

Graphene enriched with pyrrolic coordination of the doped nitrogen as an efficient metal-free electrocatalyst for oxygen reduction

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1. Calculation for in-plane crystalline size (L_a) from Raman spectroscopy¹

The crystallite size can be determined according to the Tuinstra–Koenig (TK) relation,

$$L_a(\text{nm}) = (2.4 \times 10^{-10}) \lambda^4 (I_D/I_G)^{-1}$$

Where, L_a is in-plane crystalline size, λ is the Raman excitation wavelength, I_D and I_G are peak intensity of D and G band respectively.

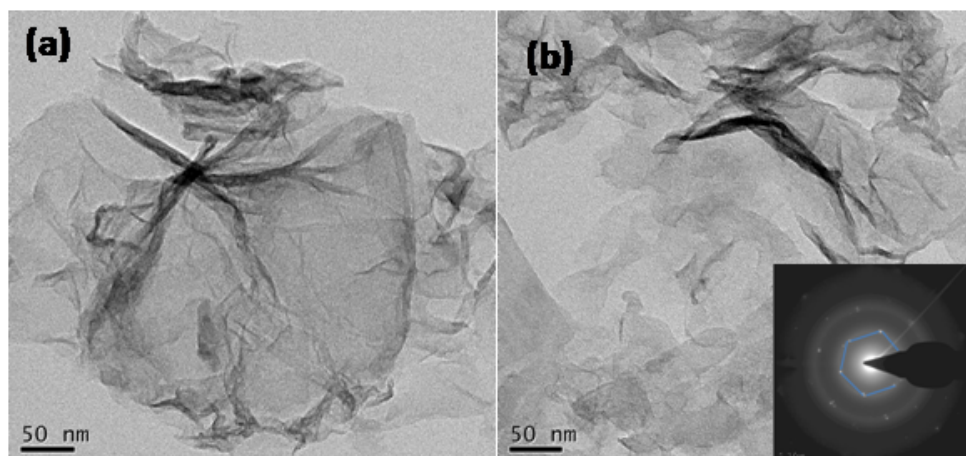


Figure S1. Transmission electron microscopic images of reduced graphene oxide prepared by using NaBH_4 as a reducing agent. (Inset: SAED of the reduced graphene oxide which shows dotted patterns indicating both the crystalline nature and presence of six sided honeycomb lattice of the carbon framework).

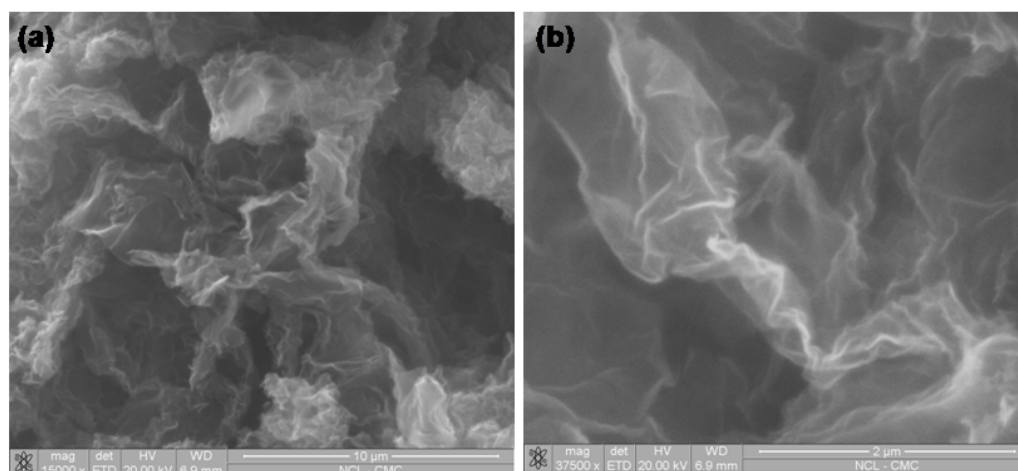


Figure S2. Scanning electron microscopic images of (a) GEPPy and (b) NGE-1000.

