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# 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 spectroscopy[1]

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

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

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

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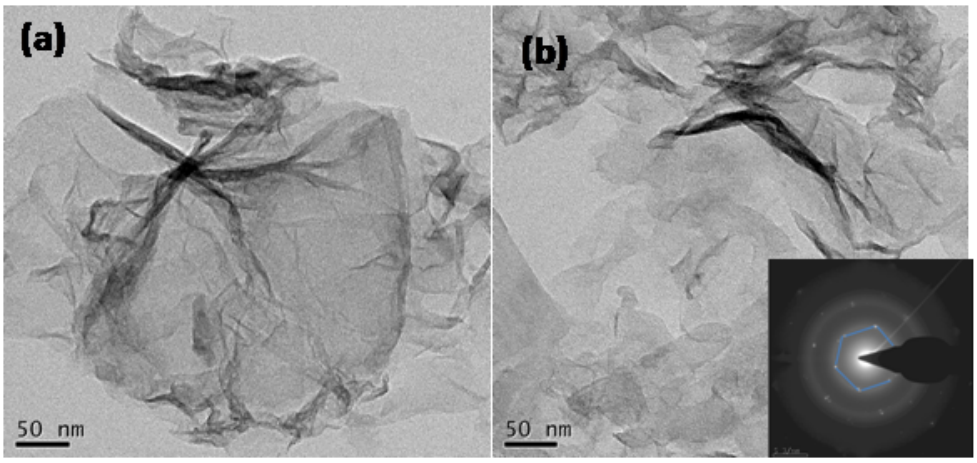


**Figure S1**. Transmission electron microscopic images of reduced graphene oxide prepared by using $NaBH_4$ as a reducing agent. (Inset: SAED of the reduced graphene oxide which shows dotted patterns indicating both the crystalline nature and presence of six sided honeycomb lattice of the carbon framework).

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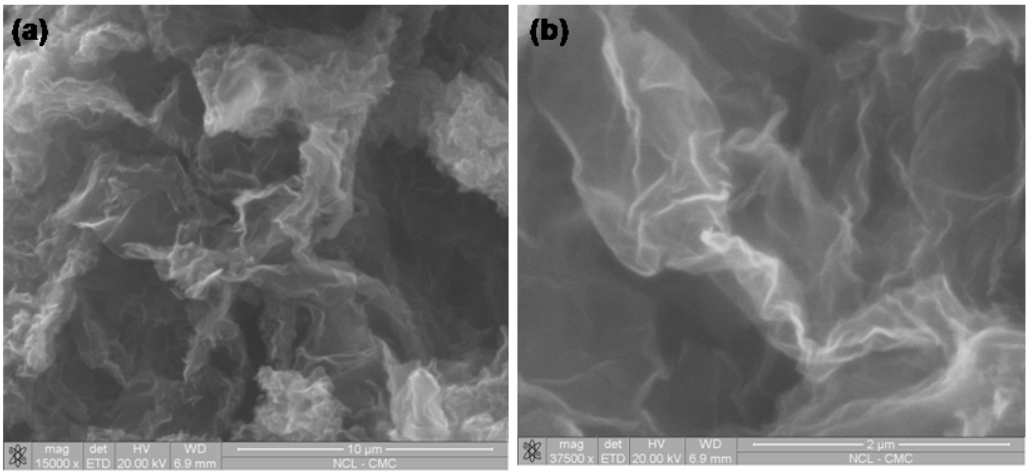


