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Introduction

Various low-Pt materials have been extensively investigated as cost-effective oxygen reduction electrocatalysts for polymer electrolyte membrane fuel cells (PEMFCs).1 Despite excellent research progress in this direction, the ultimate target obviously is to make the electrode completely free from Pt. Recently, a number of studies have been focused on developing Pt-free electrocatalysts, and this area has become a hot research topic in the field of fuel cells.² Among these, heteroatom (N, P, B and S) doped electrocatalysts have generated a great deal of research interest.3 Their capability for the oxygen reduction reaction (ORR) originates from the doped heteroatom in a graphitic network, which makes it non-electronneutral and thus favours the molecular oxygen adsorption and eventually the reduction. Nevertheless, here, control of the activity and selectivity of the sites towards the desired ORR pathway involving four-electron (4e⁻) transfer is a daunting

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

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Encapsulation of nitrogen doped graphene on Au nanoparticle (Au@N-Gr) could be accomplished through a water-in-oil emulsion technique, where the emulsion droplets act as 'nanoreactors' and the redox reaction inside the droplets results in the formation of core-shell nanoparticles. The encapsulation of N-Gr on a small guantity of Au (N-Gr : Au wt ratio of 90 : 10) made the N-Gr layer more conductive and active towards electrochemical oxygen reduction reaction (ORR). The enhanced conductivity helped the system narrow down the ohmic overpotential, and direct electronic interactions between the Au and Gr layers brought in a favourable positive shift to the onset potential for ORR. Encapsulation has helped N-Gr reduce the overpotential by \sim 121 mV as compared to N-Gr alone. Apart from this, the oxygen reduction kinetics of Au@N-Gr also appeared to be superior to N-Gr and Au nanoparticles as separate entities due to greater involvement of the preferred 4-electron reduction pathway. At -0.3 V (vs. Hg/ HqO), the percentage of hydrogen peroxide (H_2O_2) (a product formed from the undesirable 2-electron reduction pathway) was found to be 16.5% for Au@Gr, where Au was covered with undoped Gr, which gets reduced to a significantly low level of 6.5% for Au@N-Gr. Au and N-Gr as separate entities give yield of H₂O₂ as 52.2 and 47.7%, respectively. From these, it can be concluded that the coverage of N-Gr on Au helps decrease the yield of H_2O_2 drastically apart from the benefits of synergistic interactions in reducing both ohmic and activation overpotentials.

> task. The doping increases the disorder in the catalyst with a concomitant increase in the number of the active sites for ORR.3,6 The induced disorder and more active sites mainly attributed to the change in spin density and charge distribution of carbon atoms, thanks to the presence of heteroatom at next-door to it.11,12 However, due to the dislocations, the overall electronic conductivity of the catalyst will get altered due to opening of band gap between the conduction and valence bands.^{3,6} Moreover, the nitrogen doping in graphene frameworks shifts the Fermi level above the Dirac point,13,14 and the density of state near the Fermi level gets suppressed.^{15,16} Apart from this, the synthesis method also alters the overall conductivity of the N-doped systems. Gong et al. observed that the conductance of graphene annealed in ammonia atmosphere was lower than that of pristine graphene due to the N-doping in a graphene framework, whereas the N-doping in a nitrogen atmosphere apparently did not alter the electronic properties of graphene.¹⁶ Thus, the material accommodates the heteroatom with some compensation on its inherent electronic conductivity even though the mode of preparation plays a crucial role.¹⁶ In addition, Alfred et al. investigated the oxygen reduction study on graphene, N-doped graphene and non-noble metal (like cobalt) based graphene systems²¹ using DFT method. The authors found



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that the electroreduction of oxygen mainly leads to the formation of H_2O_2 by following the undesirable two electron pathway.

