Nitrogen-doped Graphene Interpenetrated 3-D Ni-Nanocage: Efficient and Stable Water-to-Dioxygen Electrocatalyst

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Herein, we report synthesis of nitrogen-doped graphene (NGr) interpenetrated 3-D Ni-nanocage (Ni-NGr) electrocatalyst by simple water-in-oil (w/o) emulsion technique for oxidation of water-to-dioxygen. Correlation of adsorption of NGr and subsequent interpenetration through the specific surface plane of nickel particles as well as concomitant interaction of N, C, with Ni at a nano-regime have been investigated. Apart from the benefits of the synergistic interactions between Ni, N, and C, the overall integrity of the structure and its intra-molecular connectivity within the framework help to achieve better oxygen evolution characteristics at a significantly reduced overpotential. The engineered Ni-NGr nanocage displays a substantially low overpotential of ~290 mV at practical current density of 20 mA/cm² in 0.1 M KOH. In comparison, NGr and Ni-particle as separate entities give overpotentials of ~570 and ~370 mV under similar conditions. Moreover, the long term stability of Ni-NGr has been investigated by anodic potential cycling for 500 cycles and observed an 8.5 % increment in the overpotential at 20 mA/cm². Additionally, chronoamperometric test has been performed for 15 h at 20 mA/cm², which highlight the better sustainability of Ni-NGr in the actual operating condition. Finally, the quantitative estimation of evolved oxygen has been monitored by gas chromatography and is found to be 70 mmol/h/g of oxygen, which is constant in second cycle as well.

Introduction

Oxygen evolution reaction (OER) is gaining substantial attention due to its growing importance in several energy conversion and storage devices, such as metal-air batteries, water splitting, etc. The water splitting reaction proceeds via two half reactions: the anodic OER and the cathodic hydrogen evolution reaction (HER). The anodic oxidation reaction, i.e. OER, is more complicated as it involves a four electron oxidation path in which two water molecules get oxidized to form one oxygen molecule. Hence, the overall efficiency of electrolytic water splitting is mainly held back due to the higher anodic overpotential of OER. Consequently, development of promising OER electrocatalyst is a challenging task than the HER catalysts. The oxides of ruthenium and iridium have been currently considered as optimal electrocatalysts having efficient OER activity. However, even these catalysts operate with overpotential higher than 200 mV at a practical current density of 10 mA/cm². The 10 mA/cm² is the current density required to achieve the splitting efficiency of 10% with one sun illumination for solar-to-fuel conversion. However, the cost and scarcity are the major challenges of these systems, which hamper the prospects of their commercialization. Moreover, efficient OER electrocatalysts have great urge in the field of sustainable energy devices in order to maintain high overall efficiencies of the systems where multiple processes are integrated to meet the efficiency requirements and challenges.

A review of literature suggests that multi-metallic structures of Co, Ni, Fe, Ru-Co, Ir-Ni, have been widely explored for OER. Moreover, the nickel based electrocatalysts (Ni-Co, Ni-Mo, or the spinels like NiCoO₂, etc) have been reported as active catalysts for multiple reactions, including OER and ORR in alkaline medium and as better oxidation electrocatalysts for alcohol and amine. However, stability is the major concern in the way of the real commercialization of these OER catalysts. Moreover, the inter- and/or intra-metallic interaction within the structure has not been explored. Along with this, the synthesis techniques like sputtering, thermal decomposition, immersion process, etc make the processes less viable for scale-up. In conjunction, the surface passivation, corrosion of metal and support and degradation of materials lead to performance loss during long-term tests. Recently, Ni-based multi-metallic heterostructures (oxides, hydroxides etc.) have been introduced as potential substitutes to the precious metal based electrocatalysts. These morphologies reveal beautiful geometry and they also have high surface area and voids, which pave their use as electrocatalysts in the field of energy devices. Unfortunately, the limited-localized electronic interaction of these structures with support material (carbon) causes carbon corrosion, and eventually, the inherent structural properties get disturbed during the long-term stability. In addition, the separate N-doped graphene (NGr) or metal-decorated NGr/Gr may not be a good solution due to its limited electronic interaction with/within the framework and have low molecular accessibility. Specifically, Ni, Fe etc. decorated on the NGr shows the innate carbon interpenetration property.