**Figure S2.** Scanning electron microscopic images of (a) GEPPy and (b) NGE-1000.

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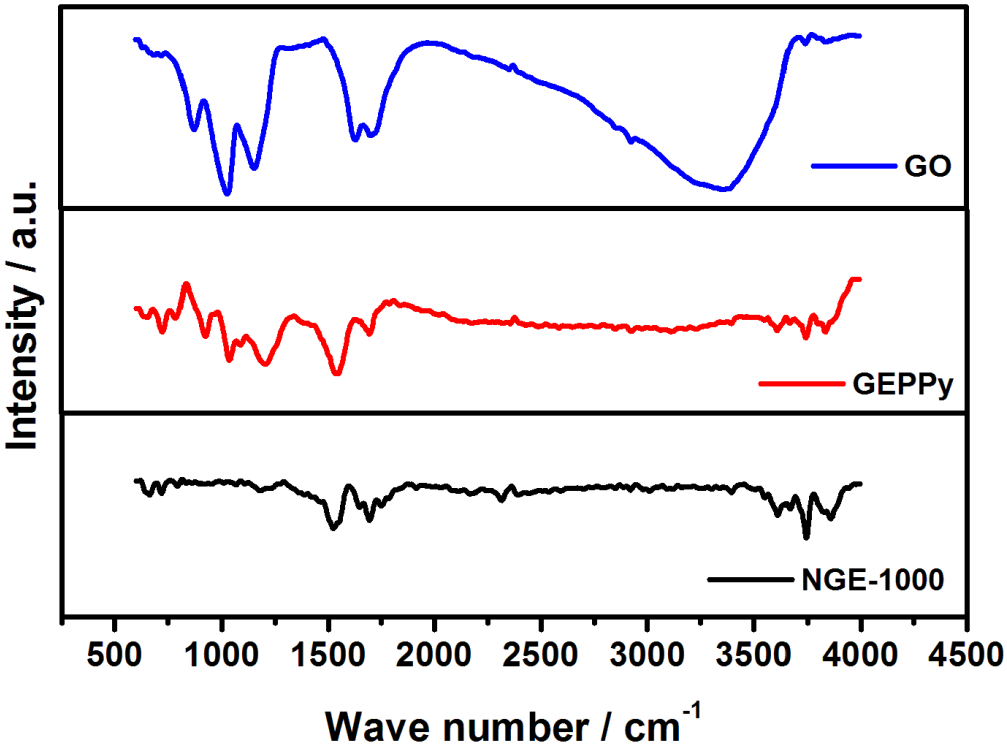


**Figure S3**. FTIR spectra of GO, GEPPy and NGE-1000.

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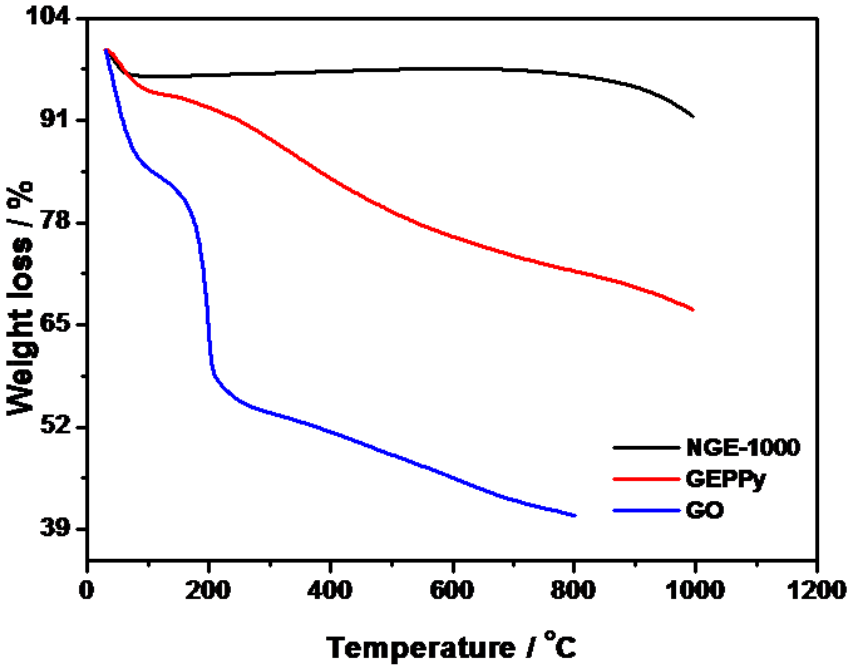


**Figure S4**. Thermo gravimetric analysis of GO, GEPPy and NGE-1000 at a temperature range of 25 to 1000 $^{o}$C by maintaining a heating rate of 10 $^{o}$C per minute in nitrogen atmosphere.