In parallel, Henkelman et al.8 reported that the difference in the Fermi energy of core and shell entities decides the direction of charge redistribution. Generally, the charge gets transferred from the higher to lower Fermi energy.8 Moreover, along with the charge redistribution, the adsorption and desorption rates of chemical species decide the activity of a catalyst. According to the Bronsted-Evans-Polanyi relationship, the energy barrier of reactions is linearly associated to the reaction energy.^{17,18} In general, a chemical species like oxygen binds very strongly with non-noble metals (like Cu, Fe, Co, etc.), with no barrier for dissociative adsorption. On the other hand, noble metals like Pt, Au, etc. bind oxygen weakly and have high barrier for dissociative adsorption.^{6,19} However, in the designing of the kinetic model of the surface chemistry by putting together the relationship between the product binding energy and energy barrier, a maxima in catalytic activity is found at an optimal compromise between the weak product binding energy and reaction barrier.20 Also, Schmickler et al. investigated the importance of gold in alkaline fuel cells with supported evidences from energy calculations.19

In this context, gathering the intrinsic properties of gold and N-doped graphene in a single nanostructure system will be helpful to understand the effect of property modulations in influencing the parameters such as ohmic overpotential, electrical conductivity and oxygen reduction kinetics. Taking the advantage of the difference in the conductivity, electronegativity and Fermi energy of Au compared to carbon, herein, we tried to synthesize a Pt-free electrocatalyst, which can show nearly comparable activity to the 20 wt% commercial Pt/C, without sacrificing the overall conductivity of metal-graphene nanostructures. This is achieved by encapsulating nitrogen doped graphene (N-Gr) on gold (Au) nanoparticle (herein after called Au@N-Gr) all the while keeping the Au concentration very low (10 wt% Au and 90 wt% N-Gr). Here, the role of the N-Gr shell is to reduce oxygen, while the Au core modulates the electronic conductivity⁴ and electrocatalytic activity of the N-Gr shell by triggering synergetic electronic interactions. The study leads to conclusive evidence on the highly influential role played by the core metal species in shifting the ORR kinetics of N-Gr towards the favourable four-electron (4e⁻) pathway. This leads to a reduced content of hydrogen peroxide (H2O2) in alkaline environment apart from its contribution in enhancing the electrical conductivity.

Experimental

Materials

Chloroauric acid (HAuCl₄), graphite, potassium permanganate (KMnO₄), phosphoric acid (H₃PO₄), melamine, sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), silicon oil and hexane were procured from Sigma-Aldrich and used as such without any further purification.

Synthesis of gold@nitrogen doped graphene (Au@N-Gr) electrocatalyst

Gold@nitrogen-doped graphene (Au@N-Gr) core-shell nanostructures were synthesized by simple water-in-oil emulsion technique without using any external reducing and capping agents in a size controlled manner (Scheme 1). Briefly, 4 mg of the as-synthesized nitrogen-doped graphene (N-Gr) was mixed with 2 ml of aqueous solution of 100 mM HAuCl₄ and the mixture was sonicated for 30 min using a bath sonicator to form a homogenous solution. The dispersed solution was added dropwise in previously taken fresh silicon oil (25 ml), under strong magnetic stirring. Furthermore, the reaction mixture was maintained for 5 h under stirring at 750 rpm 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@N-Gr core-shell nanostructures. Further, the water-in-oil emulsion was transferred into a Petri dish, and was kept in an oven at 80 °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@N-Gr core-shell nanostructures were centrifuged at 10 000 rpm for 15 min and the mixture was washed with excess hexane to obtain oil-free Au@N-Gr coreshell nanostructures. In a similar way, gold@graphene (Au@Gr) sample was also prepared by using graphene (Gr), instead of N-Gr, in the above mentioned method (detailed synthesis procedures adopted for preparing Gr, N-Gr, Au nanoparticles, and Au@Gr are given in ESI†).



