Supporting Information:

Sandwiched Graphene with Nitrogen, Sulphur co-doped CQDs: Efficient Metal Free Material for Energy Storage and Conversion Application

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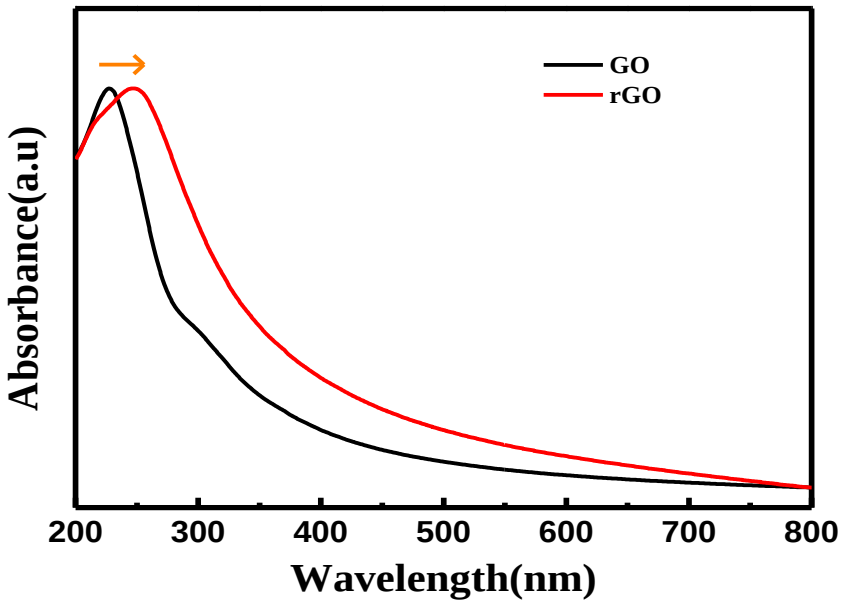


Figure S1. The UV-Visible spectrum of GO and rGO.