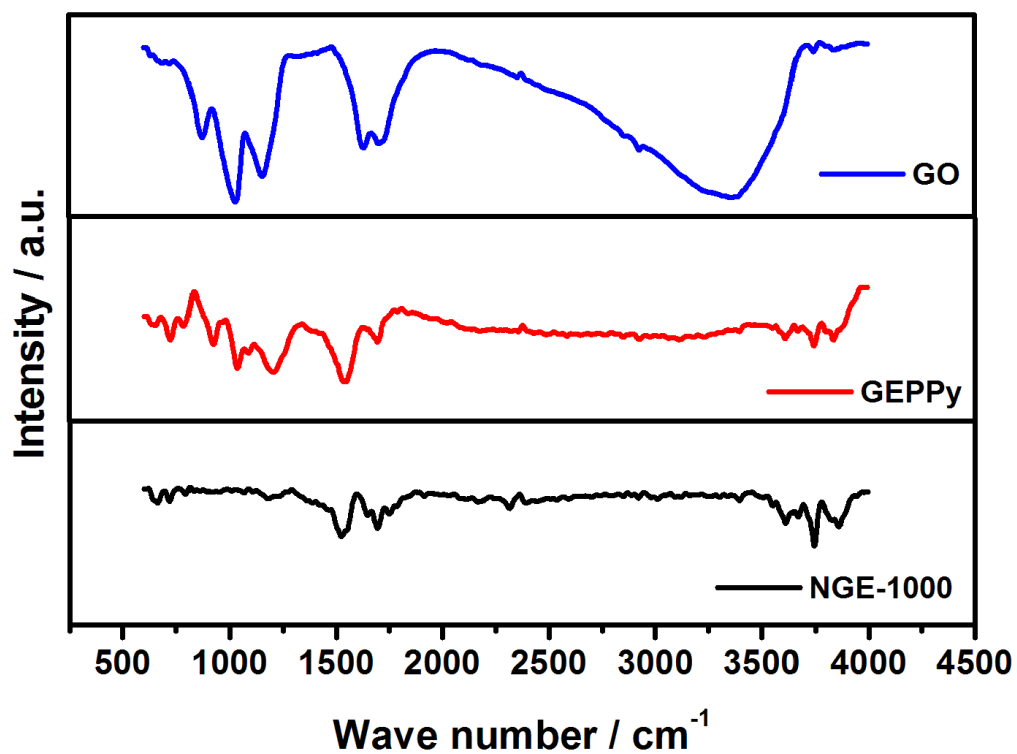


Figure S3. FTIR spectra of GO, GEPPy and NGE-1000.

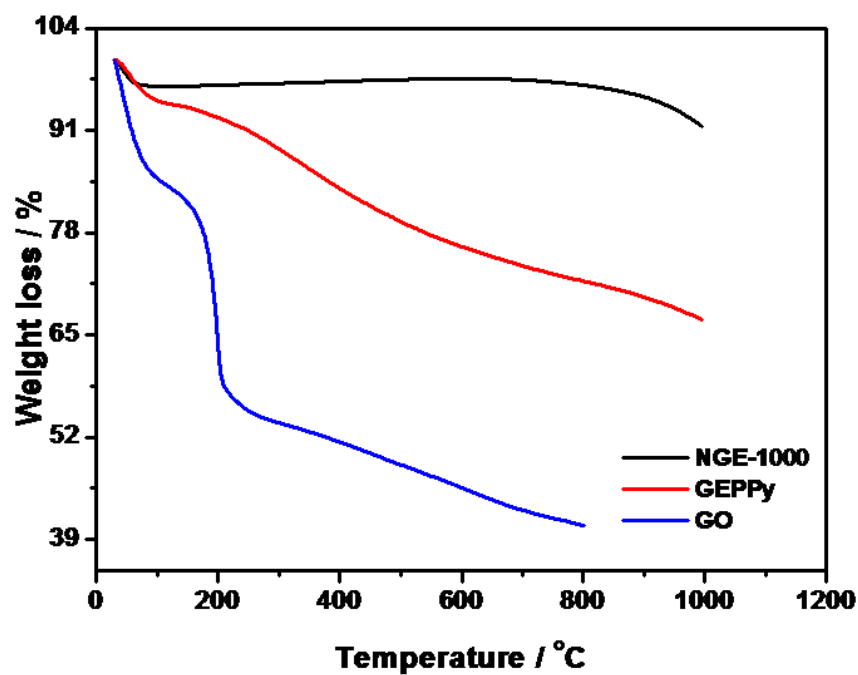


Figure S4. Thermo gravimetric analysis of GO, GEPPy and NGE-1000 at a temperature range of 25 to 1000 °C by maintaining a heating rate of 10 °C per minute in nitrogen atmosphere.