A well dispersed sample for the high resolution transmission electron microscope (HR-TEM) analysis was prepared by sonicating the catalyst (1 mg) in 5 ml isopropanol solvent. The as prepared sample was drop-coated on a carbon coated 200 mesh Cu grid and was dried under vacuum and images were obtained on FEI, TECNAI G2 F20 instrument operated at an accelerated voltage of 200 kV ($C_{\rm s} = 0.6$ mm, resolution 1.7 Å). X-ray diffraction (XRD) patterns were recorded on PANalytical instrument using Cu-K_{α} radiation ($\lambda = 1.54$ Å) at a scanning rate of 2° min⁻¹ and a step size of 0.02° in 2θ . X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Micro Tech ESCA 300° instrument at a pressure of >1 \times 10^{-9} Torr (pass energy: 50 eV, electron take off angle: 60° and the overall resolution: \sim 0.1 eV). Raman analysis of synthesized electrocatalyst was performed on an HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) using 632 nm green laser (NRS 1500 W) in order to obtain the graphitic, and defective nature of the carbon.

Electrochemical studies

A Bio-Logic instrument was used to investigate the electrochemical properties by cyclic voltammetry (CV) and rotating ring disc electrode (RRDE) studies (Pine Instruments) in a conventional three-electrode test cell with Hg/HgO as the reference electrode and a platinum foil as the counter electrode. The working electrode was prepared by sonicating 5 mg of the catalyst in 1 ml 3:2 EtOH: H₂O mixture and drop coating the slurry on a previously polished (by using 0.3 µm alumina slurry) RRDE electrode consisting of a GC disk (6 mm diameter) and a Pt ring (9 mm outer diameter and 7.5 mm inner diameter) to achieve constant 20 µg mass loading in all the cases. 5 µl of 0.01 wt% Nafion® solution was applied on the whole surface of the disk electrode to yield a uniform thin film. Followed by the coating, the electrode was dried for 4 h under IR-lamp and was used as the working electrode for the electrochemical investigations. An aqueous solution of 0.1 M KOH, de-aerated with N2 gas, was used as an electrolyte for the CV and RRDE studies. Moreover, to get the current density plots, current was divided by the geometrical area of the electrode. For the RRDE measurements, the collection efficiency (N) of the electrode was determined by a standard ferrocene couple by measuring separately the disk and ring current and the ratio of disk current to ring current gave the collection efficiency (N), which is nearly equal to 0.37. The oxygen reduction polarization data was also analyzed with standard rotating disk electrode (RDE) equations, Koutecky-Levich (K-L) plots and mass-transport corrected plots, by separately collecting the RDE data. RDE data was collected after applying 70% iR compensation. For the ohmic correction, the uncompensated resistance contribution was measured by impedance spectroscopy and positive feedback method,²² and the value was found to be 58 Ω in both the cases (details of the calculation and the corresponding graphs are given in ESI, Fig. S12[†]).

Results and discussion

Basically, the emulsion droplets will act as a "nanoreactor", where the actual reaction takes place. During the time bound heating process, water starts evaporating, and simultaneously, the metal ion and N-Gr undergo mutually assisted redox reaction,⁵ leading to the formation of Au@N-Gr core-shell nano-structures. Recently, Z. Kang *et al.*⁵ reported that, Gr gets distributed at the water-oil interface, due to the larger surface area and flexible properties of it. Moreover, three kinds of energies *viz.*, surface energy (E_s) created by bending of Gr layers, van der Waals forces (E_v) between the Gr sheets, and gravitational potential energy (E_g) of metal nanoparticles, will decide the final structure of the metal-Gr nanostructures. However, for the formation of the core-shell structures, E_v is expected to dominate over the E_s and E_g .