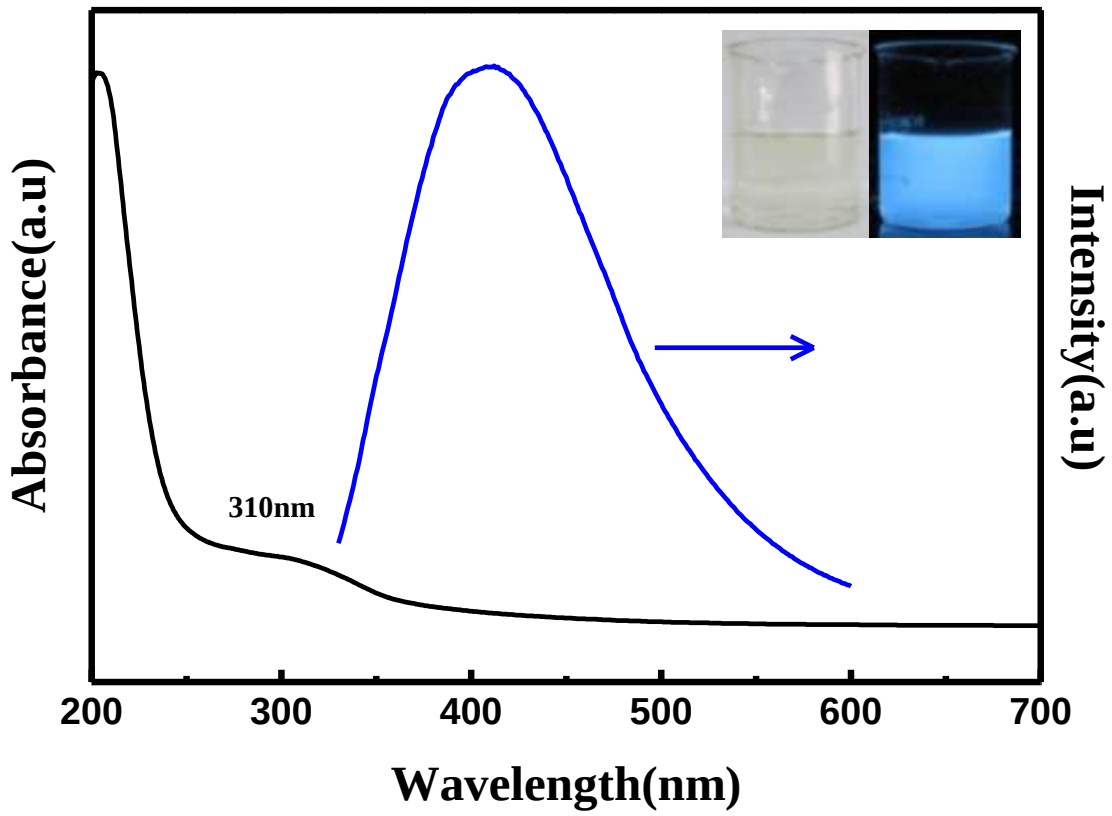


Figure S2. The UV-Visible and photoluminescence emission spectrum (at 340 nm excitation) of CQDs-HP. The inset is the optical photograph of the CQDs-HP in presence of room light and UV light (λ=365nm).

