Supplementary Information

Activated nitrogen doped graphene shell towards electrochemical oxygen reduction reaction by its encapsulation on Au nanoparticle (Au@N-Gr) in water-in-oil "nanoreactors"

Vishal M Dhavale, Sachin S Gaikwad, Sreekumar Kurungot*

Physical and Materials Chemistry Division, National Chemical Laboratory, Pune-411008, India, Fax: +91-20-25902636/15; Tel: +91-20-25902566;

E-mail: k.sreekumar@ncl.res.in

CONTENT:

1. Experimental Section:

2. Results and discussion:

1. Experimental Section:

1.1. Synthesis of gold (core)@graphene (shell) nanostructures (Au@Gr):

For the synthesis of Au (core)-Gr (shell) (Au@Gr) nanoparticles, 4 mg of the as-synthesized Gr was mixed with 2 ml of aqueous solution of 100 mM chloroauric acid and the mixture was sonicated for 30 min using a bath sonicator to form a homogenous solution. The dispersed solution was added drop-wise in previously taken fresh silicon oil (25 ml), under a strong magnetic stirring. Furthermore, the reaction mixture was maintained for 5 h at room temperature to get a uniform distribution of emulsion droplets. At this stage, the color of the reaction mixture was turned from transparent to reddish, which is attributed to the formation of Au@Gr core-shell structures. Further, the water-in-oil emulsion was transferred into a Petri dish, and was kept in an oven at 80 ^{o}C for 80 h. During this process, water in the emulsion droplets gets evaporated and crystallization of the solid components in the emulsion droplets occurs simultaneously. Finally, the formed Au@Gr core-shell nanostructures were centrifuged at 10000 rpm for 15 min and was washed several times with hexane to remove the silicon oil and the material was dried under and a lamp.

1.2. Synthesis of reduced graphene oxide (Gr):

For the synthesis of Gr, first, graphene oxide (GO) was synthesized by improved Hummer's method.[1] Furthermore, reduction of GO was done by chemical reduction method. For this, 100 mg of GO was dispersed in an 100 ml DI water and transferred in a 250 ml round bottom flask and kept under stirring for 10 min. Subsequently, 50 ml of 0.1 M sodium borohydride was added slowly from a burette and the mixture was kept under stirring for 4 h. The reaction mixture was centrifuged at 10000 rpm, washed with DI water several time and dried at 80 ^{o}C overnight in oven. The obtained black product is graphene and is termed as Gr (Figure S2).

1.3. Synthesis of N-doped Gr (N-Gr):

For the synthesis of N-doped Gr (N-Gr), the chemically reduced graphene (Gr) was mixed with melamine in the ratio of 1:6 in 100 ml DI water and the mixture was stirred for 24 h. The slurry was filtered and dried in an oven at 80 ^{o}C for overnight. Thus obtained melamine-Gr mixture was heated at about 900 ^{o}C in a tubular furnace under 200 sccm Ar flow for about 4 h. the furnace was cooled down to room temperature under inert atmosphere and finally the N-Gr was obtained (Figure S2).

1.4. Synthesis of gold (Au):

For the synthesis of Au nanoparticles, a homogeneous mixer of the as-synthesized Gr (2 mg) and chloroauric acid (100 mM, 2 ml) was obtained by sonication. Here, the concentration of Gr is maintained too less as it is required only as a moiety to facilitate *in-situ* reduction of the Au precursor (a higher concentration of Gr will trigger the formation of Au@Gr core-shell particles) The mixture was then added drop-wise in previously taken fresh silicon oil (25 ml), under a strong magnetic stirring. After the addition, the reaction mixture was maintained for 5 h at room temperature to get uniform emulsion droplets. This was then transferred into a Petri dish, and was kept in an oven at 80 ^{o}C for 80 h. During this process, Gr will reduce the gold precursor to gold nanoparticles and Gr itself will get oxidized, leading to formation of gold nanoparticles and small graphene sheets. The gold nanoparticles and gold supported graphene sheets will form separately, which could be separated after the centrifugation. The product was washed several times with hexane to remove the silicon oil and was finally dried under a lamp.

1.5. Calculation of uncompensated resistance for iR compensation study:

a) Positive Feedback method:

The uncompensated resistance value has been calculated by positive feedback method, as described in the literature (Reference No. 22, Main manuscript).

The automatic compensation of resistance has been done on Bio-Logic instrument, by determining the resistance value using positive feedback method. Basically, at any potential, where no faradaic reaction is happening, the faradaic impedance is very large and can be taken as approximately an open circuit. By applying very small amount potential, where no faradaic process takes place, the instantaneous change in the potential will takes place, and consequently the current drops to zero. Finally, the current value at time (*t*) equal to zero has been calculated by extrapolation, and used it to find the uncompensated resistance (iR_u). In between the reference and working electrode, the resistance (R_u) in series with capacitance (C_d) will be appeared. Therefore, in order to eliminate the C_d term, the feedback method is useful to get the resistance-free data. Here, the application of a small potential step (50 mV) across the reference and working electrode is given, where no faradaic reaction occurs and hence the only current that flows in this region is charging current with an exponential decay. Finally the linear regression is performed at low time scale, as shown in Figure S12a. The current response should be

$$i\,(t) = (\Delta E / R_u)\,\exp\,(-t / R_u C_d) \ldots\ldots\ldots\ldots\ldots\, Equation\,1$$

The current at t = 0 will be interpret as in equation 2, where the exponential term of Equation 1 (i.e. $-t/R_uC_d$), becames equal to unity and capacitance will disappear. Finally Equation 1 changes to,

$$i\,(0) = (\Delta E / R_u) \;\ldots\ldots\ldots\ldots\ldots\, Equation\,2$$

where, ΔE is known (50 mV) and R_u can be extracted after extrapolation at t = 0.

The plot of current (*i*) *vs.* time (*t*), extrapolation of graph at t = 0, gives the value of $\Delta E / R_u$.