Fig. 1a and c show the TEM images of the well dispersed Au@Gr and Au@N-Gr core–shell nanostructures, respectively. The inset shows the magnified views of the selected particles, displaying the core–shell features with an average particle size of \sim 10 nm. The HR-TEM images of Au@Gr and Au@N-Gr are given in Fig. 1b and d, respectively. The *d*-spacing values of the core and shell have been calculated from the lattice fringes profiling (Fig. S3 and S4, ESI[†]), which gives 0.26 nm for the core for both Au@Gr and Au@N-Gr, which is attributed to Au. In the case of the shell, the *d*-values for Au@Gr and Au@N-Gr are 0.33 and 0.36 nm, respectively, which clearly indicate the coverage of the Au core in the corresponding samples by Gr and N-Gr. It has



Fig. 1 TEM images of (a) Au@Gr nanoparticles and the inset gives the magnified image of the selected area highlighting the core-shell structure of the particles, (b) HR-TEM image of Au@Gr core-shell structure with lattice fringes (inset shows the SEAD pattern of Au@Gr), (c) Au@N-Gr nanoparticles and the inset highlights the core-shell feature of the magnified particles and (d) HR-TEM image of Au@N-Gr core-shell structure with lattice fringes (inset shows the SEAD pattern of Au@N-Gr).

been reported that N-doping leads to an increase in the *d*-value due to incorporation of N-atoms in the graphene framework, which leads to the lattice expansion.⁶ Insets of Fig. 1b and d show the selected area electron diffraction (SAED) patterns of Au@Gr and Au@N-Gr, respectively.

Fig. 2a shows the comparative X-ray diffraction (XRD) of Gr, N-Gr, Au, Au@Gr and Au@N-Gr. In all the cases except Au, a strong reflection at $2\theta = \sim 26.5^{\circ} \pm 0.3^{\circ}$ is observed which is attributed to the G (002) graphitic plane. In case of N-Gr and Au@N-Gr, the same peak is shifted to lower 2θ values ($\sim 25^{\circ}$) with broadening, indicating the incorporation of nitrogen atom in the graphene framework (Fig. 2b). Compared to N-Gr, the shift in the peak position in the case of Au@N-Gr is more and a similar trend, even though less pronounced, is also observed between Gr and Au@Gr. These shifts are attributed to the interaction of Au with the Gr shell, which is in well agreement with the calculated *d*-spacing values from TEM.

Apart from this, Raman spectroscopy serves as a powerful and non-destructive tool for the characterization of carbon based materials. A typical Raman spectrum of Gr shows a peak at 1345 cm⁻¹ (D band), which corresponds to the breathing mode of *K*-point photons of A_{1g} symmetry allied with vibrations of sp³ carbon atoms. Furthermore, a peak at 1590 cm⁻¹ (G band) has also been identified, which is attributed to the inplane vibration of sp² carbon atoms in hexagonal lattice (Fig. 2c).⁹ Explicitly, the first-order Raman scattering processes are responsible for the G-band, whereas the double-resonance process and second order scattering results into the 2D and D bands.⁶ Usually, the intensity ratio of D to G (I_D/I_G) is used to compare the structural order between the crystalline and amorphous graphitic systems. In the present case, the I_D/I_G

b

N-Gr

RGO (Gr)

d

Au@N-G

Au@Gr

(220) (311

70 80

N-Gr

Au@Gr

Au@N-G

3000

RGO (Gr)

G(101)

(200)

40 0/Deg

ID/IG = 0.7

ID/IG = 0.65

 $I_{D}/I_{G} = 0.64$

I_G = 0.62

2500

2000

Raman shift/cm⁻¹

G-band

Intensity (a.u.)

с) а) ^{D-ba}

(a.u.)

Intensity (

d)

1000

Au@N-G

Au@G

N-G

RGO (Gr

20 **20/Degree**

N-Gr

0.0 EV

Au@N-Gr

RGO (Gr) (0.50089 S/cm

(1.48612 S/cm) (2.09205 S/cm) (6.03389 S/cm)

(9.4145 S/cm)

1.0

0.5

Au

Fig. 2 Comparative (a) full range XRD, (b) magnified view of the G (002) peak of the XRD showing a shift in the peak position after N-incorporation in the graphene framework, (c) Raman spectra with the corresponding I_D/I_G ratios, and (d) electrical conductivity of the samples.