(a) Table 1

Sample (CQDs) Name	Reactant Ratio (Heparin:Protamine)
CQDs-HP	1:1
CQDs-HP (1:2)	1:2
CQDs-HP (2:1)	2:1

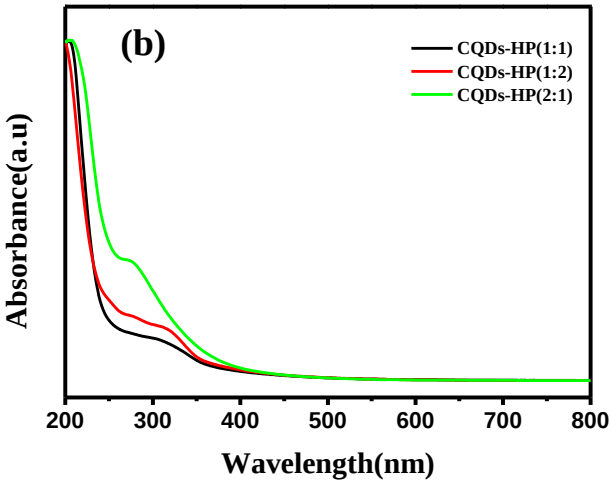
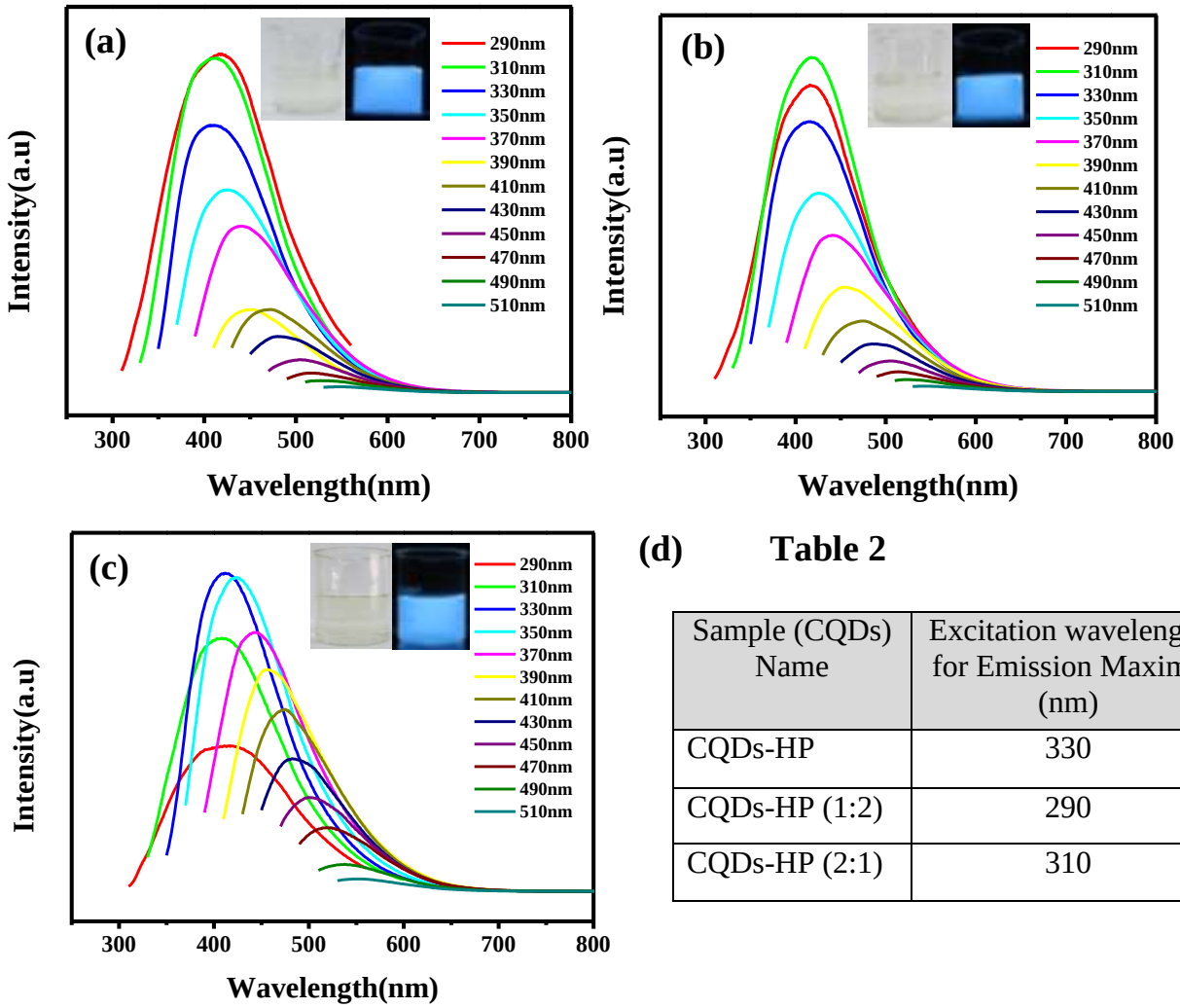