Calculation:

$\Delta E/R_u = 0.85$ m A

$R_u = \Delta E/0.85$ mA

$= 50$ mV / 0.85 mA

$\mathbf{R_u = 58.82\ \Omega}$

b) Impedance spectroscopy:

The uncompensated resistance value could also be calculated by impedance analysis. The dispersed sample is coated on the glassy carbon electrode surface, and used as working electrode. Moreover, the impedance spectra is recorded in three electrode system by using Hg/HgO as a reference electrode and platinum foil as counter electrode in 0.1 M KOH. The plot is shown in Figure S12b. The X-axis intercept gives the value of resistance (58.2 Ohms), and used for the automatic *iR* compensation study, during RDE. The obtained resistance value is matching with the obtained resistance value by feedback method.

2. Results and discussion:

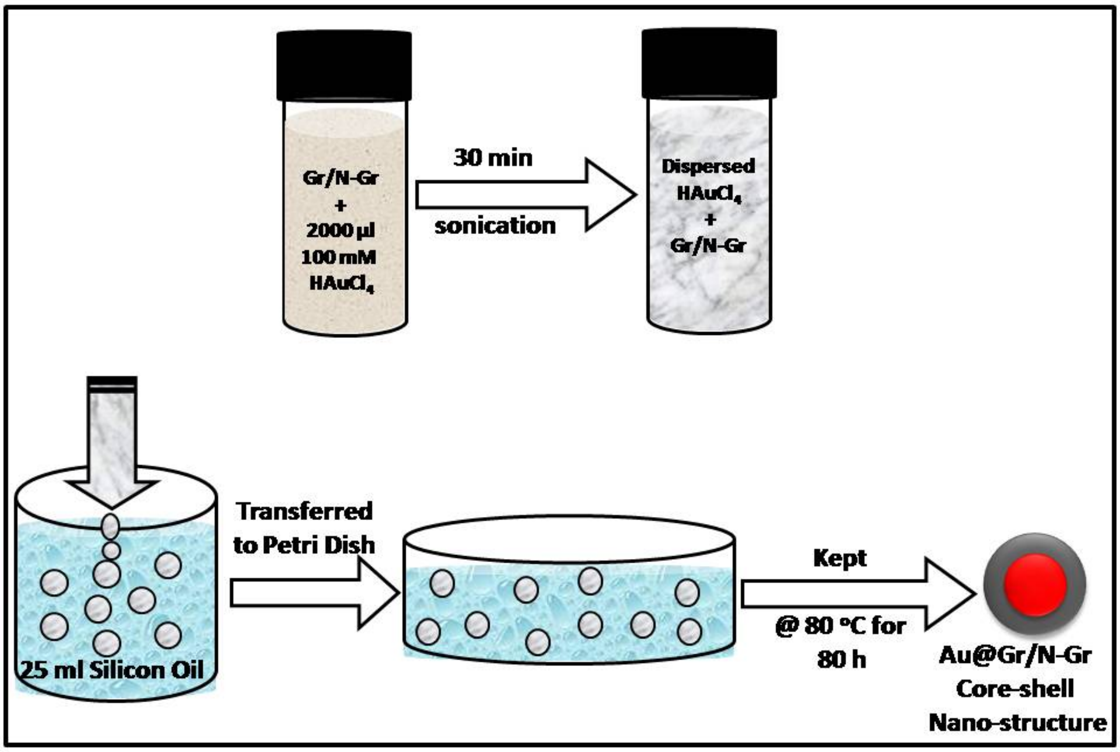

Figure S1. *Schematic representation of Au@Gr and Au@N-Gr synthesis.*

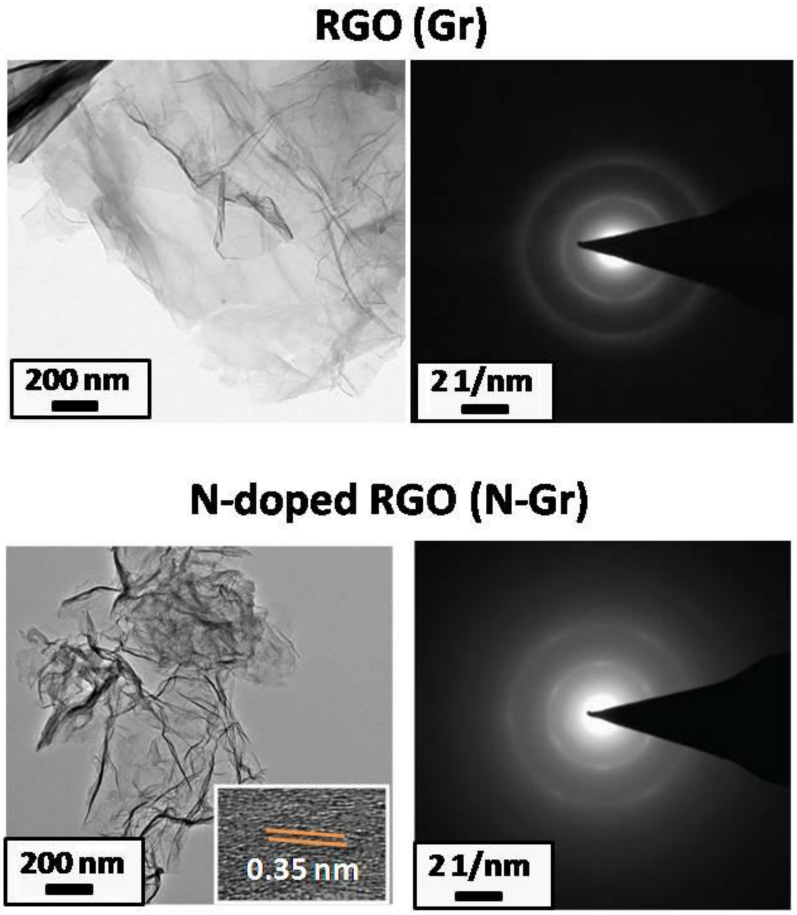

Figure S2. *(Top) TEM image of the chemically reduced graphene (Gr) and the respective SAED pattern; (Bottom) TEM image of the N-doped Gr (N-Gr) and its respective SAED pattern. The inset shows the HR-TEM image of N-Gr with higher d-spacing value of 0.35 nm, indicating the incorporation of nitrogen in graphitic network.*

