Dependence of Precursor Graphite Flake Size on Nitrogen Doping in Graphene Oxide and Its Effect on OER Catalytic Activity

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ABSTRACT: We report the synthesis of nitrogen-doped graphene oxide, with 5.7−7.0 wt % nitrogen doping, from different sizes of precursor graphite and study its effect on the oxygen evolution reaction (OER) activity of IrO$_2$ in an acidic medium. The nitrogen-doped supports are expected to have pyridinic, pyrrolic, and graphitic functionalities at different ratios responsible for their improved performance. The N-doped supports and catalysts are synthesized via pyrolysis and the hydrothermal method using natural and synthetic graphite of three different flake sizes and evaluated for their structural and electrochemical characteristics. The average size of IrO$_2$ nanoparticles deposited on the N-doped supports is independent of the flake size and doping amount of nitrogen. The catalysts show optimum current densities but improved stability with increasing flake sizes of 7, 20, and 125 μm. Our results demonstrate that the selection of the flake size of the doped support is necessary to achieve durable catalysts for the OER in an acidic medium.

INTRODUCTION

Graphene-based materials have been extensively used in the energy industry for applications in supercapacitors, batteries, and fuel cells due to their widely utilized attributes such as high surface area, large potential domains, high electrical conductivities, low background currents, and ease of modification. The common synthetic methods such as chemical vapor deposition (CVD), epitaxial growth, chemical oxidation−reduction, and ball milling are employed to provide graphene. Recently, plasma-assisted ball milling has also been reported for the controlled synthesis of few-layer graphene, paving a way for large-scale production of carbon-based energy materials. While some of these methods are adequate for the synthesis of highly crystalline and layered graphene, the chemical oxidation−reduction method enables the production of high yields of oxygen-functionalized reduced graphene or reduced graphene oxide (rGO) from the synthesis intermediate, graphene oxide (GO). The advantages, such as the ease of functionalization/doping, accessibility of restoration into graphene, and presence of defects for nucleation of metal nanoparticles, make GO a highly useful and important precursor. These properties of GO have been widely exploited for studying the behavior of heteroatom doping, such as the presence of oxygen functionalities, lattice defects, increased layer separation, and so forth, and its effect on the surface structure, as well as the properties of doped graphene for direct-type fuel cells, supercapacitors, and the oxygen evolution reaction (OER).

Nitrogen is the first atom that was doped into graphene, yielding an n-type semiconductor material, generally termed N-doped graphene. Being similar in size to the C atom (atomic radius, C: 70 pm), the N atom (atomic radius, N: 65 pm) can replace or add to a graphene lattice, forming a C−N bond. The comparable bond lengths of the C−N bond (1.41 Å) and C−C bond (1.42 Å) allow the reconfiguration of the electronic structure with a minimal structural change in the graphene lattice. Furthermore, nitrogen doping in the graphene lattice results in the formation of a few possible types of functional groups, namely, (a) substitutional or graphitic N (when an N atom substitutes a C atom in the lattice), (b) pyridinic N (usually doped N forms a pyridinic ring at the edge or defect of graphene sheets), (c) pyrrolic N (formation of the five-membered or pyrrolic ring at the edge or defect), and (d) nitrogen oxide (N−O, doped N is also attached to an oxygen atom). N-doped graphene has been comprehensively analyzed in terms of its morphology, change in electronic structure,
Our recent works show the applicability of nitrogen-doped reduced GO (N-rGO) as an advanced supercapacitor electrode and as a catalyst support material for the OER. N-rGO is similar in structure to N-doped graphene, excluding the presence of a few oxygen functional groups and defects in N-rGO that are not completely removed or restored during pyrolysis at high temperatures. In a recent research work, Yadav et al. explored the temperature-dependent synthesis of N-rGO, starting with natural graphite (flake size: 7 μm), and explained the structural effect on the supercapacitive behavior of N-rGO as an electric double-layer supercapacitor (EDLC). In this study, the properties of N-rGO such as the degree of reduction, the extent of N-doping, formation of structural and lattice defects, specific surface area, and the crystallinity of rGO were investigated as a function of synthesis temperature. Furthermore, Hara et al. demonstrated the use of N-rGO (starting from synthetic graphite, Sigma-Aldrich, flake size: < 20 μm) as the catalyst support and investigated its effect on the catalytic properties of IrO2 nanoparticles (nps) as an electrocatalyst for the OER. These results confirmed the effect of nitrogen doping on the electrochemical properties of graphene.