Therefore, systematically controlling the reaction parameters during synthesis could be possible to get new structured catalyst. Hence, dispersing NGr and Ni in an aqueous nanodroplet, and advantage of the dissolution property of one component into the other trigger the solid-state reaction and eventually leads to the formation of new morphologies with precise control on the size of the particles. We have observed that the reaction between Ni and NGr in nano-droplet leads to the formation of Ni-NGr nanocage structures possessing unique 3-dimentional (3-D) architecture. The overall structural and electronic modulations acquired by the new morphology help
the system to function as an efficient OER catalyst which display significantly reduced overpotential for the reaction.

**Experimental**

**Materials and methods**

Nickel chloride (NiCl₂), graphite, phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄), potassium permanganate (KMnO₄), melamine, and sodium borohydride (NaBH₄) were procured from Sigma-Aldrich. Hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), silicon oil and hexane were procured from Thomas Baker. All the chemicals were used as such without any further purification.

**Synthesis of Ni-NGr nanocage structures**

For the synthesis of the Ni-based nanocage structures, a homogeneous mixture of NGr (4 mg) and aqueous solution of nickel chloride (2 mL, 100 mM) was obtained by sonicating the mixture for 30 min using a Branson bath sonicator. This well dispersed solution was added drop-wise in previously taken fresh silicon oil (25 ml), under strong magnetic stirring (750 rpm) at room temperature. Moreover, the reaction mixture was maintained for 5 h at room temperature to get a uniform distribution of the emulsion droplets. Further, the water-in-oil emulsion was transferred into a Petri dish, and was kept in an oven at 80 °C for 80 h. The formed Ni-NGr nanocage structures were centrifuged at 10000 rpm for 15 min and were washed several times with hexane to remove the silicon oil and the material was dried under a lamp. Furthermore, to understand the role of nitrogen, we prepared Ni-Gr sample by employing similar synthetic procedure with RGO (Gr), instead of NGr, and ended with spherical particles (TEM image is shown in Figure S5). (detailed synthesis procedures adopted for preparing graphene oxide (GO), reduced graphene oxide (Gr), NGr, Ni-particles, and Ni-Gr particles are given in ESI†).

**Structural characterization**

Sample for the high resolution transmission electron microscopy (HR-TEM) analysis was prepared by sonicating 1 mg of the catalyst in 5 mL isopropyl alcohol and drop-coated on a carbon coated 200 mesh Cu grid. Moreover, the catalyst coated Cu grid was dried under a lamp and was used for the imaging purpose. The TEM images were obtained on FEI, TECNAI G2 F20 instrument operated at an accelerated voltage of 200 kV (Cs = 0.6 mm, resolution 1.7 Å). X-ray diffraction (XRD) and the patterns were recorded on PANalytical instrument using Cu-Kα radiation (λ =1.54 Å) at a scanning rate of 2° min⁻¹ and a step size of 0.02° in 20. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Micro Tech ESCA 300+ instrument at a pressure of > 1 x 10⁻⁹ Torr (pass energy: 50 eV, electron take off angle: 60° and the overall resolution: ~ 0.1 eV). Raman analysis of the synthesized RGO (Gr), NGr, and Ni-NGr was performed on an HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) using 632 nm red laser (NRS 1500 W) in order to obtain information on the defective and graphitic nature of the carbon.