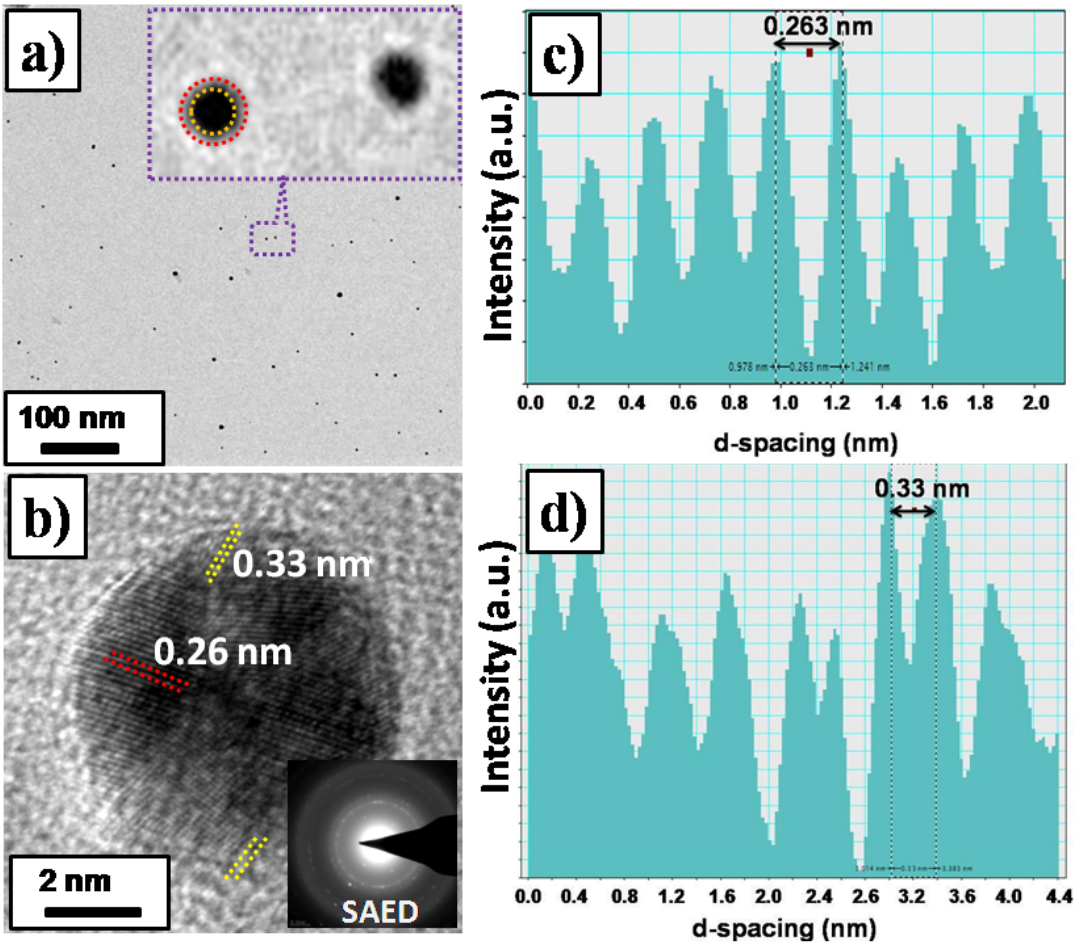

Figure S3. *a) TEM images of well dispersed Au@Gr nanoparticles and inset show the magnified image of the selected portion of a) indicating the formation of Au@Gr core-shell nanoparticles with average size of ~10 nm (core diameter = 8 nm and shell thickness = 2 nm); b) HR-TEM image of Au@Gr core-shell nanoparticles marked with the respective lattice fringes of Au (red lines) and Gr (yellow lines) and inset shows the selected area electron diffraction (SAED) pattern of Au@Gr; c and d) represent the lattice fringe profile of Au (core) and Gr (shell), respectively, indicating the core is Au and shell is Gr.*