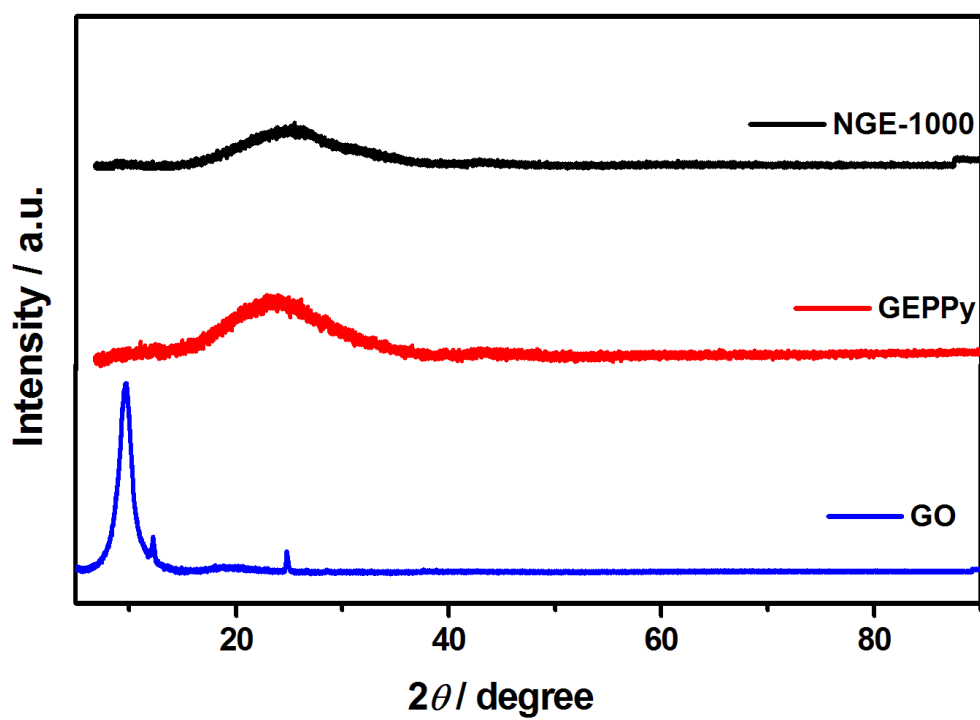


Figure S5. X-ray diffraction pattern of GO, GEPPy and NGE-1000.