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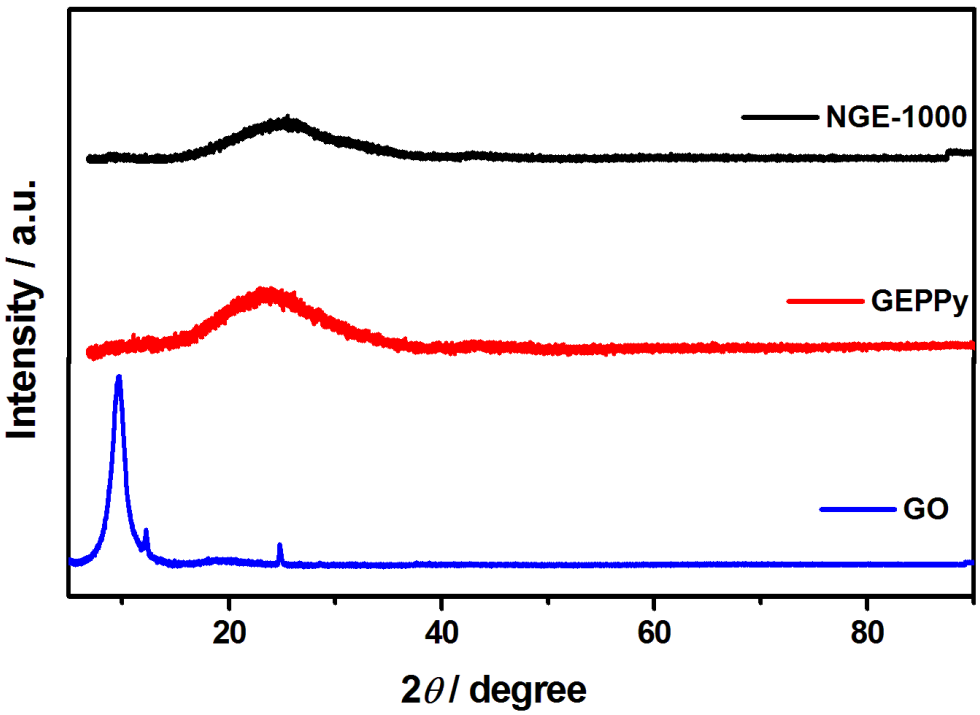


**Figure S5**. X-ray diffraction pattern of GO, GEPPy and NGE-1000.

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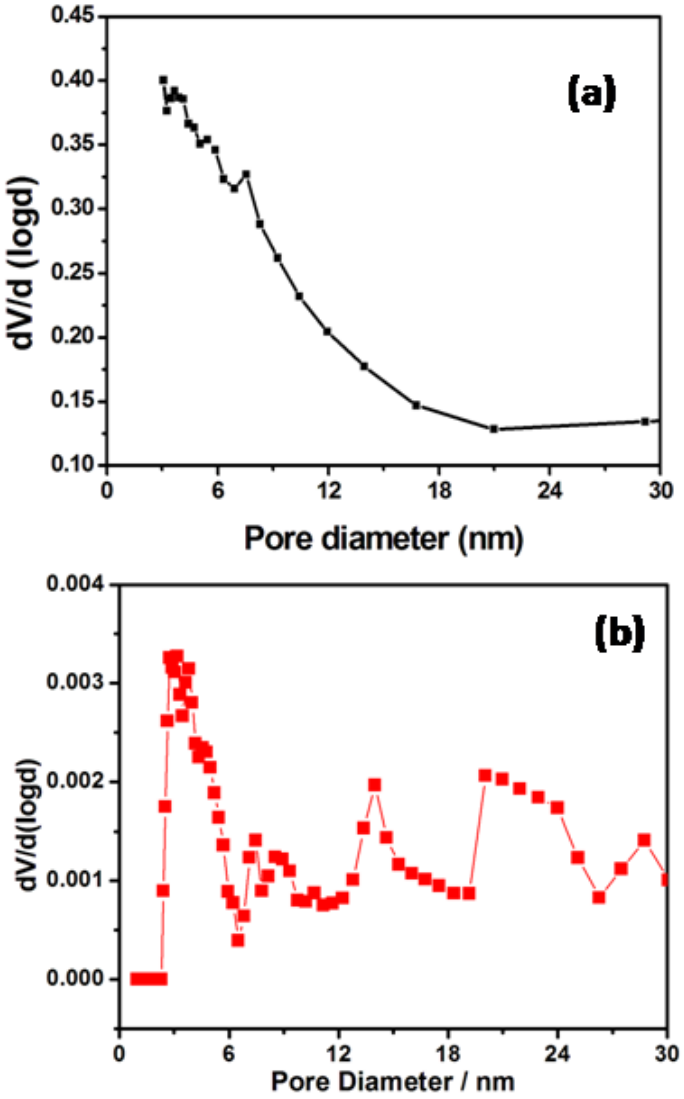