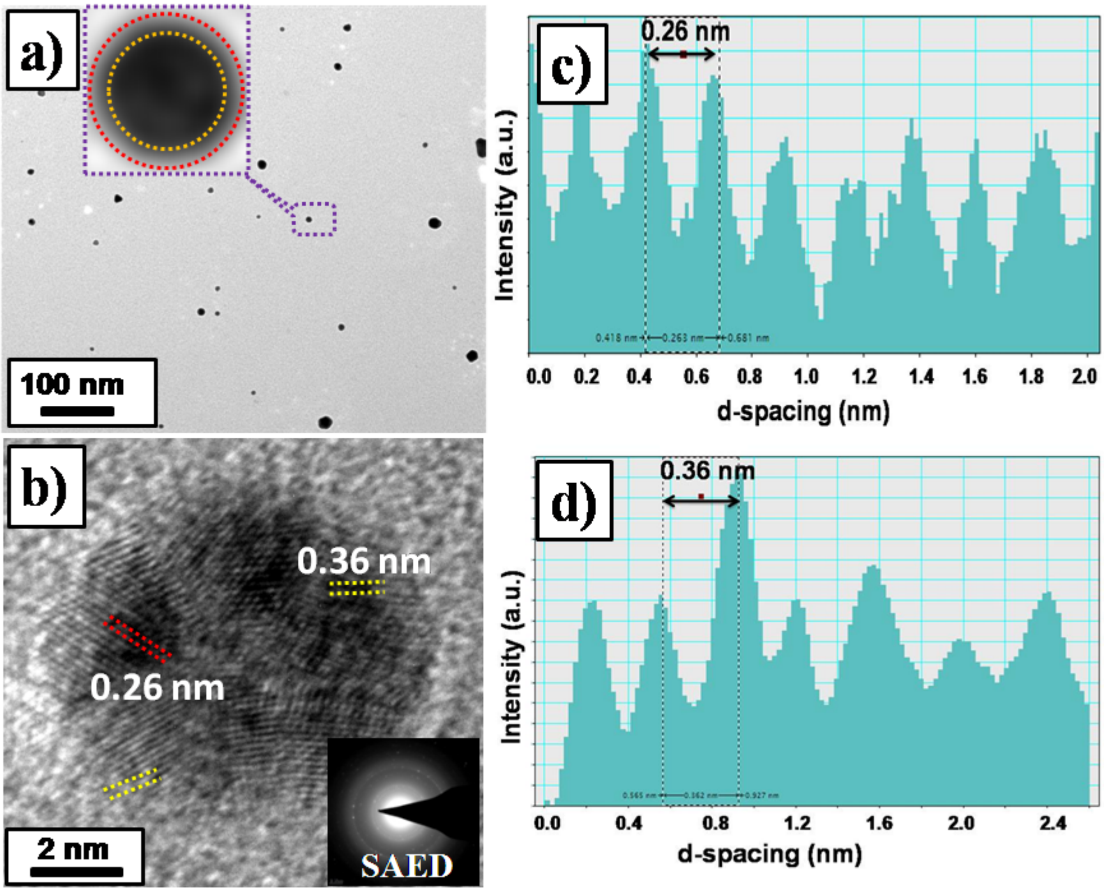

Figure S4. *a) TEM images of well dispersed Au@N-Gr nanoparticles and inset show the magnified image of the selected portion of a) indicating the formation of Au@N-Gr core-shell nanoparticles with average size of ~10 nm (core diameter = 8 nm and shell thickness = ~1-2 nm); b) HR-TEM image of Au@N-Gr core-shell nanoparticles marked with the respective lattice fringes of Au (red lines) and N-Gr (yellow lines) and inset shows the selected area electron diffraction (SAED) pattern of Au@N-Gr; c and d) represent the lattice fringe profile of Au (core) and N-Gr (shell), respectively, indicating the core is Au and shell is N-Gr.*