Evidently, the electrochemical properties of a heteroatom-doped material are highly dependent on the morphology, degree of defects, synthesis temperature, and the extent of doping in graphene lattice. Furthermore, the mentioned properties of N-rGO are dependent on the extent of functionalization of the initial precursor and, hence, can be related to the flake size of the initial graphite precursor. A very few literature reports have focused on the dependence of electrochemical properties of N-rGO or graphene as such, on the flake size of the starting graphite or the size of its corresponding GO. Adedayo reported the effect of graphite flake sizes on the mechanical properties of gray iron or steel containing carbon. Furthermore, Hooley et al. reported the effect of the thickness of the original flake size of graphite on the composition of graphitic ferric chloride. Concentrating the focus on electrochemical properties, Lee et al. in 2014 reported the large size selection of GO for size-dependent N-doping and its oxygen reduction reaction (ORR) catalysis. Their work reported the self-selection of large GO flakes is caused by biphasic phase separation of GO solution and enhanced ORR catalytic activity of graphitic planes for large size N-graphene flakes. Their work also indicated that the average size of GO sheets influences their colligative properties.

Depending on the dominant functional group, the catalytic activity for N-rGO can be altered and is expected to be dependent on the structure and morphology of rGO, which is associated with crude materials and, hence, the initial graphite precursor. N-doped graphene has been reported as an excellent catalyst and a support material for the deposition of metal nanoparticles toward electrochemical reactions, such as the ORR, hydrogen evolution reaction (HER), and the OER, and has also been reported as an excellent electrode material for supercapacitors and batteries. With regard to such a wide set of applications, this article gives us an opportunity to explore the flake size aspect of N-doped rGO formation and evaluate its effect on the OER catalytic activity of IrO2 with N-rGO as a catalyst support depending on the graphite flake size.

In this article, we have studied and discussed the effect of flake size of a N-rGO support on the electrocatalytic activity of deposited IrO2 nps toward the OER. Graphite with three different flake sizes has been examined to synthesize N-rGO, followed by deposition of IrO2 nanoparticles on the N-rGO support. The synthesized materials, IrO2-N-rGO, are well characterized for their chemical structures and morphologies. Furthermore, the electrocatalytic activity for the OER is electrochemically determined in an acidic medium. This is an approach to investigate the effect of graphitic precursor flake size on the extent of N-doping in GO and the resultant OER catalytic activity of the deposited IrO2 nps. It is worth mentioning that this is the first work that emphasizes the effect of graphite flake size on the OER activity of the resultant IrO2-N-rGO.

## EXPERIMENTAL SECTION

The catalyst was synthesized by the consecutive process of Hummers’ method, pyrolytic reaction, and hydrothermal reaction as previously described in our reported work. The synthesis details are provided in the Supporting Information. Natural graphite with two different flake sizes, 7 (G-7) and 125 μm (G-125), and synthetic graphite of flake size <20 μm (G-20) were used as initial precursors to obtain GO-7, GO-125, and GO-20, respectively. The GO precursors were pyrolyzed in the presence of urea to obtain their respective N-rGO samples as N-rGO-7, N-rGO-125, and N-rGO-20. After IrO2 nps decoration via the hydrothermal method, the obtained catalysts are denoted as IrO2-N-rGO-7, IrO2-N-rGO-125, and IrO2-N-rGO-20, respectively. All the samples were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), microwave plasma-atomic emission spectrometry (MP-AES), Raman spectroscopy, X-ray diffraction analysis (XRD), and X-ray photoelectron spectroscopy (XPS). The details for chemical and morphological characterization are provided in the Supporting Information. Figure 1 shows the schematic representation of N-rGO with the probable N-functional groups.