Figure S3. (a) Table 1 summarized CQD samples prepared at different ratio of reactants and (b) corresponding UV-Visible spectrum.



(d) Table 2

Sample (CQDs) Name	Excitation wavelength for Emission Maxima (nm)
CQDs-HP	330
CQDs-HP (1:2)	290
CQDs-HP (2:1)	310

Figure S4. Photoluminescence emission spectrum for (a) CQDs-HP (1:2), (b) CQDs-HP (2:1) and (c) CQDs-HP. (d) Table 2 summarizes the excitation wavelength for corresponding emission maxima.

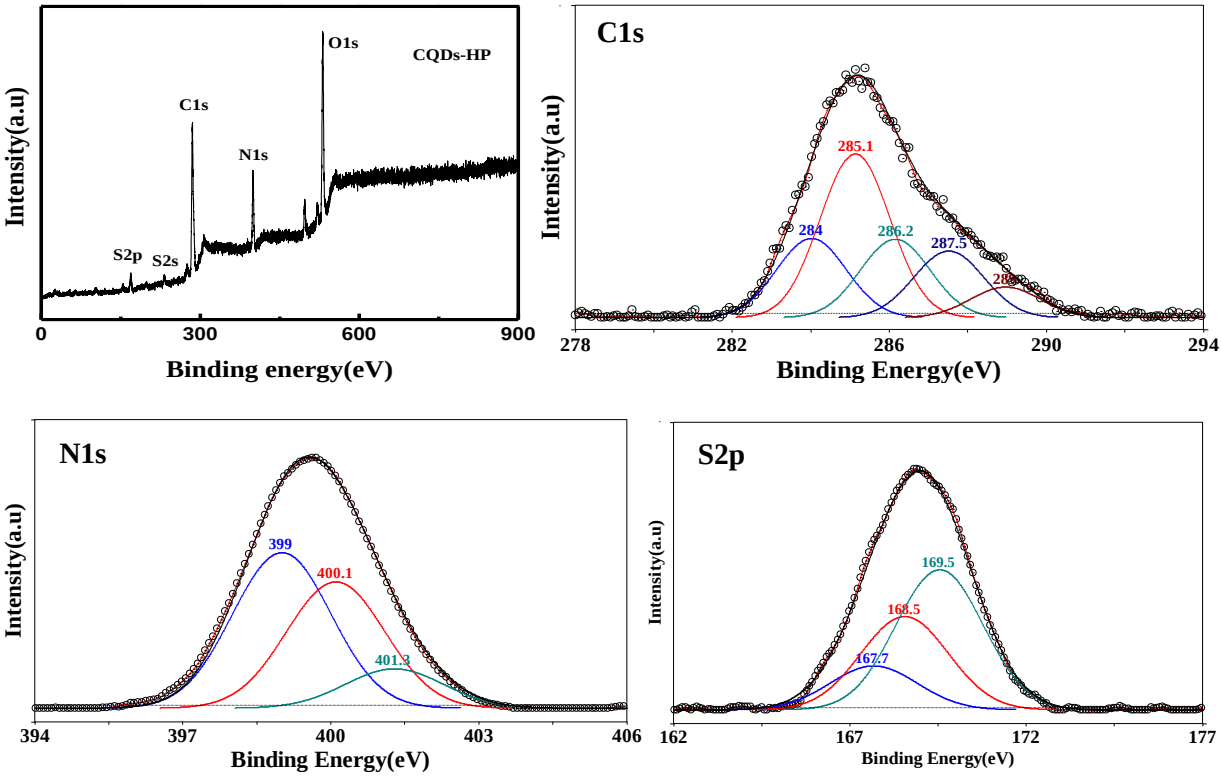


Figure S5. Full survey and the Hi-resolution XPS spectra of C1s, N1s and S2p of CQDs-HP.

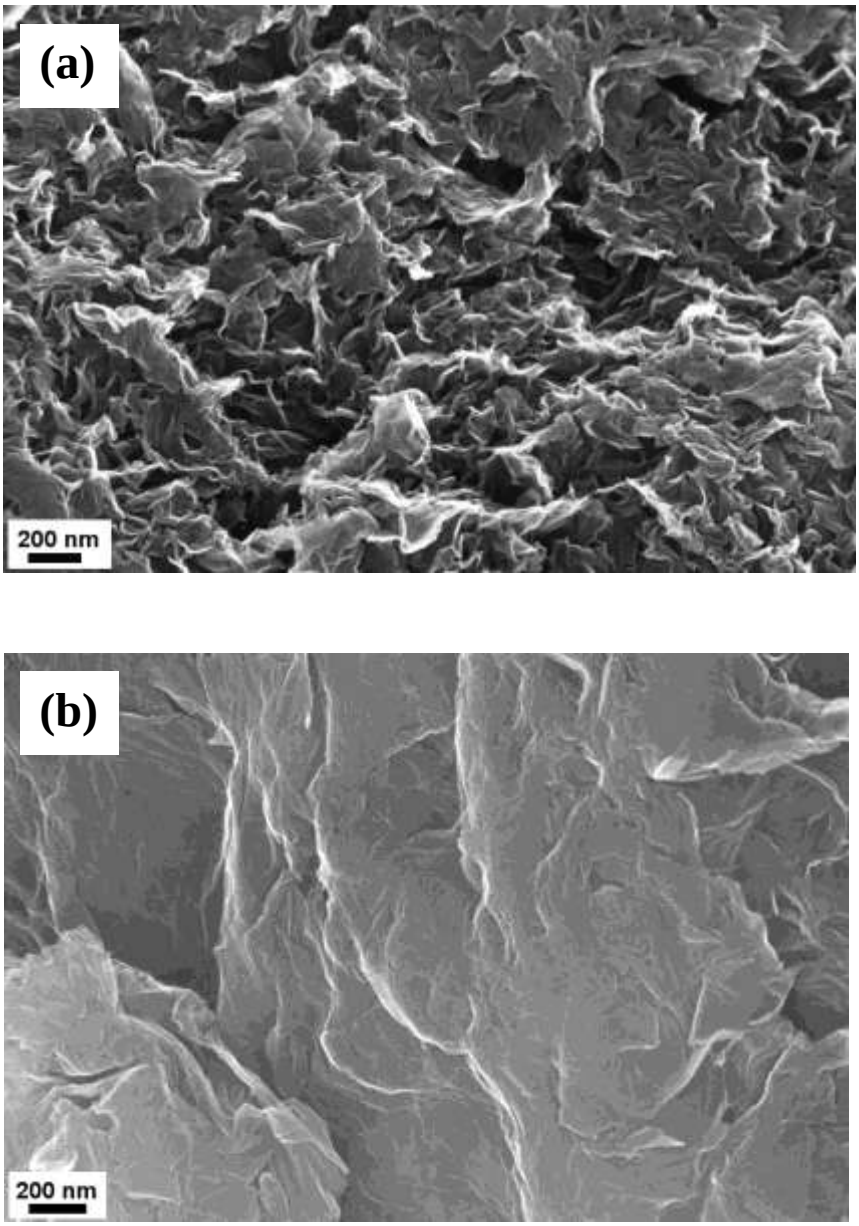


Figure S6. FESEM images of rGO (a) and rGO/CQDs-HP (b).

