

Supporting Information

Excimer Laser Patterned Holey Graphene Oxide Films for Non-Enzymatic Electrochemical Sensing

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I. Experimental methods:

1) Pulsed laser deposition and laser annealing

The substrate utilized for this study was As-doped n-type <111> Si with a resistivity of $\sim 0.005 \Omega\text{-cm}$, which was supplied by General Semiconductor (Hauppauge, NY). Before deposition, the sample was cleaned using acetone and then methanol in an ultrasonic bath for 5 minutes. These samples were later loaded into a steel chamber, and the chamber was brought to a pressure of 10^{-6} Torr. A KrF laser operating with a pulse width of 25 ns and a wavelength of 248 nm was used to irradiate the rotating glassy carbon target with a 10 Hz laser frequency. At an energy density of $3.5\text{--}4.0 \text{ J/cm}^2$, the plume generated by irradiating glassy carbon target was focused to synthesize amorphous carbon (a-C) coatings with a thickness of $\sim 20\text{--}200 \text{ nm}$ at 300 K on the Si substrate. The target to substrate distance fixed was kept at 4 cm. Subsequently, laser annealing of the a-C coatings was performed using an ArF laser ($\lambda = 193 \text{ nm}$, 20 ns) with single and multiple pulses at an energy density in the range of $0.4\text{--}1.2 \text{ J/cm}^2$ at ambient temperature and pressure. For multiple pulses, a frequency of 1 Hz was utilized. Most of the laser energy was absorbed within $\sim 40 \text{ nm}$ of a-C film. For laser annealing, a CaF_2 plano-convex confocal lens (focal distance = 50 cm) was employed to generate a $1.0 \pm 0.01 \text{ cm}^2$ spot size. Fig. 1 shows the schematic of a pulsed laser deposition system that was utilized to fabricate a-C thin films, followed by laser annealing for melting a-C to synthesize rGO by liquid phase regrowth of molten carbon.

2) Electrochemical measurements

The electrochemical reduction was studied on rGO films, which were synthesized by irradiating a-C films at varying energy density ($0.4 - 1.0 \text{ Jcm}^{-2}$) with 1 laser shot and varying laser shots (1-15) at a 0.6 Jcm^{-2} energy density [5]. Before analyte sensing, concerned electrodes were pretreated with supporting electrolytes and scanned for stabilization until a steady-state current was registered

[14]. The electrochemical measurements were carried out on an electrochemical workstation (Metrohm DropSense SPELEC, Oviedo, Spain) in a typical three-electrode configuration, which includes the Pt wire as the auxiliary electrode, Ag/AgCl (3.0 M KCl) as the reference electrode, and laser deposited 2D rGO films at different spatial resolutions on a Si substrate with the area of $2\text{ cm} \times 0.4\text{ cm}$ as the working electrode; a $5\text{ mm} \times 4\text{ mm}$ portion was dipped in the electrolyte. An electrochemical cell set up with a working volume of $\sim 4\text{ mL}$ was used for the studies. The selectivity and sensitivity of the designed electrode material against the analyte hydrogen peroxide was evaluated by cyclic voltammetry (CV) from 0 to -0.5 V (vs. Ag/AgCl) for various concentrations of hydrogen peroxide ($0.0125 - 3.2\text{ M}$) in 0.5 M pH 7.2 dibasic and monobasic phosphate buffer (PBS) with 0.1 M KCl at a scan rate of 30 mV s^{-1} . The peak current values, I_p , at onset potential were plotted with respect to absolute concentrations of H_2O_2 . The limit of detection and sensitivity of the electrodes were obtained from the calibration plots. The voltammetric responses were also recorded at a series of scan rates (2, 3, 5, 7, 10, 14, 18, 20, 30, 50, 75, 100, 120, 150, 200, 300 mVs^{-1}) to determine the values of diffusion coefficient 'D'.

3) Raman spectroscopy

A relative increase or decrease in defect concentration in graphene can be estimated by observing the trend of the intensity of the D to G peak ratio (I_d/I_g). For a fixed defect concentration, the I_D/I_G is highest for the visible wavelength (632 nm) excitation and lowest for UV wavelengths. Hence, a wavelength of 632 nm was selected for our study. An Evolution confocal micro-spectrometer (Horiba, Kyoto, Japan) was utilized to perform Raman spectroscopy measurements in a backscattering configuration with a HeCd source at a 632 nm wavelength for laser excitation in a dark room. A real time display (RTD) exposure time of 3 s, an extended scan exposure time of 25 s, and three accumulations were utilized for the measurements. The arrangement provided a spatial

resolution better than 1 μm and a spectral resolution $< 1\text{ cm}^{-1}$ to characterize the Raman-active vibrational modes in as-deposited and laser annealed samples. The Raman spectra calibrations were studied for accuracy using single-crystal silicon with a characteristic Raman peak at 520.6 cm^{-1} .