**Gas chromatography (GC)**

Oxygen evolution measurements were performed in a gas closed electrochemical cell assembly having 25 ml capacity. 0.1 M KOH (12 ml) was used as the electrolyte and the catalyst coated glassy carbon electrode (GCE) was used as the working electrode. Along with that, a Pt-flag and Hg/HgO were used as the counter and reference electrodes, respectively. The catalyst slurry was prepared by sonicating 5 mg of the catalyst in 1 ml EtOH:H₂O (3:2) mixture and this slurry was drop coated on the tip of a glassy carbon disk electrode, and was used as the working electrode for further investigations. Prior to use the tip electrode, it was polished with 0.3 µm alumina slurry and was cleaned with acetone and DI water. The same cleaning procedure was employed to clean the RRDE electrode as well, [GC disk (6 mm diameter) and a Pt ring (9 mm outer diameter and 7.5 mm inner diameter)]. In all the electrochemical studies, the mass loading was maintained to 20 µg. Finally, the electrode was dried for 4 h under an IR-lamp and was used as the working electrode. An aqueous solution of 0.1 M KOH de-aerated with N₂ gas, was used as an electrolyte for the CV, LSV and RRDE studies. Moreover, to get the current density plots, the measured current was divided by the geometrical area of the electrode. The geometrical areas of the rotating disk electrode and the rotating ring disk electrode are 0.19625 cm² and 0.2628 cm², respectively.

**Calculation:**

Scheme 1. Schematic illustration for the synthesis of Ni-NGr nanocage particles.
1) \[ O_2 \text{ (ml)} = \frac{\text{peak area} \times \text{slope} \times \text{dead volume}}{\text{injection volume}} \]

2) \[ \text{Moles of } O_2 \text{ per gm} = \left[\frac{O_2 \text{ (ml)}}{22400}\right] / \text{weight of catalyst} \times 1000 \]

**Results and discussion**

Mainly, during the synthetic process, plenty of aqueous droplets were dispersed in oil, wherein, nickel chloride was dissolved and NGr were dispersed. During time bound heating, the water starts evaporating in a nano-sized water droplet. As a result, because of the higher surface area (Es) and flexible nature of NGr, it will tend to distribute at the w/o interface. Finally, the formation of the nanocage is facilitated by the mutually assisted redox reaction of nickel chloride and NGr followed by adsorption and subsequent interpenetration of carbon in nickel particles within the tiny water droplets in the oil phase (Scheme 1) which acts as the nanoreactors and controls the growth process.

A structural illustration of the Ni-NGr nanocage is carried out by using transmission electron microscopy (TEM) (Figure 1). Figure 1a and 1b show the well dispersed nanocage structures, with clear dimensions having an average size of \(-20 \text{ nm} \pm 2 \text{ nm}\), with cubical and hexagonal structures. The ends of the N-arms seem to be connected through the metal oxide layer, which is clearly observed in Figure 1a-1b, and inset of Figure 1b. The presence of Ni-oxide has been confirmed by XPS, as explained below. HR-TEM and dark field images of Ni-NGr nanocages have been presented in Figure 1c and Figure S3, respectively. The separately calculated d-spacing values of each side from the lattice fringes profile of Ni-NGr (Figure 1d-1f, Figure S2a, S2b, ESI†) are in the range of 0.23-0.28 nm, which is attributed to the carbon interpenetration (dissolution) in the nickel lattice. The dark-field image (Figure S3, ESI†) of Ni-NGr nanocages clearly indicates the difference in Z-contrast, the white shiny part could be due to Ni, and the surrounding low contrast may be because of combined effect of nickel oxide and/or adsorbed carbon (Figure S3 and inset). TEM image of RGO (Gr) and NGr are shown in Figure S1, ESI†.

The well distribution of C, O, N and Ni in a nanocage structure has been shown by elemental mapping (Figure S4, ESI†).