-1.0

-0.5

ratios of the prepared samples follow the order: Gr (0.70) > N-Gr (0.65) > Au@Gr (0.64) > Au@N-Gr (0.62).

The slight decrease in the I_D/I_G ratio from Gr to N-Gr is due to the incorporation of nitrogen in the Gr framework at 900 °C, where the oxygen functionalities of Gr might have reduced. Furthermore, the I_D/I_G ratio is still decreased when the Gr deposition occurs over Au and this is attributed to the expected interpenetration of the lattice fringes of the component phases.^{6,8} Additionally, the 2D bands of Gr in Au@Gr and Au@N-Gr are clearly shifted to a higher wave number, due to the interaction of Au with Gr/N-Gr, leading to the electron transfer from the core to the shell.^{6,8}

An understanding on the electronic interactions in the materials has been obtained by X-ray photoelectron spectroscopy (XPS). Fig. 3a and b show the deconvoluted N1s spectra of N-Gr and Au@N-Gr, which reveal the presence of four types of nitrogen namely pyridinic-N, pyrrolic-N, graphitic-N and Noxide, with a total N content of \sim 3.5%. Basically, the nitrogen which possesses a lone pair of electrons is known to enhance the electron-donor property of the catalyst.^{6,8} As a result, it can weaken the O-O bond via the bonding between oxygen and nitrogen and/or the adjacent carbon atom, and in turn can facilitate the reduction of oxygen.6,7 Fig. 3c and d show the Au4f spectra of Au@Gr and Au@N-Gr. The higher shift in the binding energy of the Au4f peaks is attributed to the interaction of Au with the Gr/N-Gr shell. The interaction of the metal with carbon is still a matter of debate. Nevertheless, as reported, the delocalized p-orbital electrons (π electrons) of carbon overlap with the d-orbital of Au, indicating the partial covalent bonding characteristics.8 This could be due to the d-orbital electron of the metal is shared with a π^* anti-bonding orbital of the carbon. Fig. S5† shows the C1s spectra of Gr, N-Gr, Au@Gr and Au@N-Gr, which have been deconvoluted as per their spin-orbit splitting. The C1s spectra (Fig. S5[†]) of Au@Gr and Au@N-Gr



Fig. 3 (a & b) N1s spectra of N-Gr and Au@N-Gr, respectively; (c & d) Au4f deconvoluted XP-spectra of Au@Gr and Au@N-Gr, respectively.

show higher shifts in the binding energy compared to the C1s spectra of Gr and N-Gr, which is credited to the interaction of Au with the surface layer of Gr/N-Gr.

The change in the electronic configuration and interaction of Au with the Gr/N-Gr shell is reflected in the electrical conductivity as well (Fig. 2d). The measured conductivity follows the order: Au@N-Gr (9.41 S cm⁻¹) > Au@Gr (6.03 S cm⁻¹) > Au (2.09 S cm⁻¹) > N-Gr (1.48 S cm⁻¹) > Gr (0.50 S cm⁻¹). The enhancement in the conductivity of Au@N-Gr and Au@Gr originates from the Au core and its interaction (d π -p π backbonding) with the surface carbon, which improves the interfacial charge transfer.^{6,8} The shift in Raman spectra, as explained before, substantiates this kind of interfacial charge transfer from the Au core to the Gr shell. Moreover, the electronegativity of C (2.55) is slightly higher than Au (2.54), which is a determining factor in deciding the direction of the charge transfer.