4) XRD, SEM, and TEM measurements

The XRD θ -2 θ scans were performed using a Rigaku Smart Lab X-ray diffractometer (The Woodlands, TX, USA) in Bragg-Brentano mode in reflection geometry operating mode using a Cu $K\alpha$ radiation. The film microstructure was assessed by using a Verios 460L scanning electron microscope (FEI, Hillsboro, OR), which was equipped with an electron backscattered diffraction (EBSD) attachment. The structure of laser annealed rGO films was directly probed by utilizing a Talos transmission electron microscopy (TEM) system (Thermo Scientific FEI, Hillsboro, Oregon) with the capability of acquiring selected-area electron diffraction (SAED) patterns.

5) Hall effect measurements

The electrical behavior of a-C and r-GO films was studied using a HMS-3000 Hall measurement system (Ecopia, Anyang, South Korea). These measurements were calibrated using standard ITO films. This measurement procedure allowed us to understand the carrier concentration, conductivity, and mobility of the rGO films at various laser annealing energy densities. The measurements were carried out by utilizing a current of 0.1 μA and a magnetic field of 0.55 T.

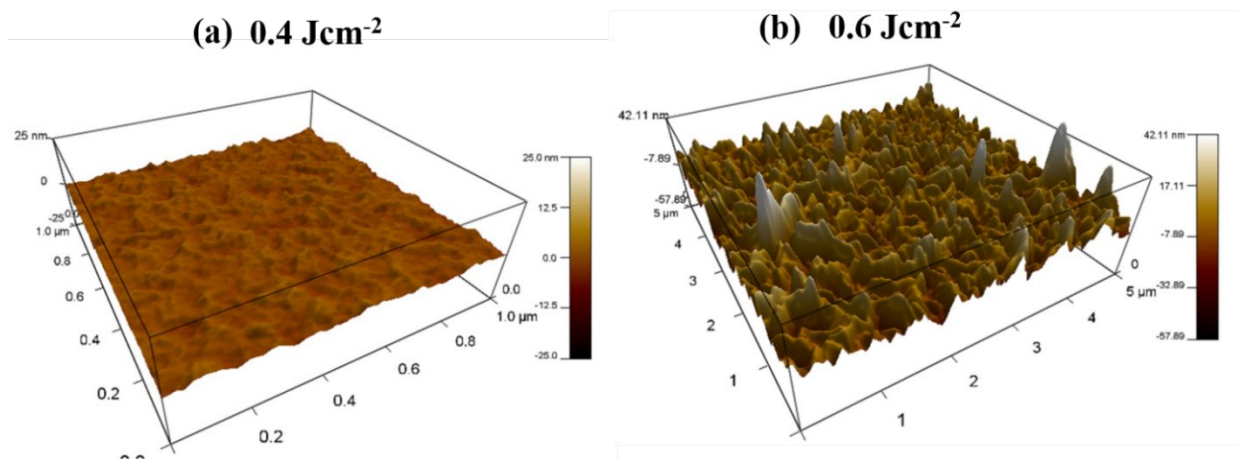


Figure S1: 3D AFM scan of LIRGO thin film synthesized at an energy density of (a) 0.4 Jcm^{-2} and (b) 0.6 Jcm^{-2} .

