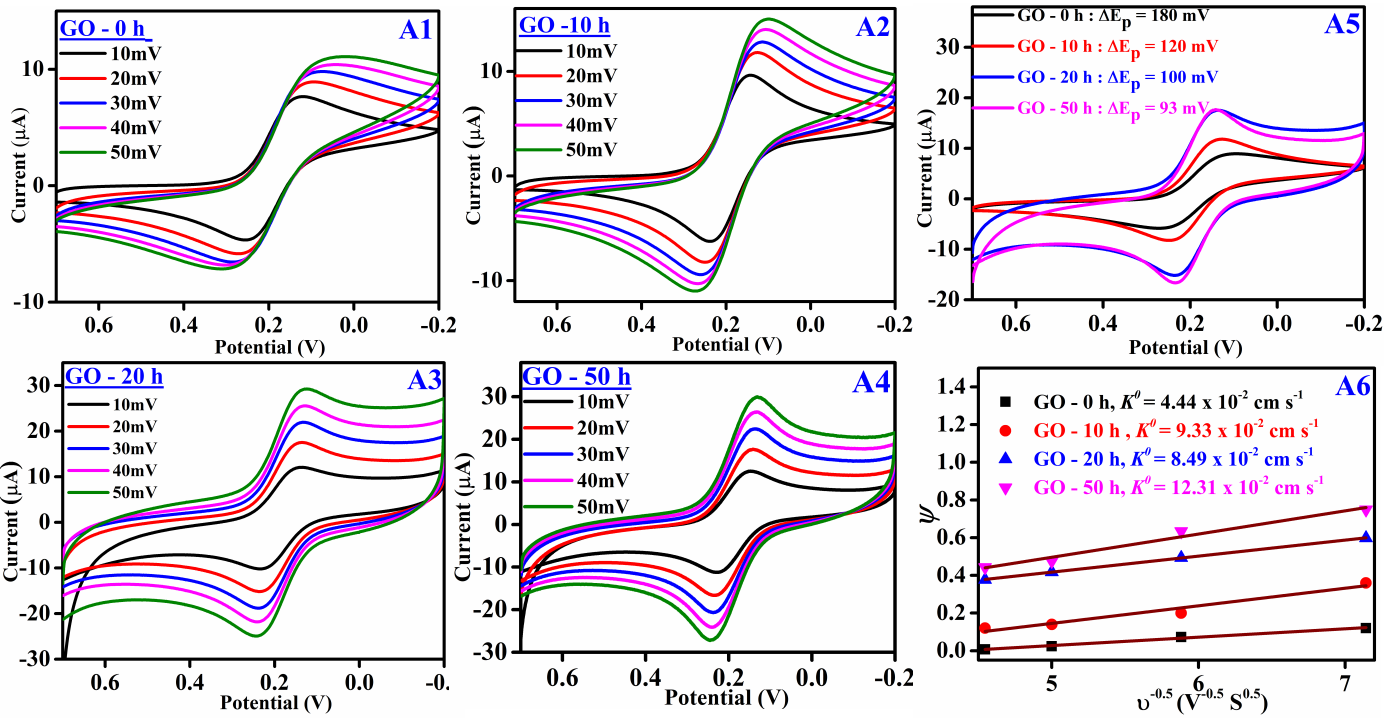


Fig. 5:Cyclic voltammogram of GO series for the redox probe $K_3Fe(CN)_6$ and plot of HET constants - k^0.

GO Series	ΔE_p (mV)	A_{eff} (cm^2) $\times 10^{-4}$	k^0 ($cm\ s^{-1}$) $\times 10^{-2}$	Ip (slope)
GO-0 h	180	0.188	4.44	0.86
GO-10 h	120	0.276	9.33	1.32
GO-20 h	100	0.968	8.49	4.42
GO-50 h	93	0.986	12.31	4.50

Table 2: Electrochemical parameters derived from CV measurements.

Discussion:

- The nature of voltammogram for the GO samples (GO – 10 h, 20 h and 50 h) produced from milled graphite appears to be different compared GO-0 h.
- The peak separation potential (ΔE_P) and peak current (Ip) increases linearly with respect to the scan rate for GO – 0 h (A1) and GO – 10 h (A2), whereas for the samples GO – 20 h (A3) and GO – 50 h (A4), ΔE_P remains approximately constant with a linear increase in the peak currents.
- The ΔE_P values among the GO series were calculated from the Fig. A5, and is in the order GO-0 h > GO-10 h > GO-20 h > GO-50 h.
- The linear increase ΔE_P can be attributed to the enhanced edge plane defects, functionalities on the electrode surface in the GO – 20 h and 50 h samples facilitating faster HET. This inference is supported by calculating the HET rate constant - k_0 (Fig.A5) using Nicolson analysis.