This enhancement in the conductivity and lattice modulation of the Gr layer are also expected to bring in favorable changes in the ORR activity of the system. A preliminary screening of the electrocatalytic activity of all the samples towards ORR in alkaline media was carried out by cyclic voltammetry (CV). More specifically, nitrogen and oxygen saturated 0.1 M KOH aqueous solution was used as the electrolyte and current-voltage curves were recorded at a typical scan rate of 50 mV s⁻¹. A catalyst loading of 20 µg on a glassy carbon disk electrode was maintained in all the cases. Accordingly, Fig. S6† shows the comparative CV profiles of Gr, N-Gr, Au, Au@Gr, and Au@N-Gr taken in an N₂-saturated 0.1 M KOH. Furthermore, the capacitive nature of Au@Gr and Au@N-Gr as compared to the Au nanoparticles indicates that Au is encapsulated by Gr/N-Gr (Fig. S6[†]). Moreover, the gold-oxide peak at \sim 0.1 V (vs. Hg/ HgO) is totally absent in the case of Au@Gr and Au@N-Gr, which also confirms the coverage of Au with Gr/N-Gr.

A quantitative estimation of the actual kinetics of ORR and H_2O_2 formation is made by recording hydrodynamic voltammograms using a rotating ring disk electrode (RRDE) set-up at a scan rate of 10 mV s⁻¹ in O₂-saturated electrolyte (Fig. S7 and S8†). The measurement of the current was done at various electrode rotation speeds of 400, 900, 1200, 1600 and 2000 rpm, by applying a constant ring potential (E_R) of 0.6 V (*vs.* Hg/HgO). The rotation of the working electrode is expected to minimize the diffusion limitation effect.⁸ As shown in Fig. S7,† from 400 to 2000 rpm, the potential regions under kinetic and oxygen mass transport limiting control are becoming more prominent and the current density increases.

Moreover, a comparison of the hydrodynamic voltammograms is performed at 1600 rpm with a scan rate of 10 mV s⁻¹ and by keeping the ring at constant potential ($E_R = 0.6$ V, *vs.* Hg/ HgO). The onset potential values (*vs.* Hg/HgO) for ORR are found in the order of Gr (-0.11 V) < N-Gr (-0.06 V) < Au (-0.08V) < Au@Gr (0.015 V) < Au@N-Gr (0.061 V) < Pt/C (0.096 V). Thus, among the prepared samples, Au@N-Gr has shown significantly higher ORR activity compared to the rest of the samples. It is clear that the encapsulation on Au has helped N-Gr to reduce the overpotential. Even with the commercial Pt/C catalyst, the overpotential is higher by only 35 mV. However, the reduction of O₂ can be accomplished *via* a 4-electron (4e⁻) pathway leading to H_2O or a 2-electron (2e⁻) route giving H_2O_2 . The latter one decreases the cell potential in a PEMFC and accelerates the degradation of membrane and catalyst with the intervention of H_2O_2 . Thus, the 4e⁻ pathway is desired in ORR, but it is well documented that carbon based electrocatalysts show high yield of H_2O_2 compared to the Pt based ones.⁷

To understand the actual mechanism, RRDE investigation was carried out by keeping the ring potential to 0.6 V (vs. Hg/ HgO). The electron pathway of the electrocatalysts towards ORR was evaluated by calculating the yield of H_2O_2 by using eqn (1).¹⁰

$$H_2O_2\% = \frac{200 \times I_R/N}{I_D + I_R/N}$$
(1)

$$n = \frac{4I_{\rm D}}{I_{\rm D} + I_{\rm R}/N} \tag{2}$$

where, $I_{\rm R}$ = faradaic ring current; $I_{\rm D}$ = faradaic disc current; N = collection efficiency (0.37); n = number of transferred electron; 200 = (2 × 100) where, 2 stands for the actual number of electron involved during H₂O₂ formation.