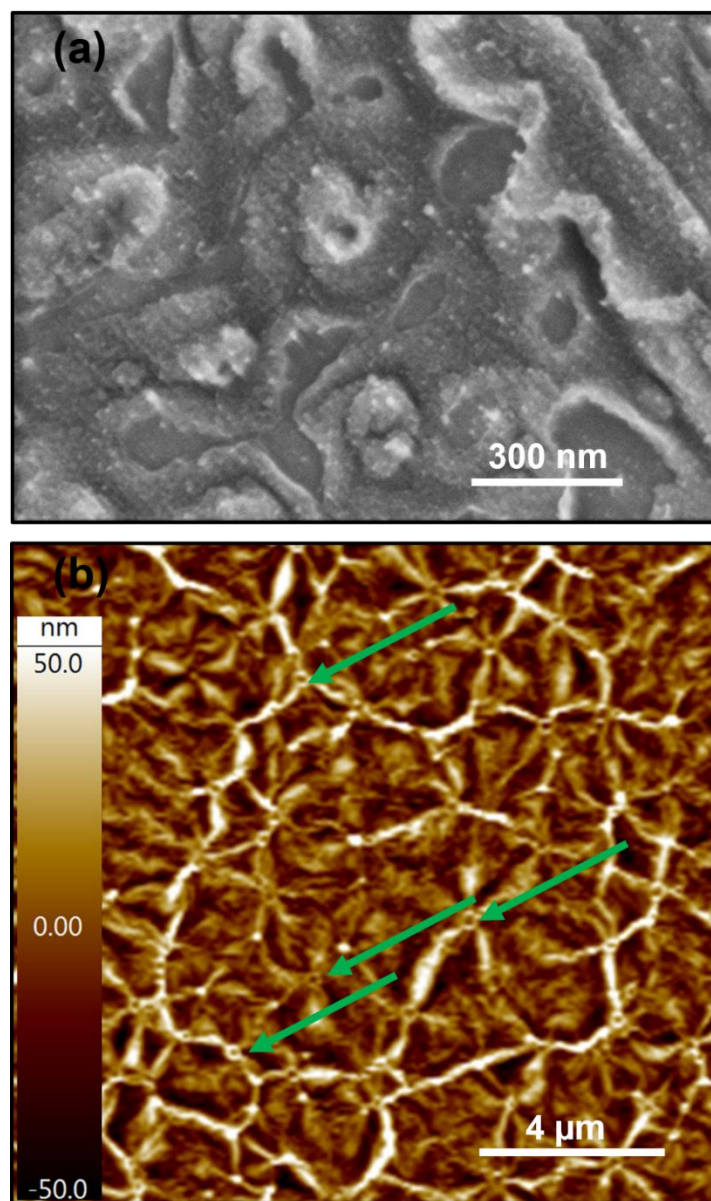


Figure S2: LIRGO thin film irradiated at an energy density of 0.6 Jcm^{-2} with 10 pulses: (a) HRSEM and (b) 2D AFM surface scan (green arrows highlight macropores).

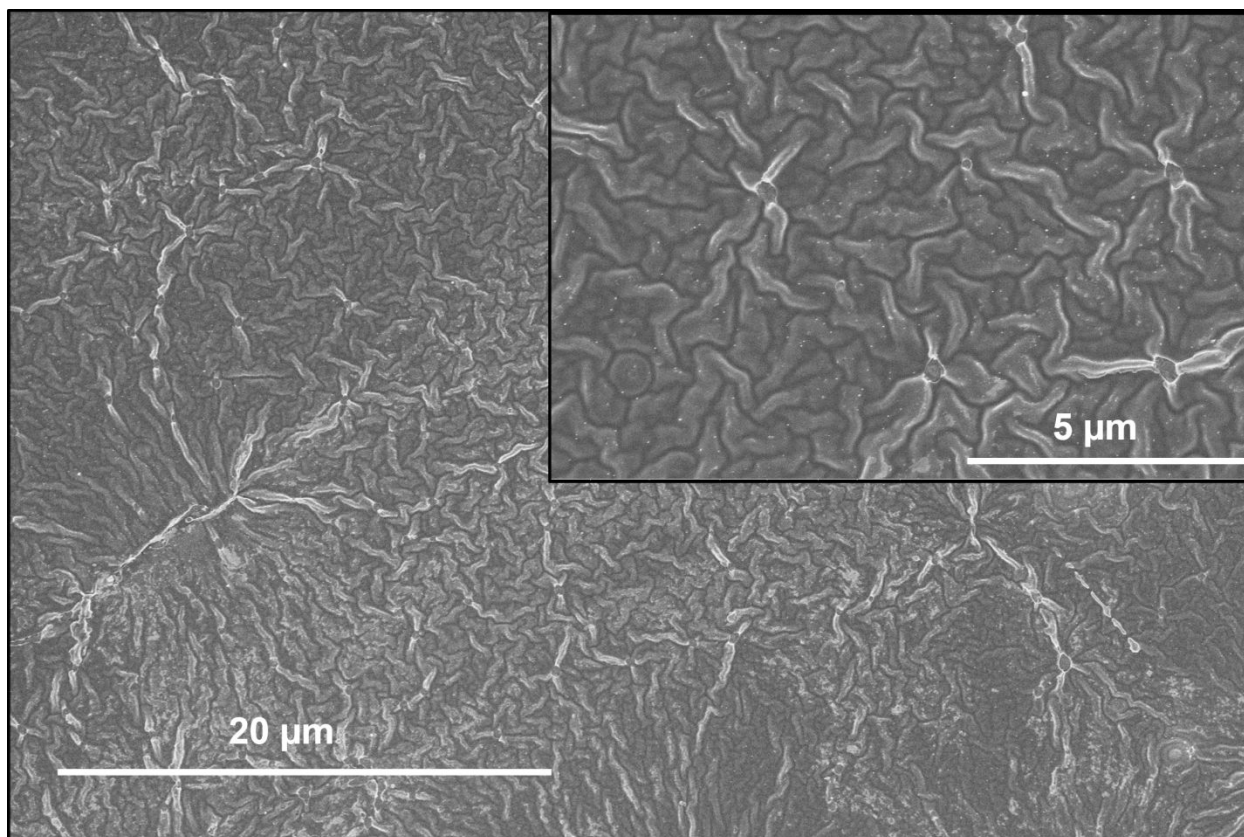


Figure S3: Low magnification SEM image of LIRGO thin film irradiated at an energy density of 1 Jcm^{-2} (inset shows high magnification image).