Moreover, the characteristic diffraction peaks in X-ray diffraction (XRD) pattern gives an idea about presence of Ni-oxide and Ni-carbide (shown in Figure 2a) in Ni-NGr. Figure 2a shows the comparative X-ray diffraction (XRD) pattern of graphite, Gr, NGr, NiCl₂ and Ni-NGr. The peak obtained at a 2θ of \(-25^\circ\) is attributed to the graphitic reflection of the (002) plane which is found to be shifted in case of NGr and even for Ni-NGr, by approximately 0.5° and 0.6°, respectively. This peak shift can be directly correlated with the d-spacing values, which clearly indicates the lattice expansion in case of Ni-NGr compared to the rest. This also could be taken as an indirect evidence of the N-doping in graphene framework. The characteristic peaks of the oxide and carbides are marked in the XRD pattern of Ni-NGr. Comparative Raman spectra of NiCl₂, RGO (Gr), NGr, Ni-NGr, and physical mixture of NiCl₂ and NGr (NiCl₂+NGr) have been provided in Figure S6, ESI†. In general, the Stokes phonon energy shift caused by laser excitation creates the main two peaks at nearly \(-1320 \text{ and } -1596 \text{ cm}^{-1}\), which could be assigned to the defective (D-band) and graphitic (G-band) nature of the carbon. In the present case, a substantial shift in the positions of the G and D-bands has been observed in the case of both Ni-NGr and NGr. The peaks appeared at a lower wavenumber in case of NiCl₂, NiCl₂+NGr and Ni-NGr could be attributed to the transverse...
and longitudinal optical (TO and LO, respectively) phonon modes of Ni.\textsuperscript{27} However, the 6 cm\textsuperscript{-1} shift in the graphitic peak of NGr (1590 cm\textsuperscript{-1}) compared to RGO (Gr) (1596 cm\textsuperscript{-1}) indicates the effective nitrogen doping in the graphene framework. Furthermore, the same peak again is shifted to a lower wavenumber by 5 cm\textsuperscript{-1} for Ni-NGr (1585 cm\textsuperscript{-1}) compared to NGr alone, which could be due to the charge transfer between the Ni and NGr. Conversely, this also could be accounted for the interaction of the Ni-N/C/O in Ni-NGr\textsuperscript{26} (confirmed through XPS and is explained below). In parallel, the calculated I\textsubscript{D}/I\textsubscript{G} ratio is found to be in the order of RGO (Gr) (1.13) < NGr (1.25) < Ni-NGr (1.26).

The NGr interpenetrated Ni, i.e. Ni-NGr, has shown more defects than that of NGr, which could be attributed to the formation of nickel carbide and/or Ni-N bond which changes the structural and electronic configuration of NGr in Ni-NGr. This type of interaction of Ni with carbon and formation of Ni-carbide has already been reported by John Thong \textit{et al.}\textsuperscript{26} On the otherhand, the oxygen functional groups present at the edges of the graphene sheets will interact with the Ni-ions and will lead to the oxidation at the particular site, which can eventually facilitate the rapturing and/or cutting of the graphene sheets. This also could increase the number of defects in graphene.\textsuperscript{26} Moreover, Raman spectrum of Ni-NGr has shown multiple peaks at 395.5, 508.7, 632.93, 805.9 cm\textsuperscript{-1}, which are assigned to the TO, LO, 2TO, and TO+LO phonon modes, respectively.\textsuperscript{27} Subsequently, the shift in the peaks at the lower wavenumber substantiates the charge transfer between the Ni and N and/or C in Ni-NGr.

Furthermore, the XPS also gives an additional proof of formation of nickel-carbon bond, evidenced by the characteristic peak of Ni-C bonding at ~283.5 eV in C1s spectra (Figure S8a) of Ni-NGr.\textsuperscript{23} Along with this, the XPS of Ni2p and O1s of Ni-NGr are provided in Figure 2b and Figure S8b, respectively. The Ni2p spectra have shown two peaks, one at 855.9 and another at 874.5 eV of 2p\textsubscript{3/2} and 2p\textsubscript{1/2} respectively, along with their corresponding satellite (S1 and S2) peaks. Moreover, the difference between the Ni2p\textsubscript{3/2} and Ni2p\textsubscript{1/2} peaks is found to be 18.4 eV and the occurrence of the satellite peaks is attributed to the presence oxide/carbide of nickel in the Ni-NGr system.\textsuperscript{21} On the other hand, the higher binding energy shift (~4-6 eV) of Ni 2p\textsubscript{3/2} and 2p\textsubscript{1/2} of Ni-NGr compared to that of NiCl\textsubscript{2} (Figure S7, ESI\textsuperscript{†}) is attributed to the change in the electronic configuration of Ni present in Ni-NGr, which substantiates the interaction between the Ni and N/C/O.\textsuperscript{23} For comparison, XPS spectra of C1s, N1s, and O1s of NGr have been provided in Figures S10-S12, respectively. More importantly, the numbers of defective sites is seemed to be more as observed in C1s of NGr (Figure S10) compared to Ni-NGr (Figure S8a). However, the Raman investigation highlights the slight variation in the I\textsubscript{D}/I\textsubscript{G} ratio. Overall, the defects in NGr are due to the combined effects of functional groups, N-doping and change in the bond length after the N-doping. Conversely, in case of Ni-NGr, the carbon is in coordination with the Ni and N (which has been confirmed by XPS). Therefore, only the type of the defect is changed in Ni-NGr compared to NGr. Similarly, the presence of low binding energy peak (~398 eV) in N1s of Ni-NGr (Figure S9, ESI) also gives the evidence of interaction between the N and Ni.