The ring current in Fig. 4a and S8,† which corresponds to the formation of H_2O_2 , shows an increase in its yield in the kinetic region and exhibits a gradual increase in the diffusion region (<-0.2 V, *vs.* Hg/HgO). Fig. 4c shows the change in the H_2O_2 percentage with respect to the potential during the ORR process. At -0.3 V (*vs.* Hg/HgO), Au@Gr gives a yield of 16.5% for H_2O_2 which gets reduced to 6.5% for Au@N-Gr. On the other hand, the H_2O_2 yield of RGO and N-Gr are 68.7 and 47.7%,



Fig. 4 (a) Comparative hydrodynamic voltammograms for ORR and H_2O_2 oxidation performed in an O_2 -saturated 0.1 M KOH solution at 1600 rpm with a scan rate of 10 mV s⁻¹ and at a constant ring potential ($E_R = 0.6$ V, vs. Hg/HgO), (b) highlighted portion of the selected area of (a), indicating the higher positive potential for Au@N-Gr compared to Au and N-Gr, (c) H_2O_2 percentage calculated from the ring current–potential curves recorded in (a) at 1600 rpm using different samples coated on the electrode in an O_2 -saturated 0.1 M KOH (figure represents the change in H_2O_2 percentage with respect to the potential) and (d) number of electron transferred during the ORR study as calculated by using eqn (2).

respectively. Moreover, Au itself gives 52.2% of H_2O_2 . This means that when Au is covered with Gr and N-Gr, the H_2O_2 % from Au has came down by 68 and 87%, respectively (Fig. 5). The enhanced ORR activity and the reduced H_2O_2 yield for Au@N-Gr is attributed to the favourable push towards the nearly $4e^-$ pathway through the mutual interactions of the metallic core with the non-metallic shell (Fig. 4d).

Furthermore, to substantiate the obtained results from RRDE, mainly the transferred electron number and its co-relation with the H₂O₂ formation during ORR, we have separately examined the disk current data after iR compensation (70%). The obtained RDE plots (Fig. S7†) have three different regions, namely, diffusion-controlled region (\sim -0.3 to -0.8 V), mixed diffusion-kinetic limitation region (-0.3 to -0.1 V) and kinetic region or Tafel region (\geq -0.1 V). The obtained current density (*j*) is a combination of diffusion-limiting (*j*_L), film diffusion (*j*_f) and kinetic (*j*_k). However, in an actual practice, the amount of Nafion used to bind the catalysts on the electrode surface is significantly very low and, hence, the film diffusion resistance can be negligible. Hence, the *j*_f term can be neglected, and the final kinetic parameters can be analyzed by considering the K–L equations:

$$1/j = 1/j_{\rm L} + 1/j_{\rm k} \tag{3}$$

$$1/j = 1/B\omega^{1/2} + 1/j_k \tag{4}$$

where,

$$B = 0.62 n F A C_0^* D_2^{2/3} v^{-1/6}$$

$$j_{\rm k} = nFAkC_0^*$$

where, *j* is the measured current density, j_k and j_L are the kinetic and diffusion-limiting current densities, respectively. ω is the angular rotation ($\omega = 2\pi f/60$, *f* is rotation speed), *F* is the Faradays constant (*F* = 96 500 C), *n* is the number of electron transferred during ORR, C_0^* and D_0 are the O₂ bulk concentration (1.22 × 10⁻⁶ mol cm⁻³) and diffusion coefficient of O₂ (1.9 × 10⁻⁵ cm² s⁻¹), respectively, ν is the kinematic viscosity of electrolyte (0.01 cm² s⁻¹) and k is the electron transfer rate constant.

The total current obtained under various rotating rate is plotted in the form of current density (j^{-1}) versus angular rotation ($\omega^{-1/2}$) and a straight line with good linearity has been obtained in Fig. S9[†] at different potentials. The slopes remain approximately constant over the potential range from -0.16 to -0.56 V (vs. Hg/HgO) for Pt/C, Au@N-Gr and Au@Gr, which suggest that the electron transfer numbers for ORR at different electrode potentials remain similar in these systems. However, slight deviations in the slopes with potential have been noticed in the case of Au, Gr and N-Gr, which is in accordance with the RRDE results. Linearity and parallel behaviour of the plots are usually taken as an indication of first-order reaction kinetics with respect to the concentration of dissolved oxygen. Moreover, the comparative K-L plots are shown in Fig. 6. The number of electron exchanged during ORR for each catalyst has been deduced from the slope of the straight lines. The calculated nvalues for Pt/C, Au@Gr and Au@N-Gr fall in the range of \sim 3.4 to 4, whereas, in case of Gr (RGO), N-Gr and Au the value ranges from 2.1 to 3.4 (Fig. S10[†]), which is in well harmony with the results obtained from RRDE. The results thus indicate that Au@Gr and Au@N-Gr reduce the oxygen molecule into water, whereas, the *n* values of Gr (RGO), N-Gr, and Au are showing that oxygen molecule gets reduced with the formation of higher amounts of H₂O₂ compared to the core-shell structures.