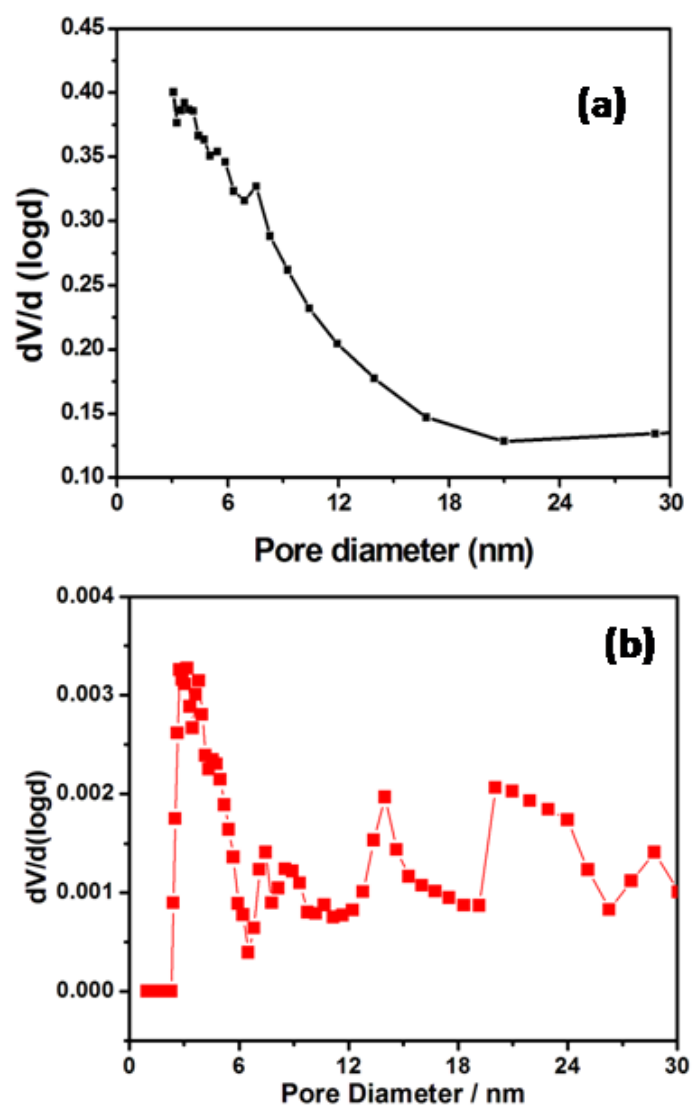


Figure S6. Pore size distribution of (a) NGE-1000 and (b) GEPPy

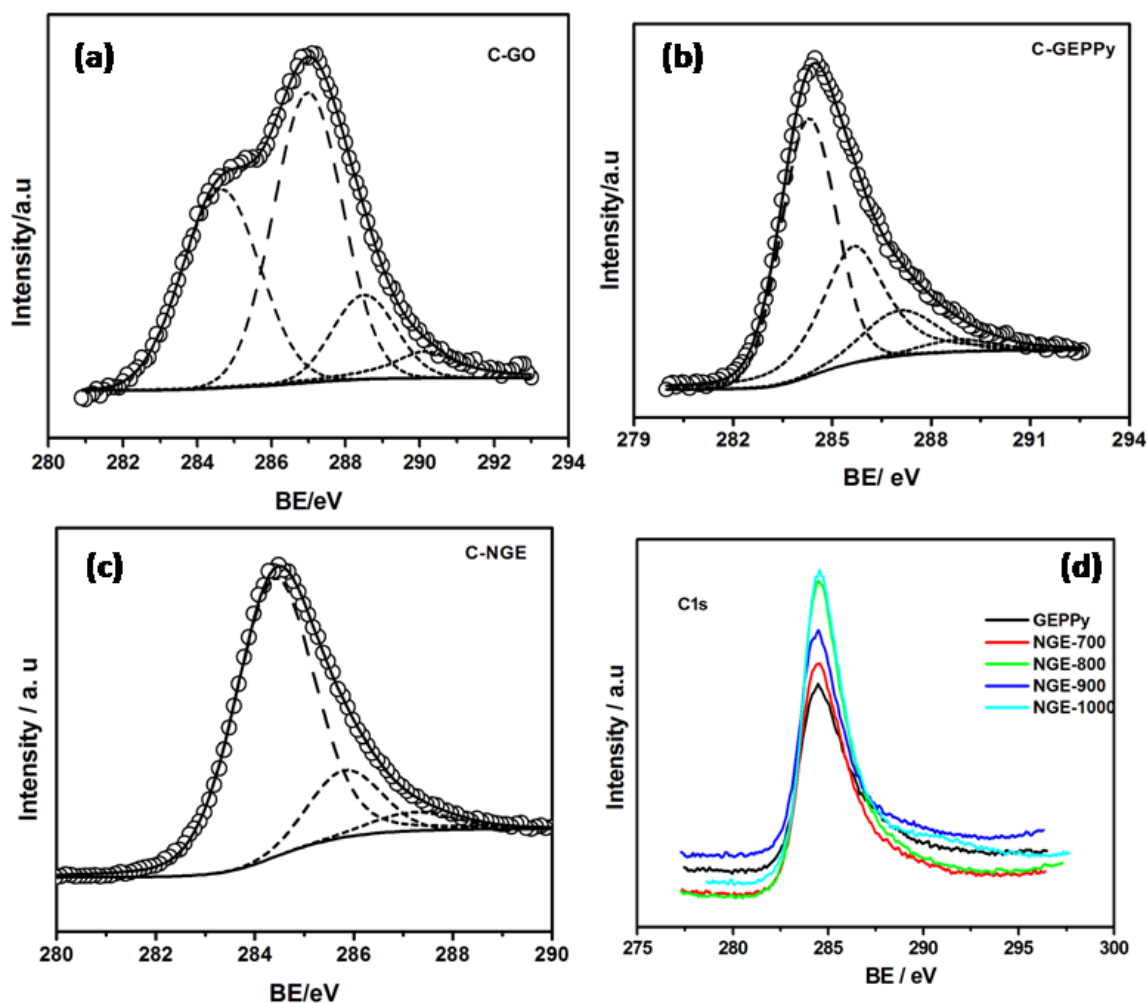


Figure S7. Deconvoluted XPS spectra of carbon 1s of (a) GO, (b) GEPPy and C (NGE). (d) C 1s spectra of GEPPy, NGE-700, NGE-800, NGE-900 and NGE-1000. Narrowing of the C1s peak at higher temperature indicates high degree of graphitization as the heat treatment temperature increases.