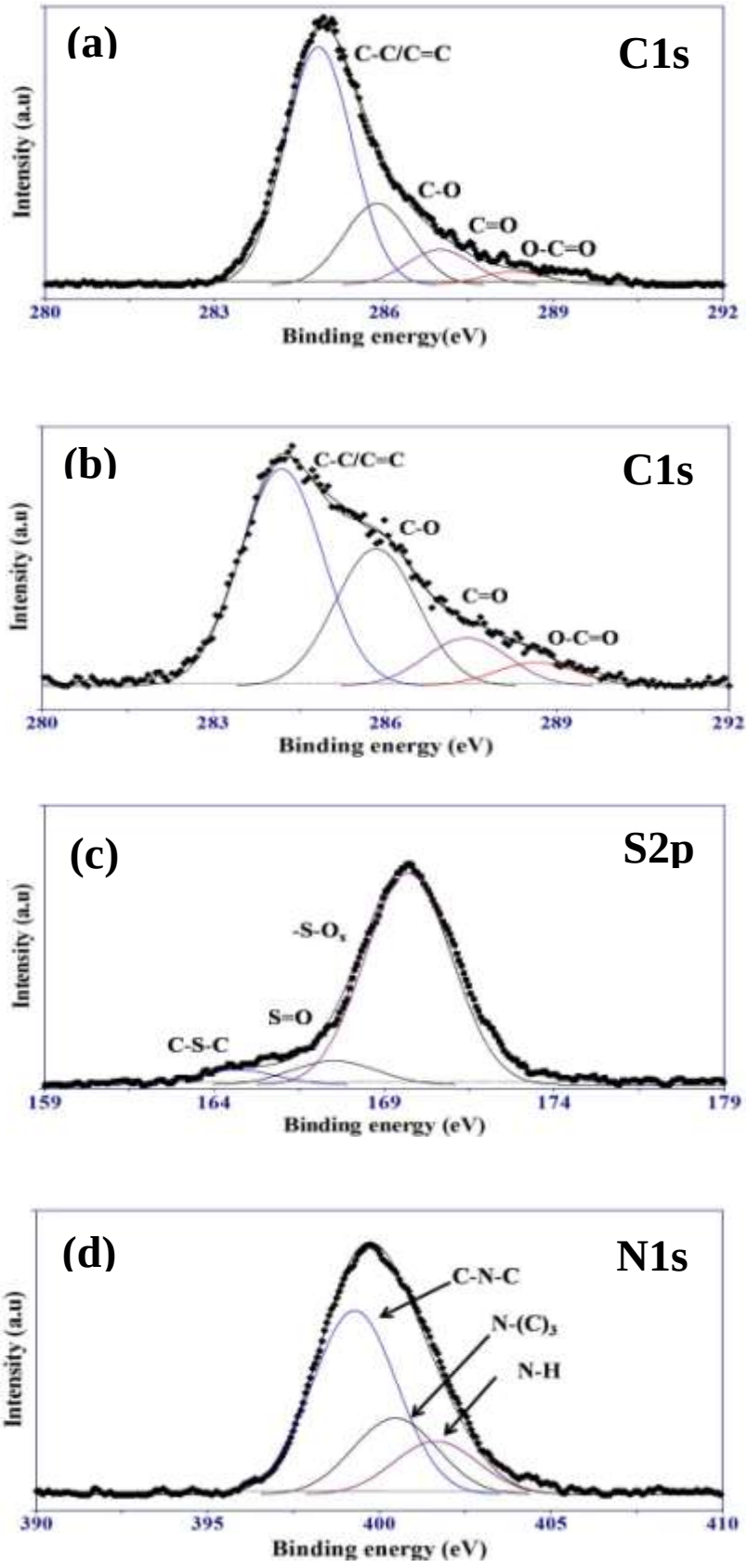


Figure S7. The Hi-resolution XPS spectra of (a) C1s of rGO and (b-d) C1s, S2p and N1s spectrum of rGO/CQDs-HP respectively.