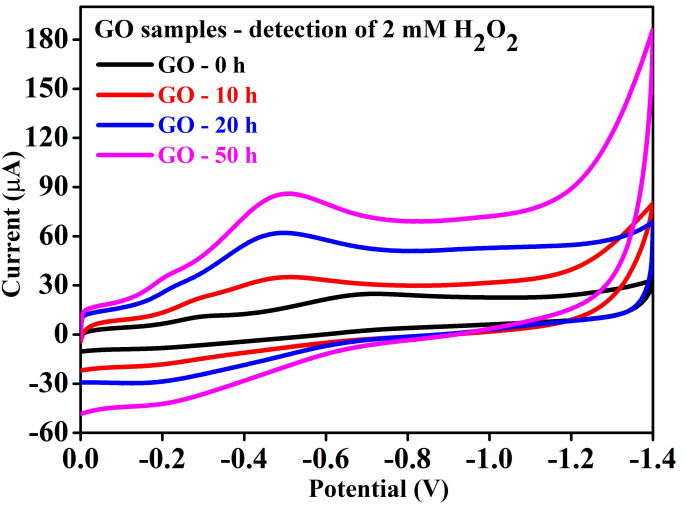


Fig.6: Cyclic Voltammograms for GO series in 2mM H_2O_2 at a scan rate of 40 mV/s.

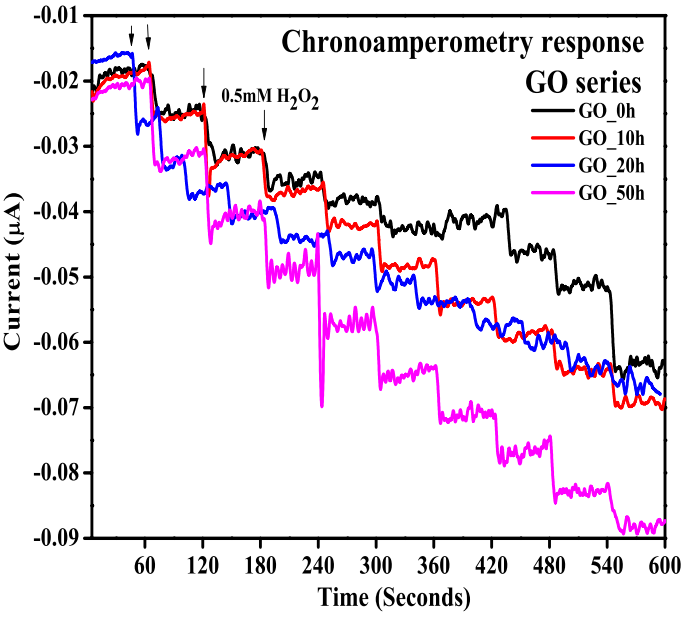


Fig.9: Chronoamperometry response for GO series at applied potentials of -0.6 V for GO-0h and -0.4 V for GO-10h, 20h and 50h.

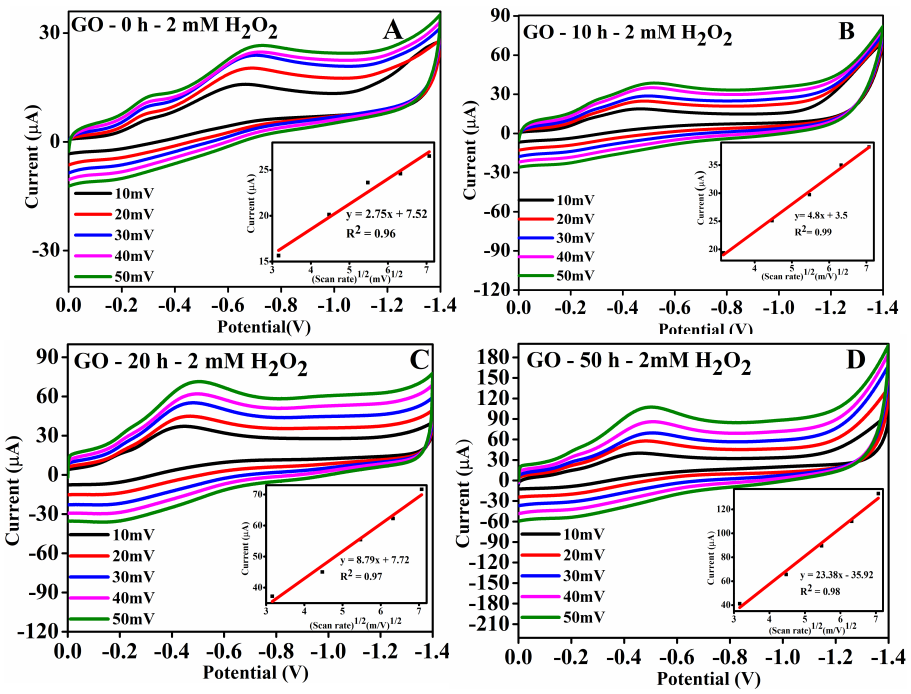


Fig.7: The cyclic voltammograms from GO series for 2 mM H_2O_2 at different scan rates.