**Figure S6**. Pore size distribution of (a) NGE-1000 and (b) GEPPy

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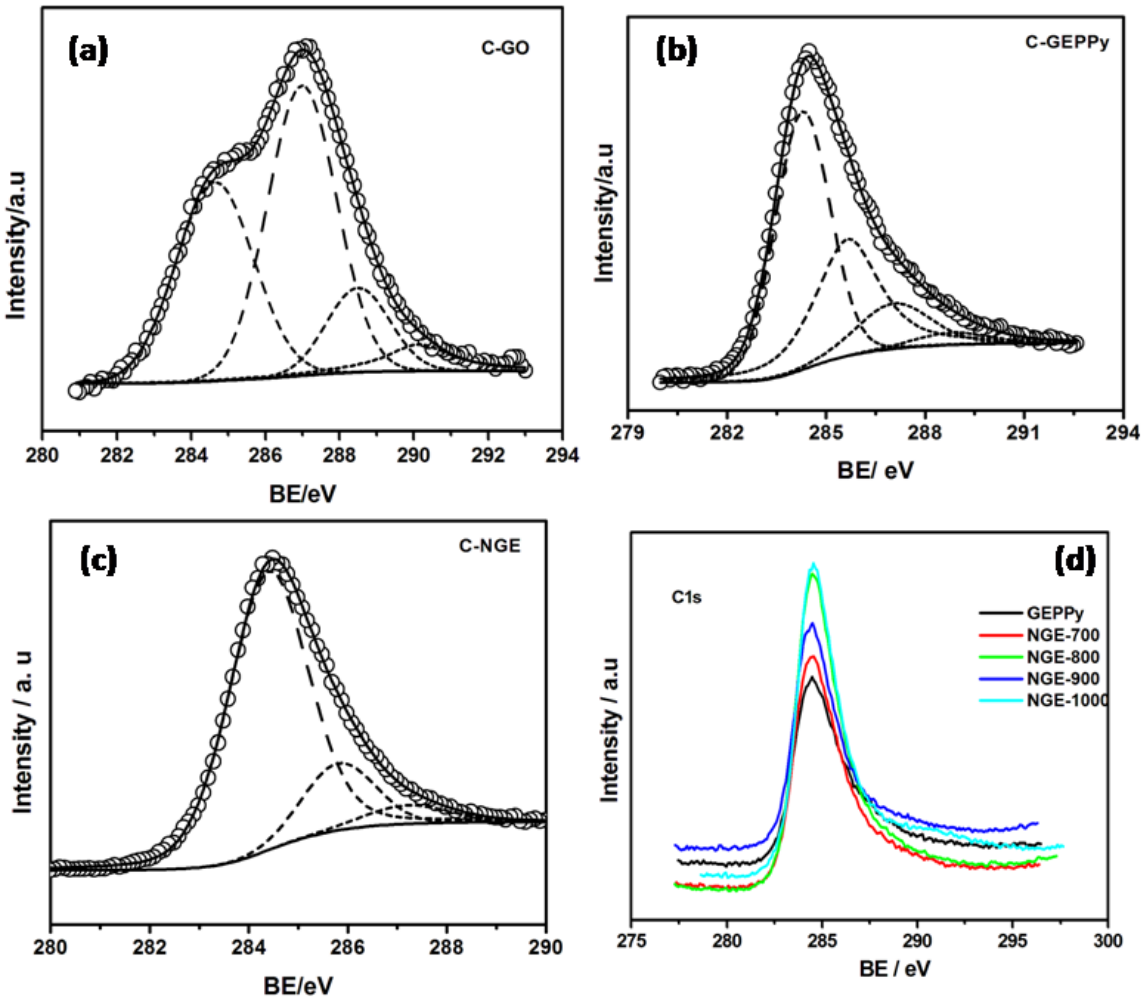