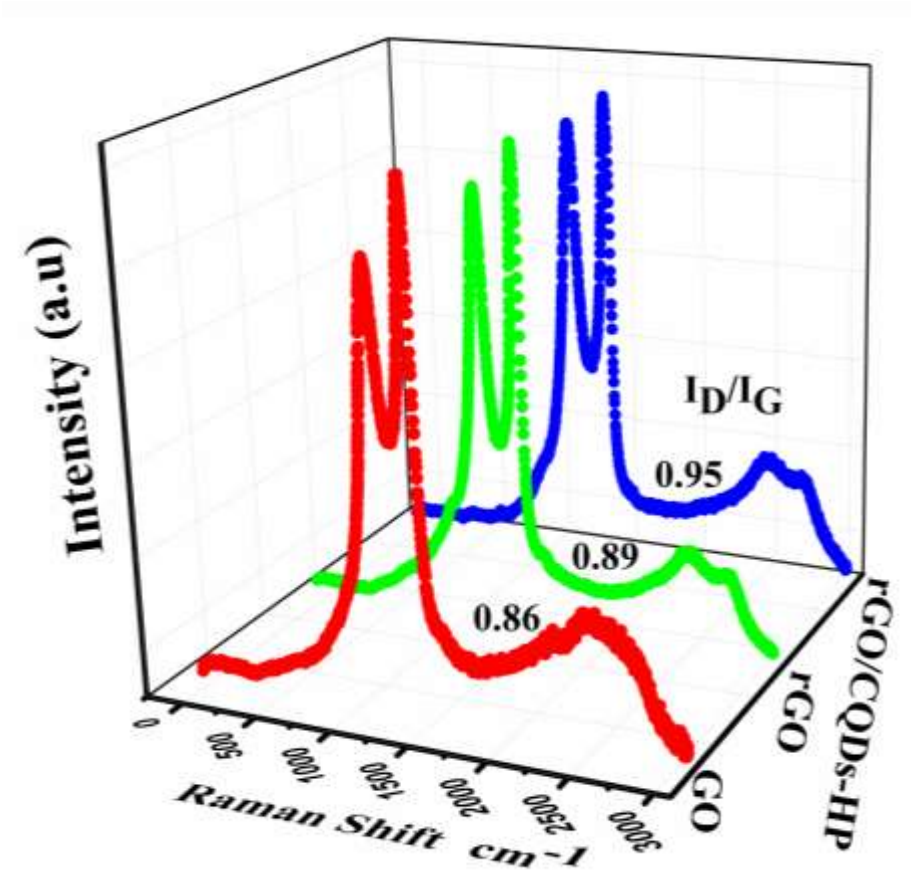


Figure S8. The Raman spectrum of GO, rGO and rGO/CQDs-HP.