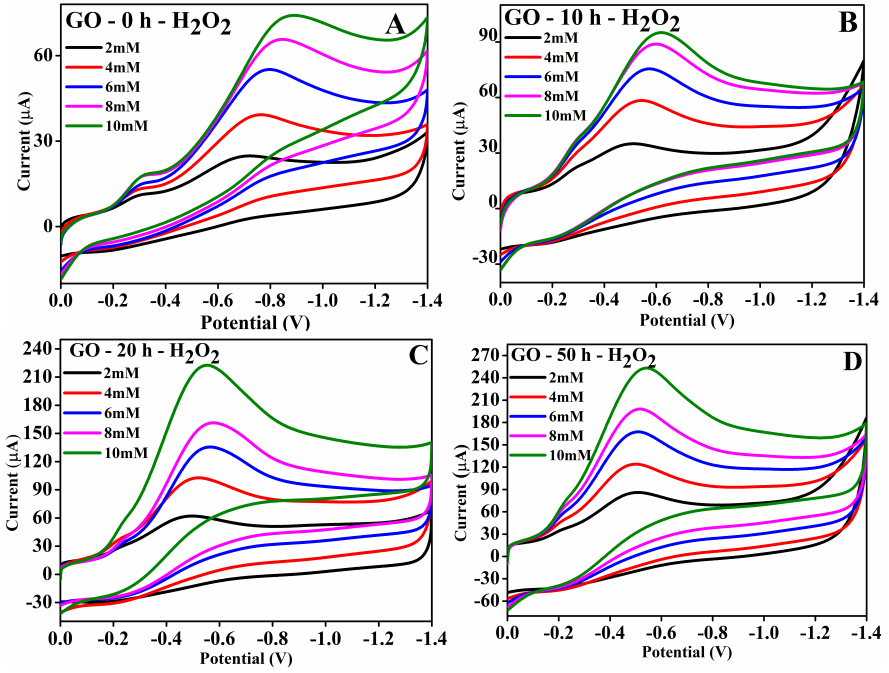


Fig.8: Cyclic Voltammograms of GO series with different concentrations of H_2O_2 at a fixed scan rate of 40 mV/s.

Electrode	Sensitivity (µA/µM)	Detection limit (µM)
GO_0 Hour	0.0062	376.83
GO_10 Hour	0.0075	278.96
GO_20 Hour	0.018	152.30
GO_50 Hour	0.02	133.93

Table 3: Detection limit and linear sensitivities

The presence of varied oxygen functionalities among the GO series due to different degree of oxidation can contribute to the greater interaction of H_2O_2 on GO sheets. This facilitates a faster electron transfer that can reduce the working potential for the reduction of H_2O_2. In addition, the edge plane carboxyl functional groups lead to an early onset of reduction potential.

Conclusion:

- The graphene oxide produced from milled graphite flakes showed a better HET rate constant k_0, electrochemical active surface area, enhanced sensitivity and detection limit in the detection of H_2O_2 as compared to the GO produced from un-milled graphite.
- Among the GO produced from milled graphite (GO - 10h, 20h and 50h), GO-50h exhibited better results with respect to k_0, peak separation potential ΔE_P, sensitivity and detection limits.
- An improvement in the reduction potential from -0.6 V (GO-0h) to -0.4 V (GO-10h, 20h, 50h) in the detection of H_2O_2 infers a betterment in the catalytic nature among the GO series.
- The milling of graphitic precursor increases the catalytic activity of the produced GO series, which opens a new dimension to understand the surface phenomenon and encourages future researchers to develop applications based on such materials that influence the heterogeneous electron transfer [HET] kinetics and the sensitivity required for a multitude of applications.

Publications:

1. **R. Ashwini**, Zinia Mohanta, M.K. Punith Kumar, Mysore Sridhar Santosh, Chandan Srivastava, "**Enhanced heterogeneous electron transfer kinetics in Graphene Oxide produced from mechanically milled Graphite**", *Carbon Trends* 5 (**2021**) 1000095.
2. **R. Ashwini,** V.G. Dileepkumar, K.R. Balaji, R. Viswanatha, C.R. Ravikumar, Chandan Srivastava, Mysore Sridhar Santosh, "**Ternary Alkali Metal Chalcogenide Engineered rGO as a New Class of Composite ($NaFeS_2$-rGO) and its Electrochemical Performance"** *Sensor International* 2 (**2021**) 100125.
3. **Ashwini Ravi**, M.K.P. Kumar, M.Y. Rekha, M.S. Santosh, C. Srivastava, **Graphene based Nanocomposites: Synthesis, Properties and Application as Electrochemical Sensors**, *Comprehensive analytical chemistry*, **(2020)** Volume 91.
4. **R. Ashwini**, M.K. Punith Kumar, M.Y. Rekha, M.S. Santosh, Chandan Srivastava, **Optimization of high entropy alloy nanoparticle – graphene (HEA-G) composite for the enhanced electrochemical sensitivity towards urea oxidation**, Materials Today Communications (under review).

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