**Figure S7**. Deconvoluted XPS spectra of carbon 1s of (a) GO, (b) GEPPy and C (NGE). (d) C 1s spectra of GEPPy, NGE-700, NGE-800, NGE-900 and NGE-1000. Narrowing of the C1s peak at higher temperature indicates high degree of graphitization as the heat treatment temperature increases.

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

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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 |

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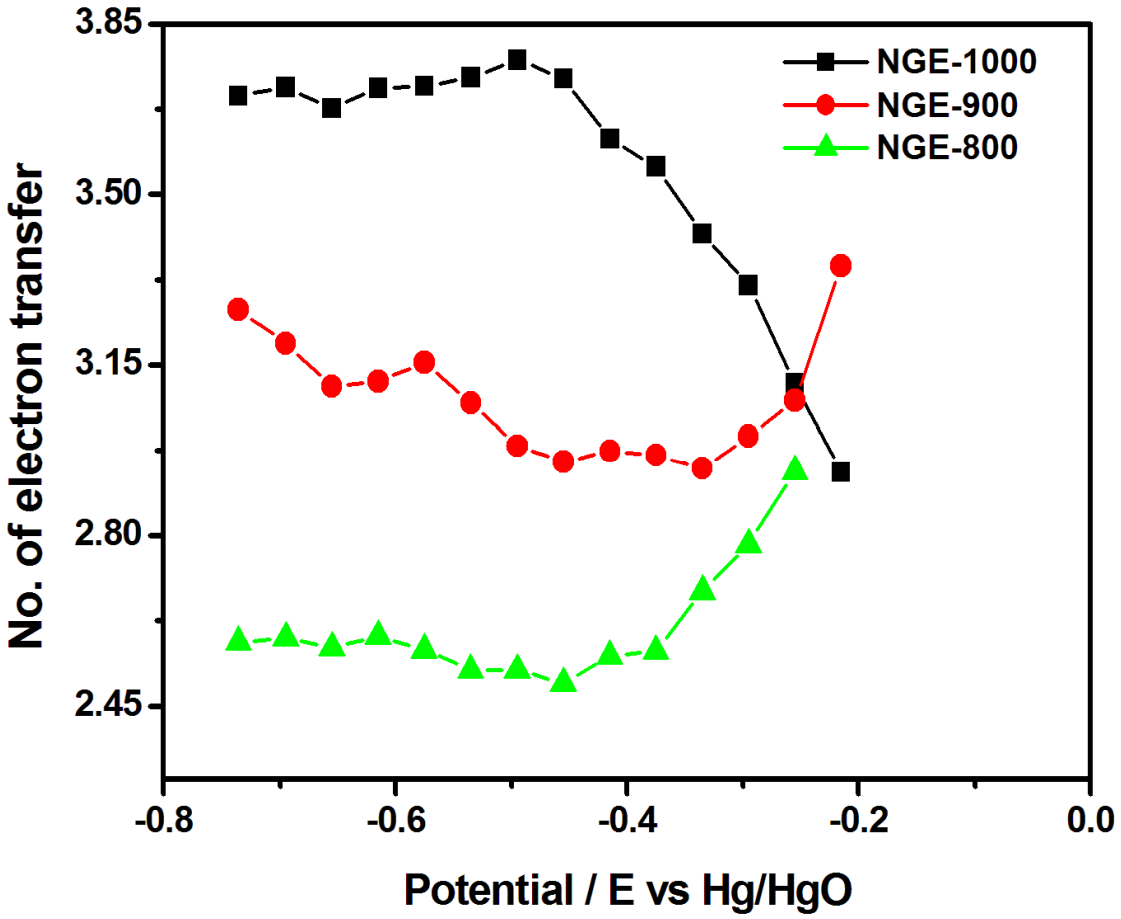


**Figure S8**. The number of electrons transferred versus the potential as calculated from the K-L plots.

## 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.