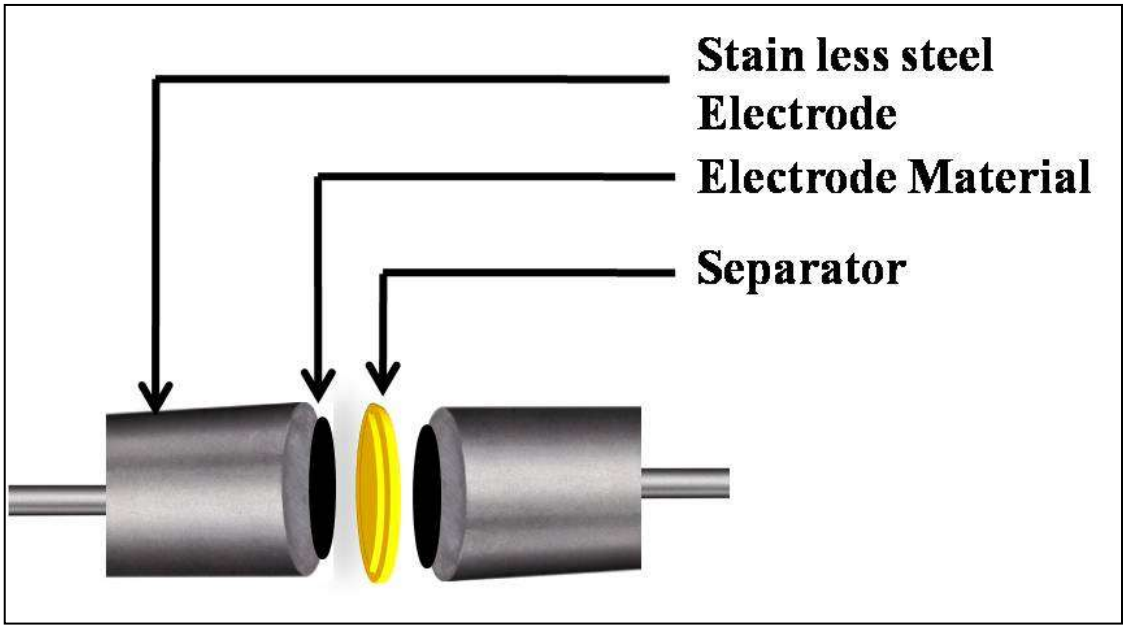
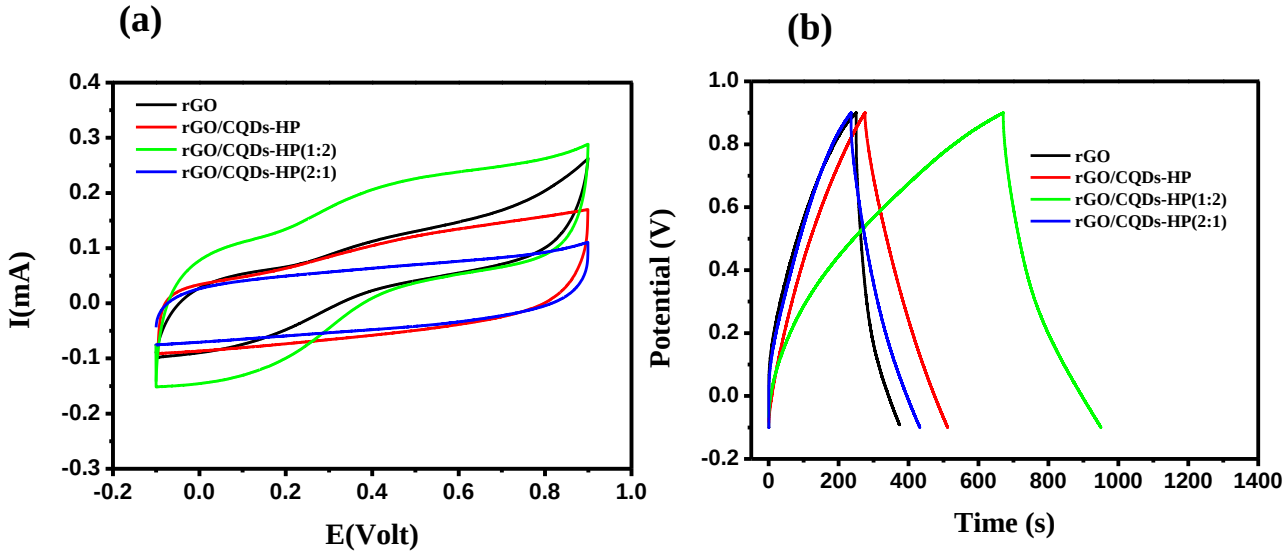


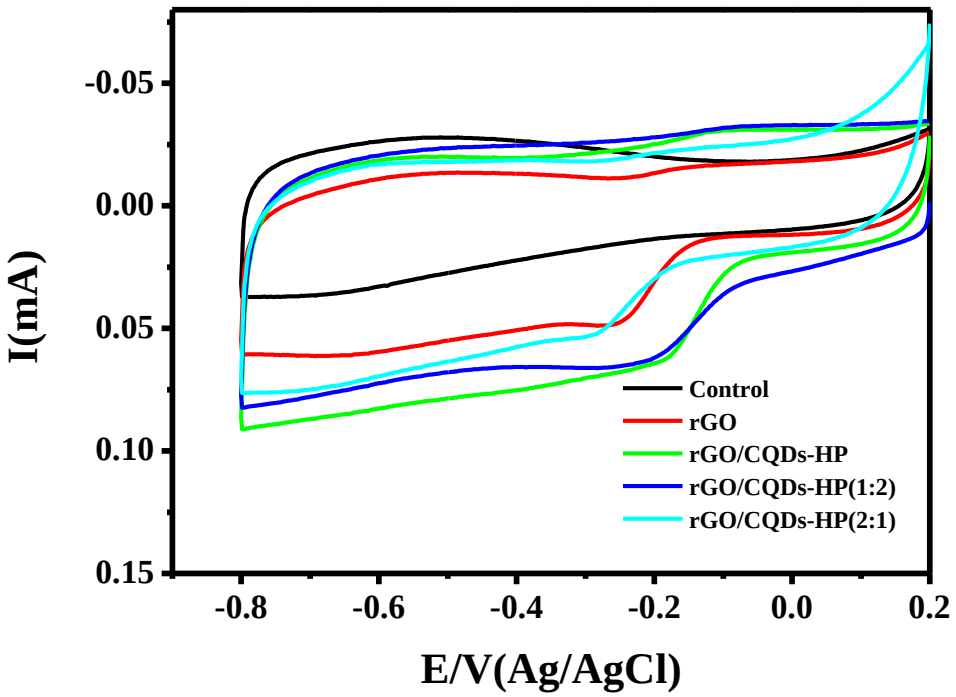
Figure S9. Scheme showing the arrangement of the symmetrical electrode. The sample was placed on the well polished stainless steel electrodes and the arrangement was carried out by placing a cellulose nitrate membrane as separator.