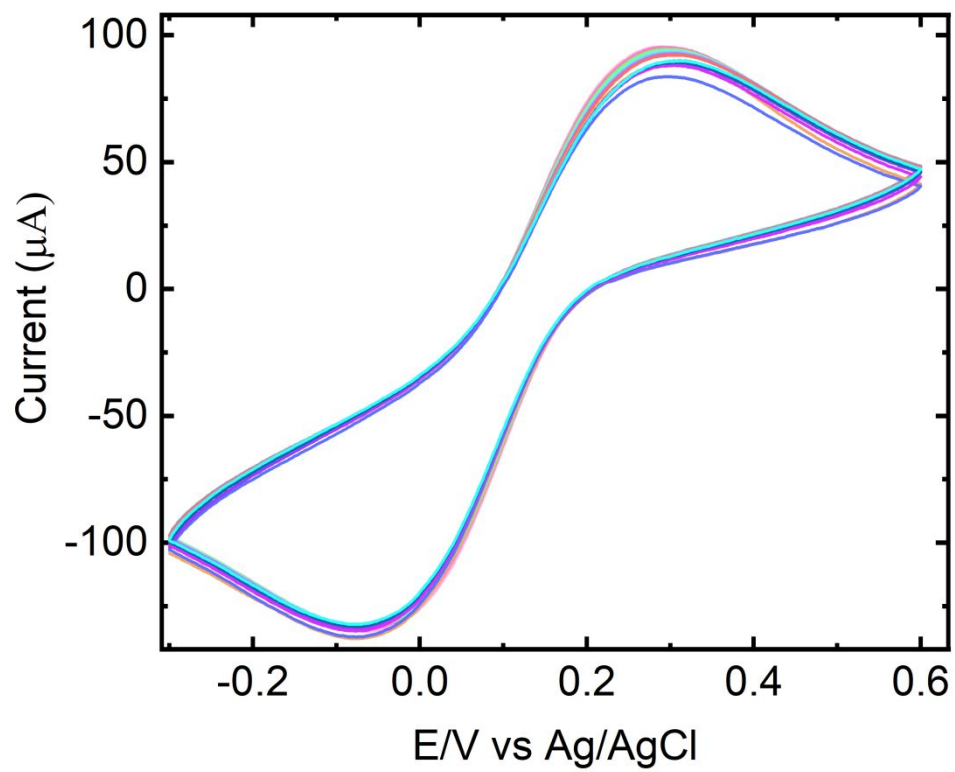


Figure S4. Cyclic voltammogram of 2D-rGO-film modified Si electrodes in a 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ solution with 0.1 M KCl with repeated scans at a constant scan rate of 0.03 V s^{-1} .

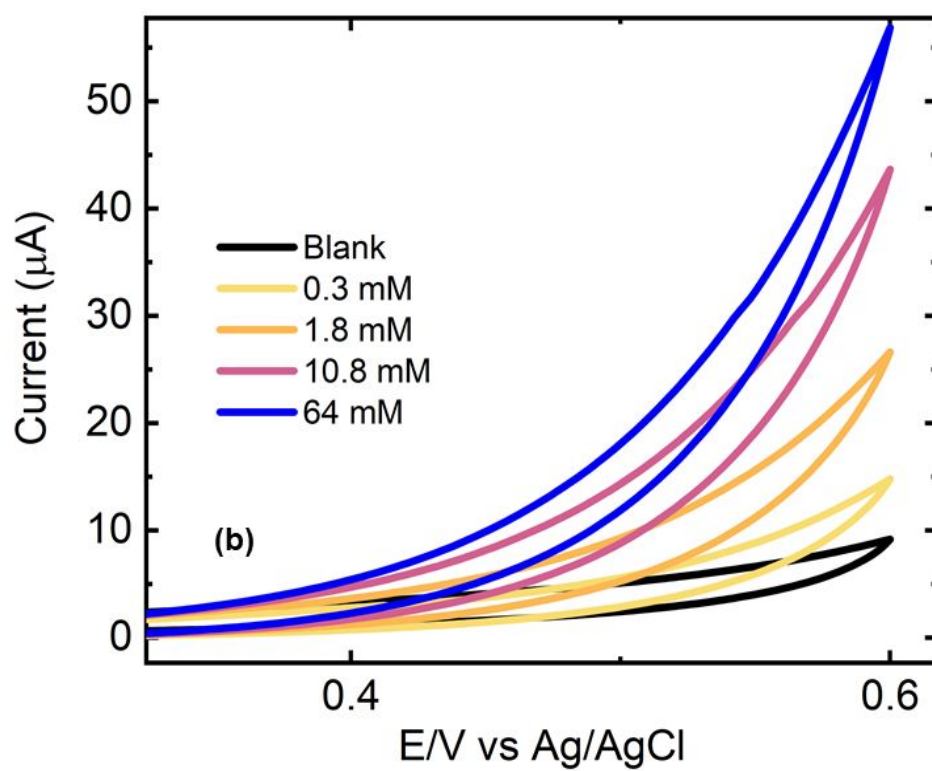
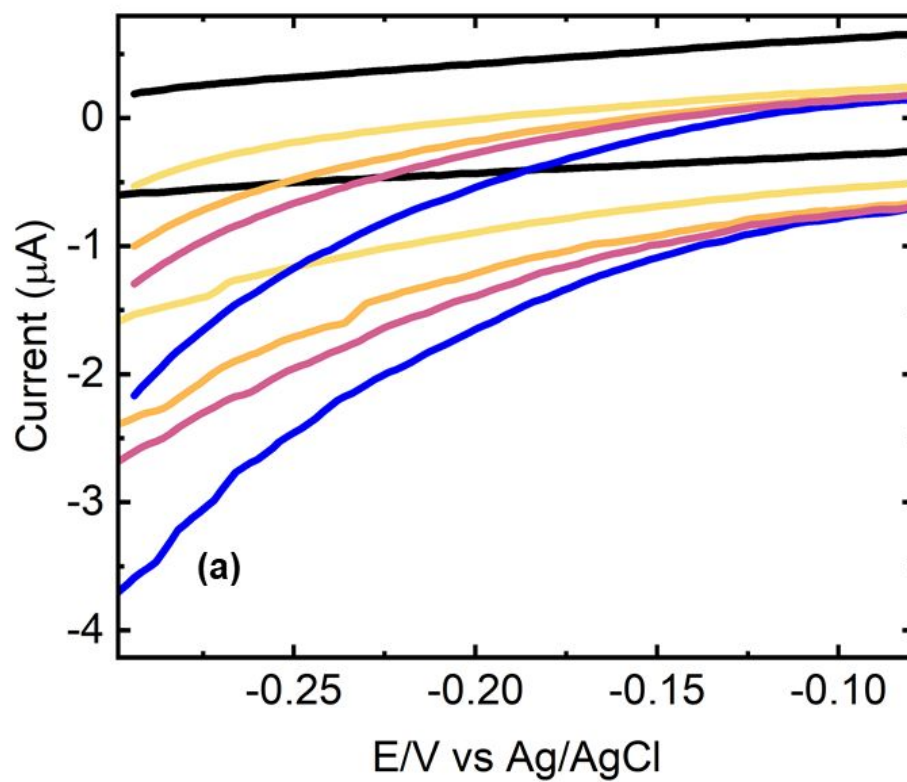