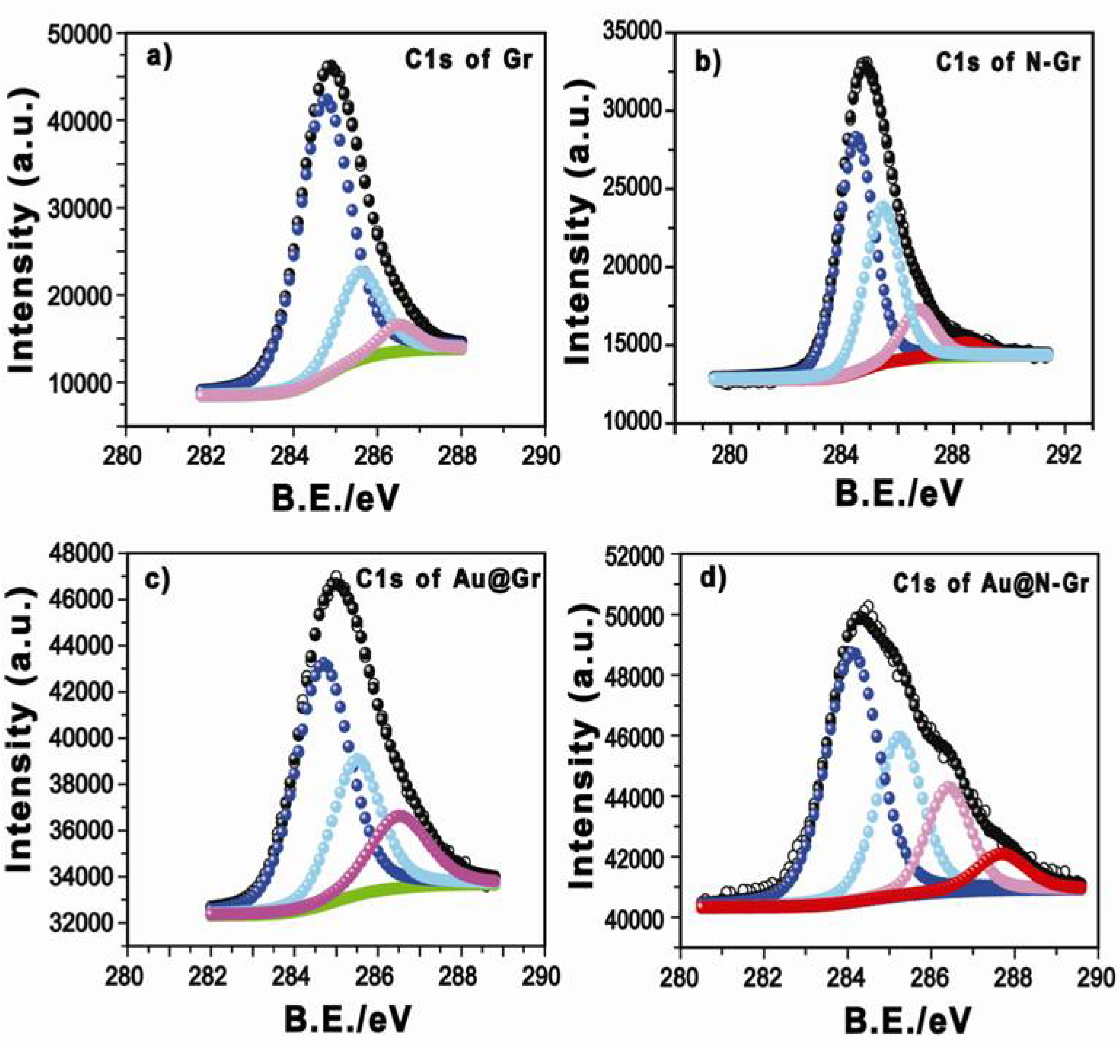

Figure S5. *C1s XP-spectra of Gr (a), N-Gr (b), Au@Gr (c), and Au@N-Gr (d).*

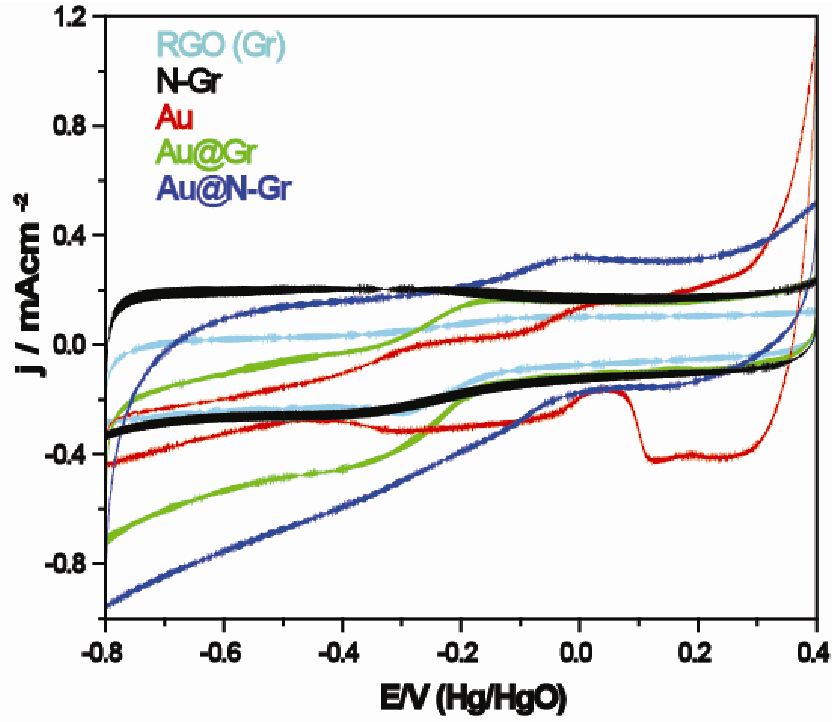

Figure S6. *Comparative cyclic voltammograms taken in* N_2*-saturated 0.1 M KOH electrolyte with a scan rate of 50 mV/s, after 70% iR compensation.*

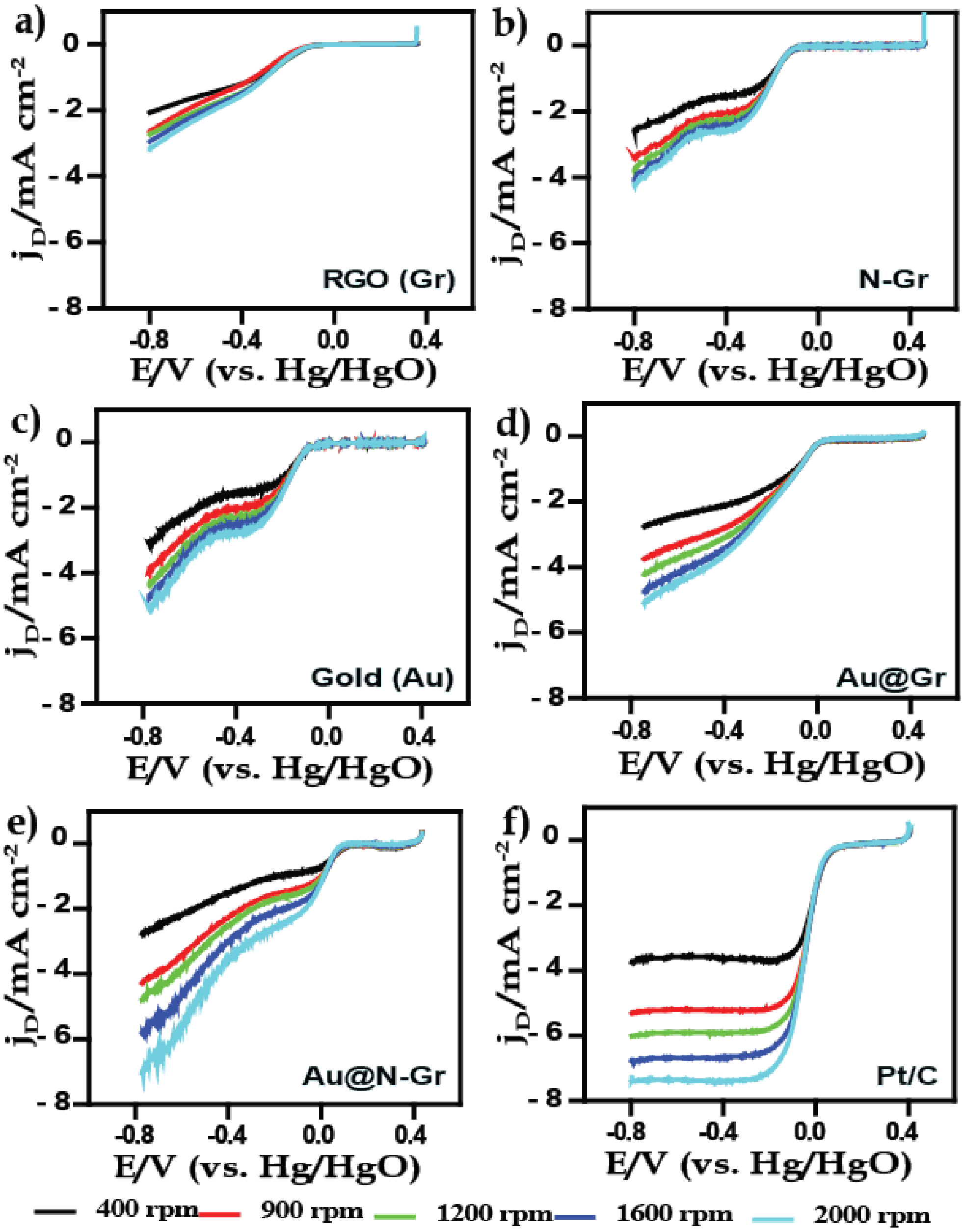

Figure S7. *70% iR compensated hydrodynamic voltammograms of different prepared samples monitored for ORR. Conditions: Scan rate, 10 mV/s; rotation speeds, 400, 900, 1200, 1600, and 2000 rpm; electrolyte,* O_2*-saturated 0.1 M KOH.*