More importantly, to understand the exact mechanism of the formation of Ni-NGr nanocage structures, we have followed a similar synthetic protocol by using Gr instead of NGr and ended up with spherical particles (Figure S5, ESI\textsuperscript{†}). This means that the presence of nitrogen has a crucial role during the formation of the Ni-NGr nanocage structure. Moreover, nickel has higher carbon solubility and also, it forms an ordered surface carbide.\textsuperscript{15} In fact, during the entire synthesis process, the carbon of the NGr gets adsorbed on the in-situ formed nickel nanoparticles, because of the dominance of van der Waals forces (Ev) between the NGr layers compared to the gravitational potential energy of metal nanoparticles and surface energy of NGr. The dominating role played by the van der Waals interaction in forming the graphene based core-shell structure has already been reported by Kang \textit{et al.}\textsuperscript{28} Consequently, the presence of nitrogen may increase Ev of NGr layer as well as the pressure build by the water vapors in the oil phase leads to controlled and/or enhanced interpenetration (dissolution/diffusion) of the carbon in the nickel crystal.
The peak at ~1.42 V during the anodic scan is the characteristic oxidation peak of the active Ni-center, which is followed by a sharp augment in current due to the oxygen evolution (Figure S13a and S15, ESi). The probable mechanism of OER on the Ni-active center (A) is given in ESi.\(^{15,16,28}\) In brief, the active center (A) will form hydroxide (A-OH), followed by chemical association between OH\(_{\text{ads}}\) and OH\(_{-}\), with the reaction involving two electrochemical steps, viz. OH\(_{-}\) discharge and O\(_{\text{ads}}\) discharge, which finally leads to the evolution of oxygen.

The electrochemical surface active area (ESCA) has been deduced from the electrochemical double layer capacitance (\(C_a\)) of the catalytically active surface.\(^{17}\) The calculation of \(C_a\) is done by measuring the non-faradaic capacitive current associated with double layer charging by merely recording the scan rate dependent CV as shown in Figure 3a.\(^{17-18}\) To obtain the double layer charging from CV, at first, the potential window corresponding to the non-faradaic contribution is determined from static CV.

Principally, this potential window will be of ~0.1 V, centered at open circuit potential (OCP) of the system. The CV of Ni-NGr electrocatalyst in the non-faradaic potential window is displayed in Figure 3a, and the \(C_a\) is calculated by using Equation 1.

\[
i = \gamma C_{dl} \quad \text{Equation 1}
\]

where ‘\(i\)’ is the measured cathodic/anodic current and ‘\(\gamma\)’ is the scan rate. The plot of \(i\) vs. \(\gamma\) gives a straight line with \(C_{dl}\) as a slope (Figure 3b). The obtained \(C_a\) is 0.1985 mF for Ni-NGr.

To evaluate the electrochemical activity of the synthesized Ni-NGr electrocatalyst for water oxidation, experiments with cyclic voltammetry (CV) and linear sweep voltammetry (LSV) have been carried out in aqueous 0.1 M KOH solution. The CV is scanned in a potential window of 0.7 to 1.7 V (vs. RHE). Ni-NGr has shown the characteristic property of oxygen evolution with lower overpotential. Figure S13a shows the comparative CV of NGr and Ni-NGr performed in \(\text{N}_2\)-saturated 0.1 M KOH.