Figure S5. (a – b) CV curves for LIRGO electrode $E_{0.4}$.

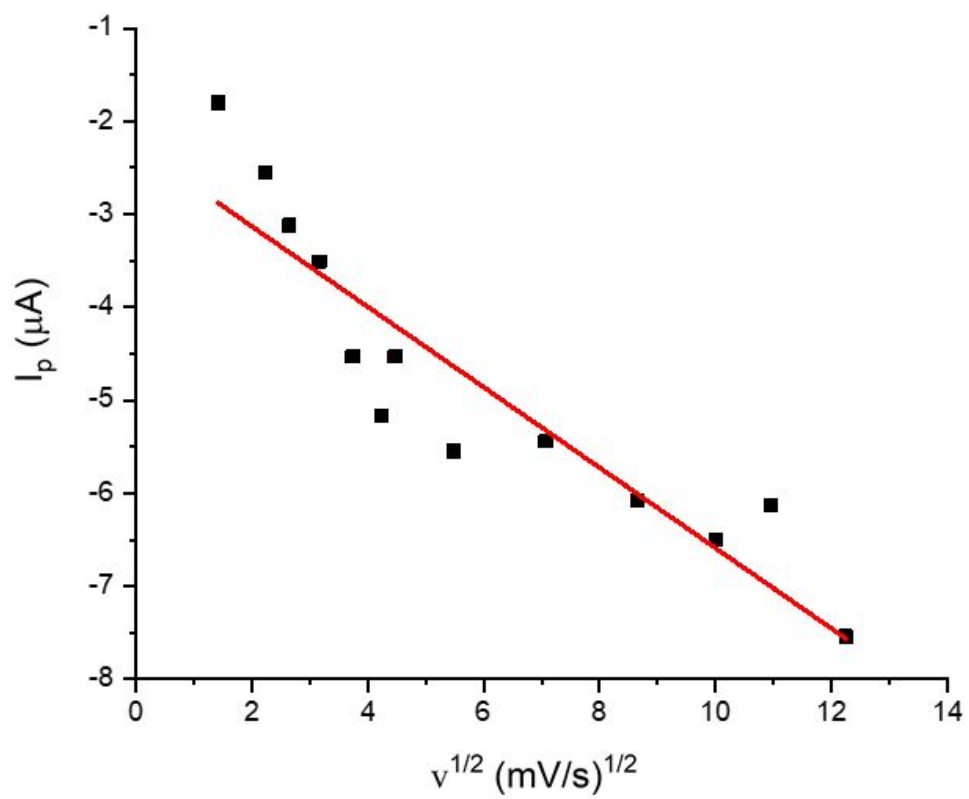


Figure S6. Plot of I_p vs scan rate for E_5 pulses electrode.