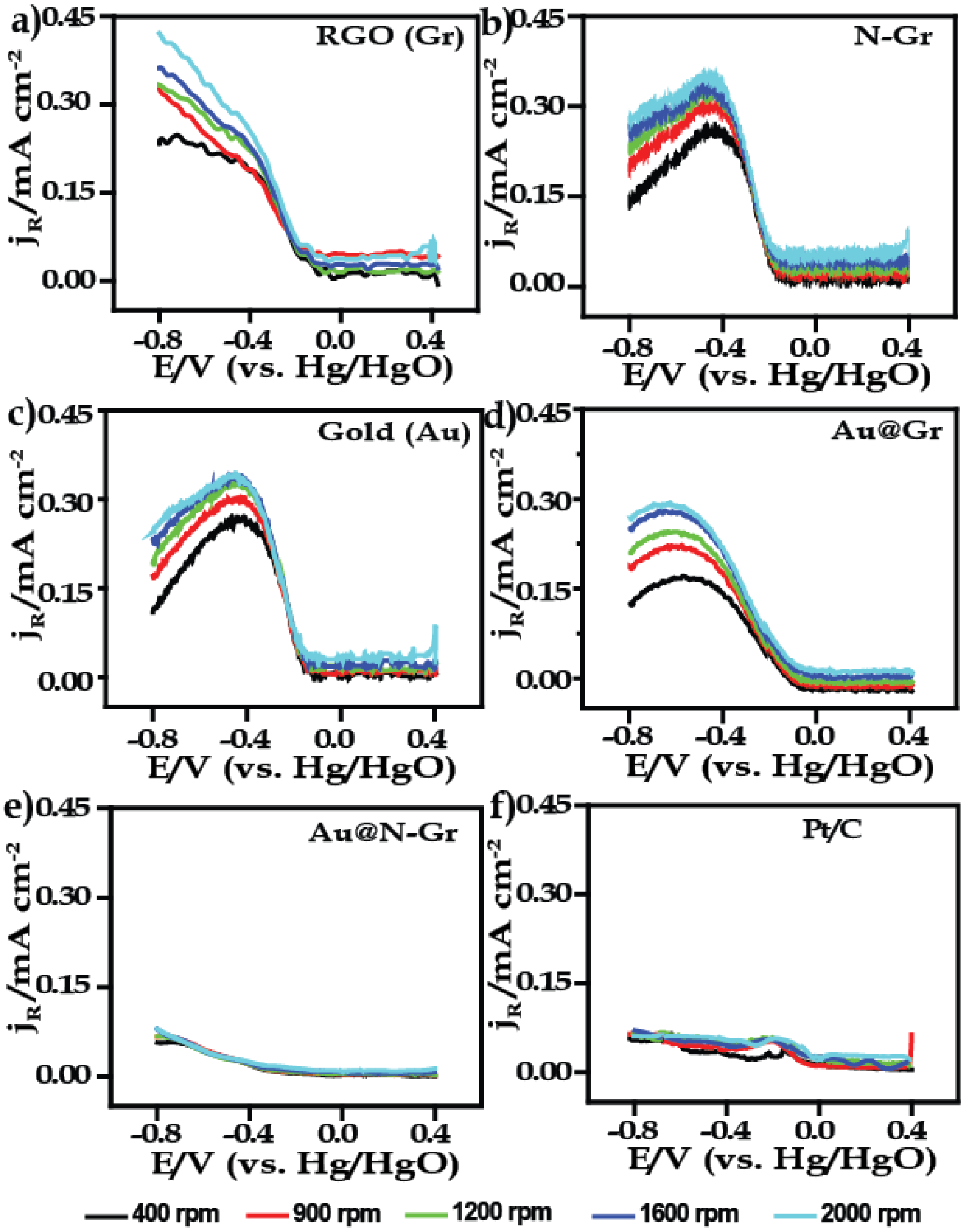

Figure S8. *Current-voltage profile of as prepared samples by monitoring the reaction occurring at a Pt ring electrode, held at 0.6 V (vs. Hg/HgO) during potential scan with varying rotation speeds of RRDE. Conditions: Scan rate, 10 mV/s; rotation speeds, 400, 900, 1200, 1600, and 2000 rpm; electrolyte,* O_2*-saturated 0.1 M KOH.*