The peak at ~1.42 V during the anodic scan is the characteristic oxidation peak of the active Ni-center, which is followed by a sharp augment in current due to the oxygen evolution (Figure S13a and S15, ESi). The probable mechanism of OER on the Ni-active center (A) is given in ESi. In brief, the active center (A) will form hydroxide (A-OH), followed by chemical association between OH\(_{\text{ads}}\) and OH\(_{-}\), with the reaction involving two electrochemical steps, viz. OH\(_{-}\) discharge and O\(_{\text{ads}}\) discharge, which finally leads to the evolution of oxygen.

Moreover, the ratio of \(C_{dl}\) to specific capacitance (\(C_s\)) will directly give the ESCA, and it is found to be 7.26 cm\(^2\) for Ni-NGr (used C, value is 27µF/cm\(^2\)). As per the literature, the typical C, values reported for metals in alkaline medium are in
the range of 22-130 μF/cm²,24,25 and for the Ni-based electrocatalysts fall in the range of 23-28 μF/cm² (Table S2, ESI†).24,25 C, is the capacitance of an atomically smooth planar surface of the material per unit area under the similar electrolyte conditions. Moreover, the roughness factor (RF) is obtained by taking the ratio of ESCA to geometrical surface area of the electrode (0.19625 cm²), and is found to be 36±3. Furthermore, to investigate the importance of nanocage structure and chemical combination, we have determined the ESCA and RF of the Ni-Gr particles by using similar method. Ni-Gr has shown the ESCA and RF values of 4.11 cm² and 20.9, respectively (Figure S16, ESI†). The 1.7 order improved ESCA and RF of Ni-NGr nanocages compared to Ni-Gr particles is mainly credited to the 3D morphology with its controlled chemical composition, higher molecular accessible space, higher surface-to-volume ratio and more number of active sites. Importantly, it is just to be noted that, the calculated ESCA and RF are the precision average values of three independent measurements with standard deviations of 0.03 and 1.73, respectively. These measurements are a sign of precision of the measurements and not obligatory the meticulousness to the obtained ESCA and RF. The estimated values must be considered only for comparing the surface roughness.

Figure 4: a) O₂-evolution curve of Ni-NGr nanocages before and after cycle stability performed in a potential window of 0.7 to 1.7 V (vs. RHE), in N₂-saturated 0.1 M KOH electrolyte, b) chronoamperometric stability profile performed at a current density of 20 mA/cm² for 15 h.

Linear sweep voltammograms of NGr and Ni-NGr has been recorded to monitor the anodic reaction by scanning in a potential window of 0.7 to 1.9 V and 0.7 to 1.7 V (vs. RHE), respectively. The onset potential is found to be 1.7 V (Figure S14, ESI†) and 1.5 V (Figure 4a) (vs. RHE) for NGr and Ni-NGr, respectively. The overpotential calculated at 20 mA/cm² for Ni-NGr nanocage is found to be ~290 mV, which is even less compared to the literature data of the Ni-based electrocatalysts (~400 mV) which is reported at a lower current density of i.e. 10 mA/cm² (tabulated in Table S3, ESI†). In short, the reported Ni-based electrocatalysts might give 10% efficiency for water splitting with one sun illumination to convert solar-to-fuel; conversely, double efficiency could be obtained from Ni-NGr even at a lower overpotential. Consequently, the Tafel slope (Figure S13b, ESI†) has been obtained by plotting the log I vs. potential, and is found to be 69 mV/decade. The Tafel slope directly gives an idea about good intrinsic electrocatalytic activity. For comparison, we have recorded the anodic LSV scan of Ni-particles and Ni-Gr (Figure S15, ESI†). The obtained overpotential of the samples at 20 mA cm² is in the order of Ni-NGr (~290 mV) < Ni-particles (~370 mV) < Ni-Gr (~570 mV). The obtained results in-terms of lower overpotential and higher current signifies the importance of nanocage structure over the Ni-particles and Ni-Gr.