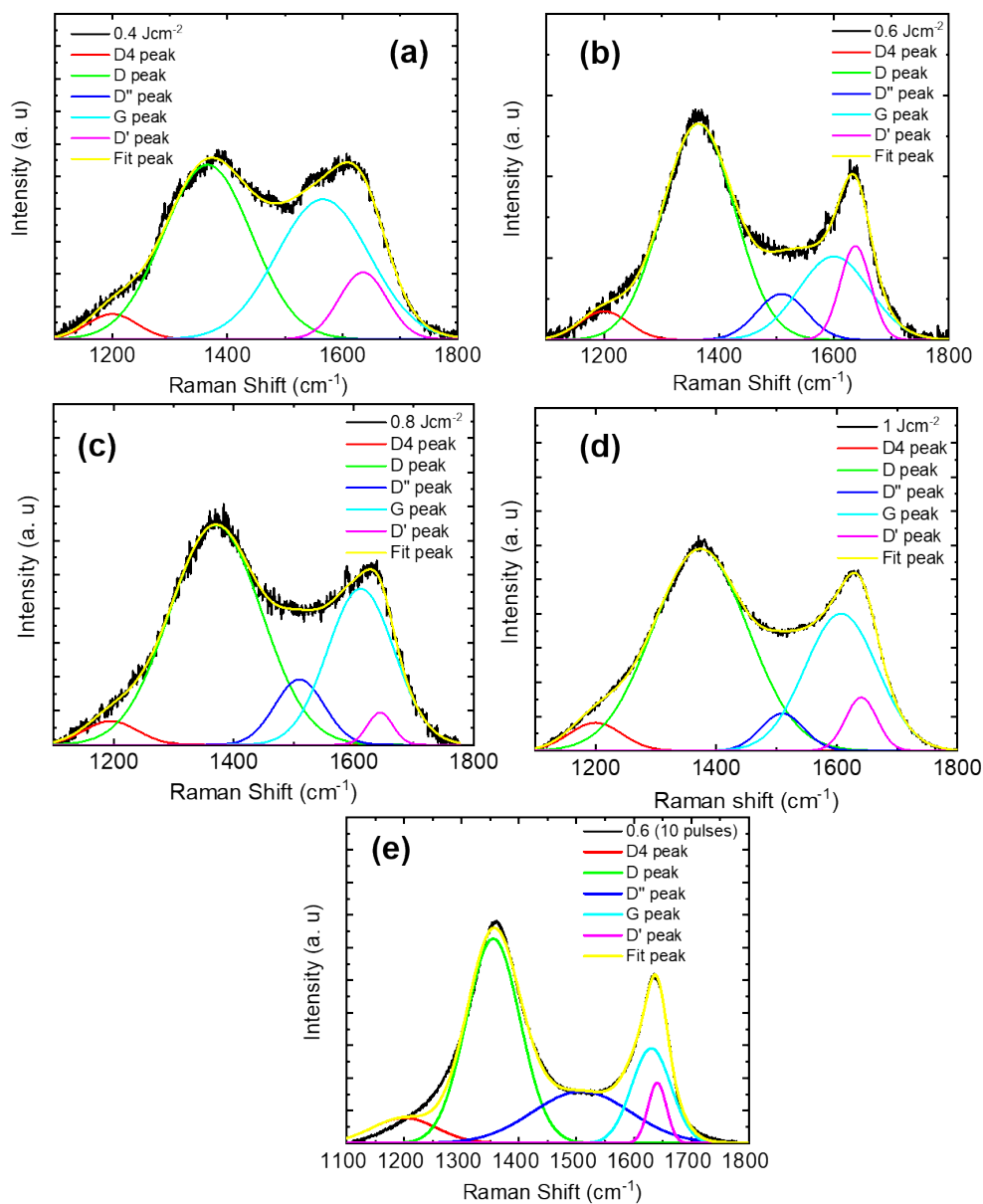


Figure S7. Peak fitting of Raman spectra obtained from rGO synthesized at various laser annealing conditions (a) 0.4 Jcm⁻², (b) 0.6 Jcm⁻², (c) 0.8 Jcm⁻², (d) 1 Jcm⁻², and (e) 0.6 Jcm⁻²-10 pulses.