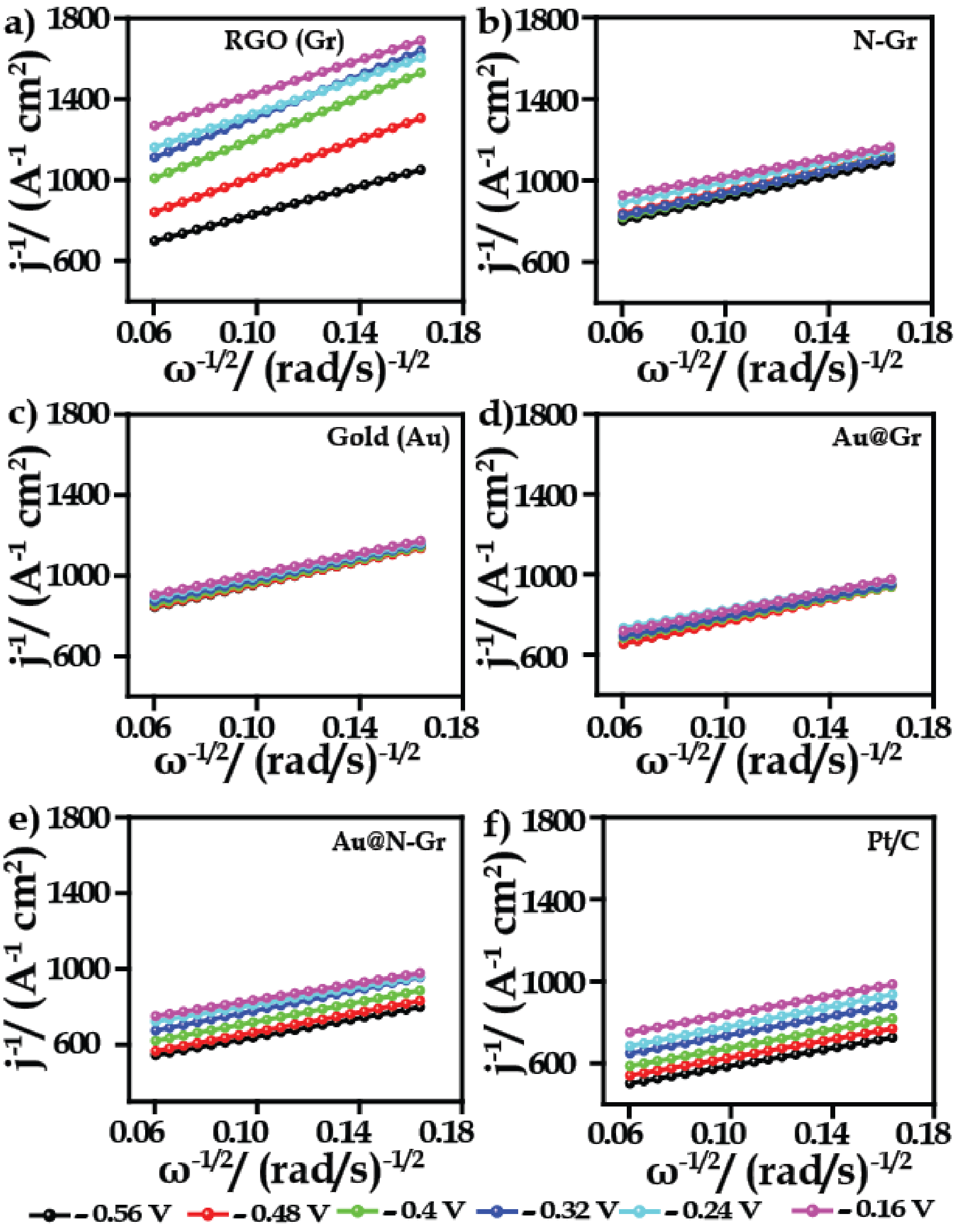

Figure S9. *K-L plots of a) RGO (Gr), b) N-Gr, c) Au, d) Au@Gr, e) Au@N-Gr, and f) Pt/C at different potentials generated from the iR corrected RDE data of Figure S7.*

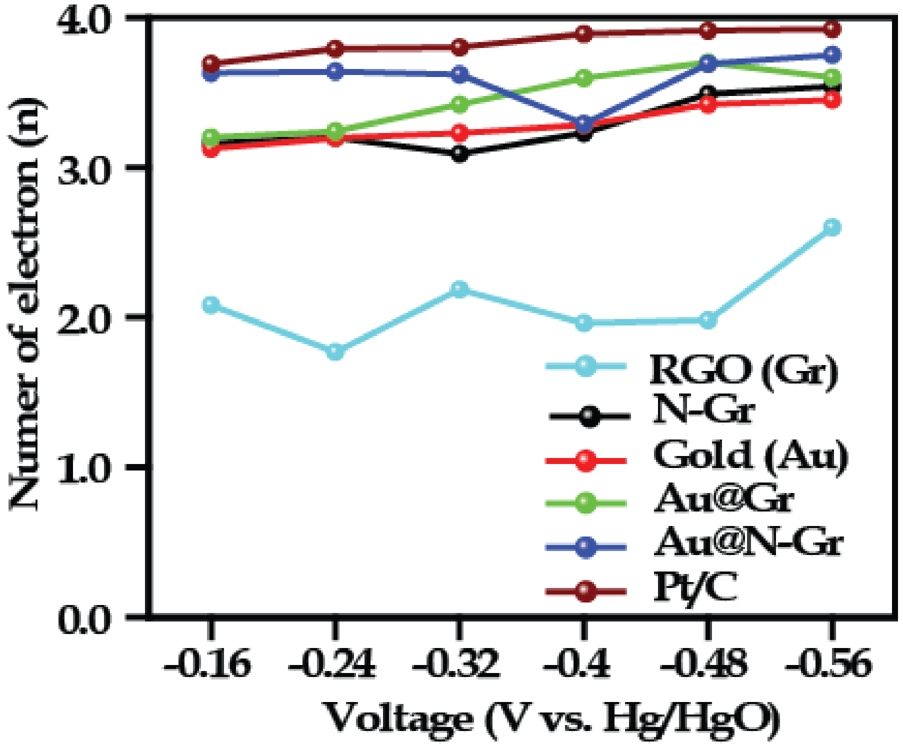

Figure S10. *Number of electron transferred during ORR at different potentials as calculated from the K-L plots.*