Reduction of graphene oxide using pyrrole is clear from the figure S7 (a & b) that the peak corresponds to sp^2 (284.5 eV) carbon intensity increased in GEPPy compared to graphene oxide. These clearly indicate the improved conjugation by the retention of double bonds in reduced graphene oxide after reduction. Similarly, oxygen to carbon ratio of GEPPy is reduced dramatically to 0.24 from 1.11 that of graphene oxide clearly indicate the reduction

of graphene oxide to reduced graphene oxide using pyrrole as reducing agent. Elemental composition of graphene oxide and GEPPy are tabulated in the Table S1.

Table S1: Weight percentage of carbon, oxygen and nitrogen in graphene oxide and reduced graphene oxide.

	Carbon	Oxygen	Nitrogen	O/C
GO	47.24	52.76	0.0	1.11
GEPPy	70.19	17.29	12.50	0.24

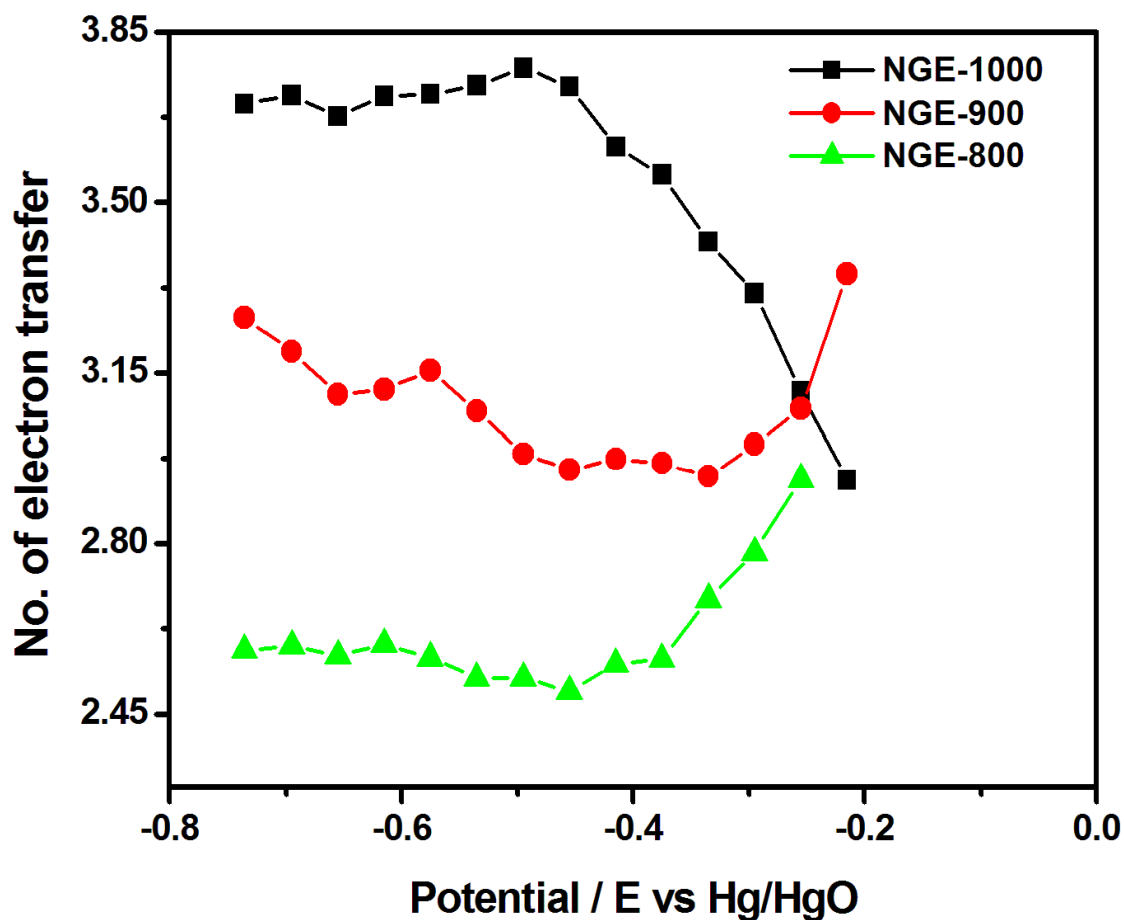


Figure S8. The number of electrons transferred versus the potential as calculated from the K-L plots.

Reference

(1) Cancado, L. G.; Takai, K.; Enoki, T.; Endo, M.; Kim, Y. A.; Mizusaki, H.; Jorio, A.; Coelho, L. N.; Magalhaes-Paniago, R.; Pimenta, M. A. *Appl. Phys. Lett.* 2006, 88, 163106-163103.