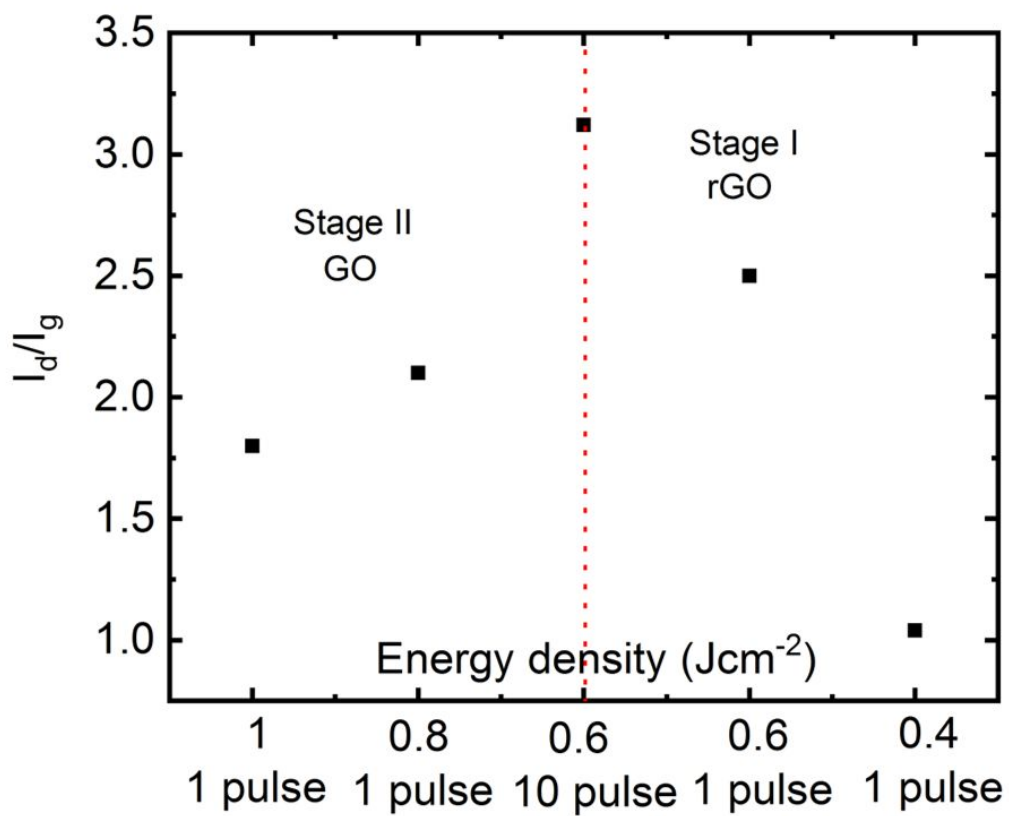


Figure S8: I_d/I_g ratio as function of laser energy density and pulses.