The mass transport (mass diffusion) corrected Tafel plots (*E vs.* log $|j_k|$) are shown in Fig. S11[†] for the entire synthesized samples along with 20 wt% Pt/C. The measured current values were corrected for diffusion to give kinetic current (j_k) in the mixed activation–diffusion region, as calculated from eqn (5).²³

$$j_{k} = \frac{j \times j_{L}}{j_{L} - j} \tag{5}$$



Fig. 5 Calculated hydrogen peroxide percentage over the various systems measured at -0.3 V (vs. Hg/HgO).



Fig. 6 Comparative Koutecky–Levich (K–L) plots at -0.32 V (vs. Hg/ HgO) obtained from the iR-free RDE data.

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where, $j_{\rm L}//(j_{\rm L} - j)$ is the mass transfer correction factor. This equation is valid only for the first order kinetic reactions. The Tafel slopes for Pt/C and Au@N-Gr are -65 and -69 mV per decade, respectively. However, Gr, N-Gr, and Au show higher Tafel slope compared to Au@N-Gr (Table S1, ESI†). The Tafel slope is an indication of the actual mechanism on the electrode surface, which can be co-related with the changing nature of the adsorbed O₂ species and its coverage variation with respect to potential. Moreover, the higher Tafel slope of Gr, N-Gr and Au compared to Au@N-Gr gives a judgment of decreased ORR rate, which may be due to the insufficient coverage of adsorbed intermediates. In contrast, the core-shell structures show nearly same Tafel slope values, attributed to the similar adsorption mechanism and coverage of the adsorbed species and subsequently its effective reduction.²⁴

The mass-transport corrected plots have thus given additional information of improved kinetic current for Au@N-Gr in comparison to all other synthesized samples. The calculated n value from K-L plots and mass-transport corrected results support the obtained RRDE results. Moreover, the change in the nature of RDE curve for Gr, N-Gr and Au compared to Pt/C, may be due to the less number of electrons involved during ORR, which is directly reflected from the yield of H₂O₂ and Tafel slopes as well. In contrast to this, the Au@N-Gr core-shell has shown better activity towards ORR with favourable electron pathway. Overall, the better ORR activity calculated from the iR compensated RDE data and reduced H2O2 yield for Au@N-Gr can be attributed to the healthy talk between the core metal with the covered N-Gr shell. The interaction of the phases through the transfer of electrons from the core to shell due to the π backbonding effect, further helps to improve oxygen adsorption prior to its reduction.

Conclusions

We have successfully synthesized an efficient core-shell structured electrocatalyst possessing N-Gr as the shell and Au nanoparticle as the core (Au@N-Gr) through a simple water-inoil emulsion technique. The process involves milder experimental conditions and very easy workups, concurrently guarantees distinct core-shell features of the metal-graphene nanoparticles. The system shows enhanced electrical conductivity and significantly reduced overpotential for ORR compared to N-Gr and even Au as independent entities. Apart from this, the study reveals the critical role played by a highly conducting metal core, in its low concentration, in influencing the active sites located at the shell layer to shift the reaction kinetics to the favorable $\sim 4e^{-}$ reduction pathway. Thus, the pertaining issue of the high ohmic drop on the heteroatom doped system could be effectively tackled here. Such property modulations have far reaching effects in devising active cost-effective electrodes for fuel cells and other potential electrochemical devices.

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