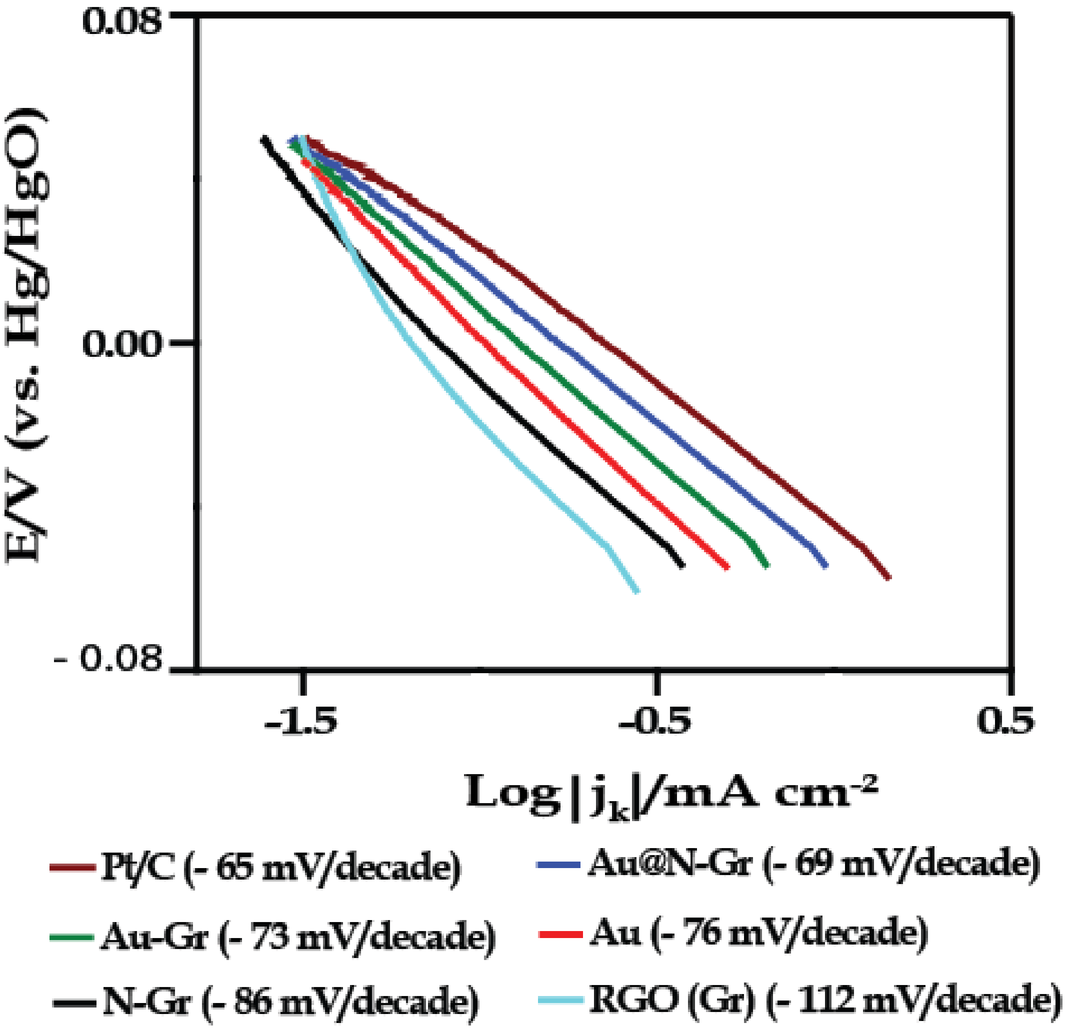

Figure S11. *Comparative mass corrected Tafel plots for ORR obtained from the iR corrected ORR data, at low current density region. Conditions: rotation of electrode, 1600 rpm, scan rate, 10 mV/s. The kinetic current density calculated by RDE analysis is used for generating the Tafel plots.*

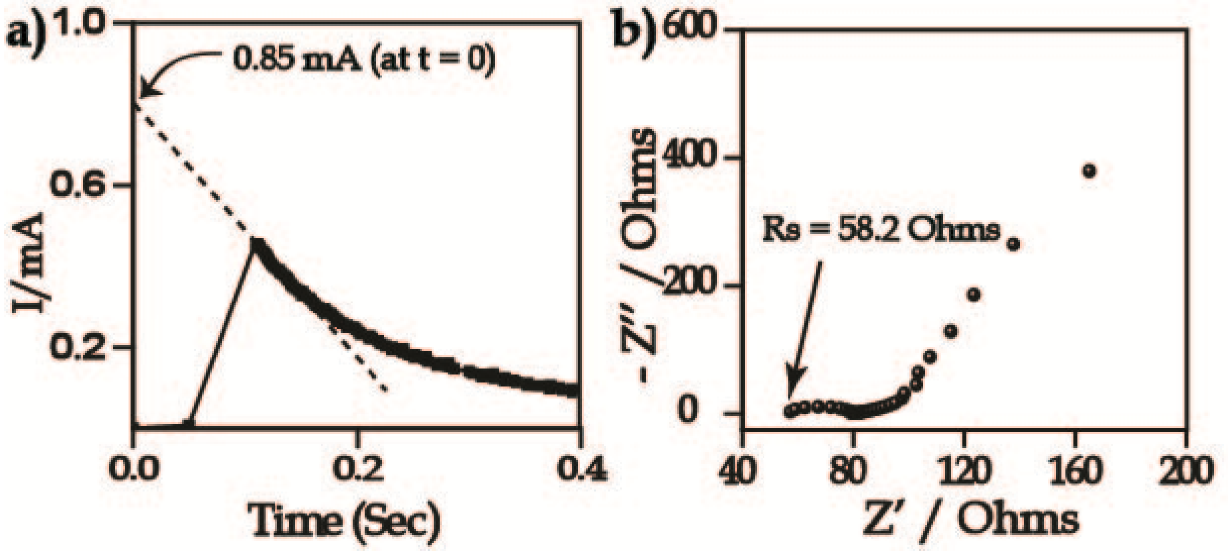

Figure S12. *Determination of uncompensated resistance value by a) positive feedback method, and b) impedance spectroscopy*

Table S1. *Summary of the electrochemical results*

	RGO (Gr)	N-Gr	Gold (Au)	Au@Gr	Au@N-Gr	Pt/C
Electrical conductivity (S/cm)	**0.5**	**1.48**	**2.09**	**6.03**	**9.41**	**--**
Onset potential (V) (Vs. Hg/HgO)	**-0.11**	**-0.06**	**-0.08**	**0.015**	**0.061**	**0.096**
n values @ -0.32 V, from iR free RDE data	**2.18**	**3.17**	**3.24**	**3.49**	**3.69**	**3.89**
Tafel slope from mass-corrected plots (mV/decade)	**-112**	**-86**	**-76**	**-73**	**-69**	**-65**
H_2O_2 % @-0.3 V (vs. Hg/HgO)	**68.7**	**47.7**	**52.2**	**16.5**	**6.5**	**2.9**

References:

1. Marcano, D. C.; Kosynkin, D. V.; Berlin, A.; Sinitskii, Z.; Sun, A.; Slesarev, L. B.; Alemany, W. ; Tour, J. M. *ACS Nano*. **2010**, 8, 4806-4814.