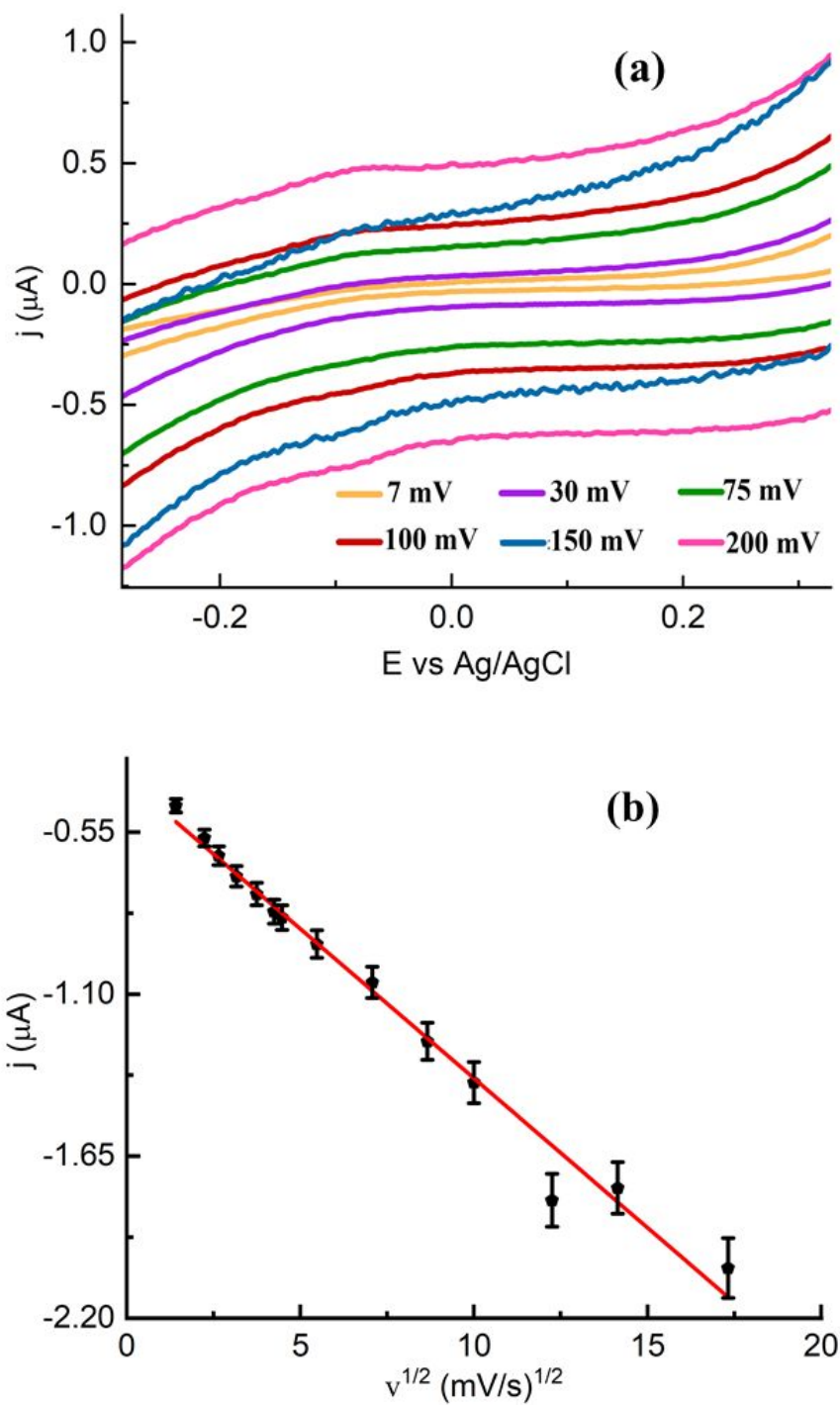


Figure S9. (a) Cyclic voltammograms $E_{10\text{ pulse}}$ rGO film in 0.5 M PBS with 0.1M KCl at various scan rates between 0.007 V s^{-1} and 0.2 V s^{-1} , (b) corresponding calibration plot of current density vs. square root of scan rates.

Calculation of effective ECSA

In order to further analyze the efficiency of electrodes, The electrical double layer capacitance (C_{dl}) approach^{55,56} has been applied to probe effective ECSA using the relation (8):

$$ECSA = C_{dl}/Cs \quad (8)$$

The process was performed as a) consecutive CV curves at different sweep speeds (7–200 mV s⁻¹) were recorded, b) An intermediate value of the applied potential range was selected (-0.06 V), c) the difference in current density under that potential was calculated ($\Delta j = j_1 - j_2$ or the sum of the absolute value of the current, d) the slope is obtained by linear fitting of the plot with different sweep speeds as X-axis and Δj as Yaxis (**Fig. S9**), The slope (-0.10292) is twice the value of C_{dl} (0.05146 mF), e) The larger value was obtained for $E_{10 \text{ pulse}}$ as compared to $E_{5 \text{ pulse}}$, $E_{1 \text{ pulse}}$, $E_{0.4}$, $E_{1.0}$ LIRGO films, i.e., the larger value represents the higher surface area and more exposed surface reactive sites. Further, the specific capacitance (Cs) was calculated using the relation (9):

$$Cs = A/2km\Delta V \quad (9)$$

Where A is the area under a particular I – V curve, k is scan rate, m is the active mass of film – mass dipped in electrolyte and ΔV is the potential window. For $E_{10 \text{ pulse}}$ electrode the Cs was calculated as 4.548 mFcm⁻². Further, the ECSA was obtained as 0.01133 cm².

Calculation of charge transfer kinetics

The defect density is parallelly related to electron transfer kinetics, hence quantifying the effect on electrochemical sensitivity. Electron transfer rate kinetics (k^0) can be directly calculated from the equation:

$$k^0 = 2.18(\alpha n F D / R T)^{1/2} e^{-[(\alpha^2 F / R T) n \Delta E_p]} \quad (10)$$

where α is the transfer coefficient, n the number of electrons involved in the reaction, F the Faraday constant, D the diffusion coefficient, R the gas constant, T the absolute temperature, and v the scan rate, ΔE_p is peak-to-peak potential separation. ΔE_p was obtained from the electrochemical performance of rGO films, using $[\text{Fe}(\text{CN})_6]^{3-/4-}$. This factor being sensitive to surface chemistry was narrow for $E_{10 \text{ pulse}}$ as compared to the bare electrode, $E_{5 \text{ pulse}}$, $E_{1 \text{ pulse}}$, $E_{0.4}$, $E_{1.0}$ LIRGO films.

From the Nicholson method of electron transfer rate calculation, it was assumed that the reduction and oxidation were symmetrical, so $\alpha \approx 0.5$, $n=1$ (one-electron processes) for reversible and quasi reversible reactions, as obtained in the case of $E_{10 \text{ pulse}}$. Putting the values of constants α , n , F , R , T , v , as 0.5, 1, 96500, 8.314, 273, 0.03 in SI units. And the variables D , ΔE_p for working electrodes $E_{10 \text{ pulse}}$, $E_{5 \text{ pulse}}$, $E_{1 \text{ pulse}}$, $E_{0.4}$ were taken as 1.71×10^{-4} , 1.01×10^{-5} , 0.15×10^{-5} , $0.01 \times 10^{-6} \text{ cm}^2/\text{s}$; 0.34 V, 0.21V, 0.11V, 0.05 V respectively. The value of k^0 were obtained as 0.117, 0.063, 0.033 and 0.0217 cm/s.