Moreover, cyclic stability (Figure 4a) has been confirmed by anodic potential scanning for 500 cycles and chronoamperometric (Figure 4b) study at practical overpotential value (i.e. required to achieve the 20 mA/cm²) for 15 h. From the chronoamperometric investigation, it is found that the current density is steady up to 15 h at the applied overpotential (η = 290 mV). However, in potential cycling nearly 15% decrease in the current is observed after 500 cycles, which is showing good stability in operating conditions. The observed overpotential (η) at the current density of 20 mA/cm² is found to be ~290 mV before the stability test (i.e. η₁ = 290 mV, where, n = number of cycle) and after 500 potential cycles, η is found to be increased to 317 mV (i.e. η₅₀₀ is 317 mV). Therefore, the percentage of overpotential increment after the 500 cycles is 8.5% at 20 mA/cm², which is far better than the available reports.

Figure 5: Quantitative analysis the evolved oxygen and cycle stability evaluation of the catalyst by gas chromatography during the electrochemical water oxidation.

The better activity and stability of Ni-NGr nanocage is attributed mainly to high surface-to-volume ratio, and 3-D surface molecular accessibility, which provides more active
sites. The exact reason for the increase of overpotential after 500 cycle and decrease in the current after 15 h chronoamperometric test could be assigned to the electrode surface passivation due to the evolved oxygen and/or formation of nickel oxyhydroxide.

Finally, a gas tight electrochemical cell assembly has been constructed for the quantification of the generated oxygen during the electrochemical water oxidation. The quantification is done by analyzing the gas sample from headspace of the assembly by using gas chromatography (GC) technique. Mainly, before starting the experiment, the electrolyte is purged with N₂ for 30 min and complete gas evacuation is ensured by applying vacuum for 10 min. Afterwards, we recorded the GC spectrum and confirmed the absence of any gas in the assembly. Subsequent to this, the system is subjected to a chronoamperometric testing at 1.5 V (vs. RHE) and the generated oxygen is recorded by GC for 1 h with an interval of 15 min, named as I° cycle in Figure 5. A systematic increase in the amount of oxygen has been observed from 0 to 70 mmol/h/g. Furthermore, to understand the stability of the catalyst, the assembly is completely evacuated and made it free from the gas and the same experiment is repeated, termed as II° cycle in Figure 5. The amount of O₂-generated is almost same in both the cycles, which highlights the higher stability of the catalyst under the operating conditions.

Faradaic efficiency of the Ni-NGr nanocage structure is determined by rotating-ring disk electrode (RRDE) investigation at 1600 rpm of the working electrode in a 0.1 M KOH. The disk electrode is subjected to a series of current steps from 2 to 15 mA/cm², and the corresponding potentials are measured (Figure S13c, ESI†). The oxygen evolution from the carbon disk is monitored by reducing it on the Pt ring, whose potential is kept constant at 1.3 V (vs. RHE). The estimated value of the faradaic efficiency (ε) is found to be 0.9 (Figure S13c, detailed procedure is given in ESI†).

In summary, Ni-NGr nanocage structure has been synthesized by simple water-in-oil emulsion technique by optimizing the reaction occurring inside the nanoreactors of the aqueous droplets. Ni-NGr has shown significantly reduced overpotential for OER at the practical current density of 20 mA/cm² compared to the literature results. Moreover, the chronoamperometery evaluation highlighted its better sustainability in alkaline medium. Nearly 70 mmol/h/g of oxygen is generated after 1 h and the catalyst displays good reproducibility in the second cycle as well. Ni-NGr is relatively cheap and it displays excellent corrosion resistance property in aqueous alkaline system. Hence, it offers an efficient and cheap alternative to the energy intensive and expensive Ru/Ir-oxide catalysts. The method demonstrated here can be useful to synthesize many more multi-metallic nanocage structures for ORR, OER, alcohol oxidation, etc. Still, the exact type of nitrogen which triggers the formation of the nanocage structure is an open question for further studies.

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Notes and references