(c)

SI. No.	Sample	Csp (F/gm)	Energy Density (Wh/kg)	Power Density (W/kg)
1	rGO	98	13.61	49.00
2	rGO/CQDs-HP	156	21.70	78.12
3	rGO/CQDs-HP (1:2)	196	27.17	98.10
4	rGO/CQDs-HP (2:1)	102	15.03	54.27

Figure S10. (a) Cyclic voltamograms and (b) GCD plots for rGO and its composites with CQDs-HP. (c) Table shows the corresponding specific capacitances, energy and power densities of the samples.



SI. No.	Sample	Onset Potential (V)	Reduction Potential (V)
1	rGO	-0.060	-0.254
2	rGO/CQDs-HP	+0.020	-0.170
3	rGO/CQDs-HP (1:2)	+0.022	-0.185
4	rGO/CQDs-HP (2:1)	-0.055	-0.281

Figure S11. Cyclic voltamograms for ORR by rGO and its composites with CQDs-HP in O_2 saturated 0.1M KOH. The control experiment was carried out in argon saturated 0.1M KOH. Scan rate: 10 mV/s.

Calculation of Capacitance

The cyclic voltammetry was performed at different scan rates (from 1 to 200mV/s) and Galvanostatic charge-discharge (GCD) was recorded at their corresponding current densities. The specific capacitance (Csp) of the materials were calculated both from the CV and CD data by using the equation 1 and 2, [1]

$$C_{sp}=2\times\frac{\int I(V)dV}{ms(V_a-V_b)} \quad \text{..... (1)}$$

$$C_{sp}=\frac{4I}{m\frac{dV}{dt}} \quad \text{..... (2)}$$

Where $\int I\,(V)\,dV$ is the integrated surface area obtained from the CV curve, m, s, I, dV/dt, and (V_a - V_b) are the mass of the electrode material, scan rate, current, slope of the discharge curve and the working potential window, respectively. After the calculation of specific capacitance, the energy density (ED) and power density (PD) were calculated by using the following formulas (equation 3 and 4), [2]

$$ED=\frac{C_s(\Delta V)^2}{2} \quad \text{..... (3)}$$

$$PD=\frac{C_s(\Delta V)s}{2} \quad \text{..... (4)}$$

Calculation of the Number of electrons involved in the ORR

The number of electrons involved in the ORR was calculated by following the Koutecky-Levich (K-L) equation as, [3,4]

$$\frac{1}{i}=\frac{1}{i_k}+\frac{1}{i_{dl}} \quad \text{..... (5)}$$

Here i_k is the kinetic current and idl is the limiting current value. Where, $i_{dl}=B\omega^{1/2}$, ω is the rotation speed and B can be calculated from the K-L equation as,

$$B=\frac{0.62nFC_0D_0^{2/3}}{\eta^{1/6}} \quad \text{..... (6)}$$

Here n is the no. of electrons involved in the ORR. F, Co, Do, and η are the Faraday constant (96485.33C), bulk concentration of Oxygen (for 0.1M KOH it is 1.2×10^{-6} Mol s^{-1}), diffusion coefficient of Oxygen (for 0.1M KOH 1.9×10^{-5} Cm^2s^{-1}), kinematic viscosity of the electrolyte (for H_2O it is 0.01 Cm^2s^{-1}) respectively.[5]

References

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5. Z. Lin, G. H. Waller, Y. Liu, M. Liu and C. Wong, *Nano Energy*, 2013, **2**, 241.