![Figure 1. Schematic representation of the structure of IrO2-N-rGO.](https://doi.org/10.1021/acsomega.2c03496)
refractory electrode (RE), and an IrO$_2$-N-rGO catalyst coated on an alumina (0.05 μm)-polished glassy carbon (GC, 3 mm diameter) electrode as the working electrode were used. A GC electrode with the catalyst was prepared as follows: IrO$_2$-N-rGO was dispersed in a mixture of distilled water (DI), isopropyl alcohol (IPA, Tokyo chemicals Ltd.), and NaBon (added 10 wt % of the catalyst, Sigma-Aldrich) by ultrasonic for 30 min to prepare catalyst ink. The aliquot of the catalyst ink was added dropwise on the GC electrode and spin-coated at 400 rpm. The coated electrode was, then, dried at 60 °C for 1 h. The Ir metal amount on each electrode was kept similar (100 μg cm$^{-2}$ for IrO$_2$-N-rGO-7, -20, and 143 μg cm$^{-2}$ for IrO$_2$-N-rGO-125), which is ∼15 times less than the Ir loading amount used in commercial WEs). The potentials in the article are reported with respect to the RHE. Prior to the electrochemical measurements, a gentle N$_2$ flow was also maintained over the solution. Ultrapure water (18.2 MΩ cm) was used for the preparation of all the catalysts and electrochemical measurements. The change in morphology of nps after ADT was also observed by TEM.

RESULTS AND DISCUSSION

Structural Characterization. The difference in the chemical structure of three different graphite forms, their chemically oxidized form, GO, and the defective reduced form (N-rGO) was confirmed by Raman spectroscopy. Figure 2 shows the comparison of Raman spectra for (a) graphite (G$_a$), (b) GO, and (c) N-rGO. The Raman spectrum of graphite consists of a sharp G peak, corresponding to in-plane C=C sp$^2$ bond vibration, at ∼1580 cm$^{-1}$ for all three graphite forms. A very significant 2D peak, the second order of the D peak, was also observed in G$_r$-7, G$_r$-20, and G$_r$-125 at ∼2690 cm$^{-1}$. The 2D peak in bulk graphite comprises two components 2D$_b$ and 2D$_w$ which are roughly 1/4 and 1/2 the height of the G peak, respectively, as can be seen for all three graphite precursors. These components depend on the excitation laser and the interactions between the stacked layers of graphite. For graphene, the shape and the position of the 2D peak are highly useful in deriving the number of layers. For G$_r$-7 and G$_r$-20, the 2D peak was observed at a lower intensity (35–50% lower) than for G$_r$-125. For G$_r$-7 and G$_r$-20, a small D peak, corresponding to the breathing mode of the sp$^2$ C ring, was also observed at ∼1351 cm$^{-1}$; however, the ratio of the intensities of D and G peaks (I$_D$/I$_G$) was very low, as shown in Table S1.

The Raman spectra of GO consisted of distinct peaks at ∼1350 cm$^{-1}$ (D peak) and ∼1598 cm$^{-1}$ (G peak). Similar two peaks were observed for N-rGO at ∼1358 and ∼1590 cm$^{-1}$. After reduction from GO to N-rGO, both D and G peaks were observed at a slightly shifted position. A red shift of the G peak was attributed to the lattice restoration of the graphene structure during high-temperature pyrolysis.$^{28,30}$ Furthermore, the doping of heteroatoms in the graphene lattice also causes a shift in the G peak as it is dependent on the charge carriers and dopant concentration.$^{28}$ Interestingly, the calculated I$_D$/I$_G$ ratio for N-rGO-20 was the highest, indicating the high density of defects in N-rGO-20. The defect introduction occurred in all three N-rGO due to N-doping and high-temperature treatment, leading to the breaking of sp$^2$ carbon bonds. We further calculated the crystallite size of all the samples obtained from different precursors, following the work by Tunistra and Koenig,$^{28}$ using the formula

$$I_a(nm) = (2.4 \times 10^{-16})\lambda_i^4 \left(\frac{I_D}{I_G}\right)^{-1}$$

where $\lambda_i$ is the laser excitation used in the Raman measurement in nanometer units. The crystallite size ($L_c$) thus calculated from the equation is listed in Table S1 along with the peak positions and $I_D/I_G$ ratio. The crystallite size decreased from graphite to GO and further, to N-rGO, as a large number of defects are introduced while thermal annealing due to mechanical stress and easy breaking of N-rGO sheets. Since crystallite size is highly dependent on the intensities of D and G peaks, the lowest crystallite size in case of N-rGO-20 indicates that the defects induced are the highest in this case.$^{31}$

We also tried to obtain a size distribution for the GO sheets obtained after Hummer’s method.
Figure 3. XRD profiles of the three IrO\textsubscript{2}-deposited catalysts.

The structures of N-rGO sheets and IrO\textsubscript{2} deposition were confirmed by TEM to understand the effect of nanostructure on the morphology and size of the supported IrO\textsubscript{2} nps, which are critical for the OER electrocatalytic activity. Figure S2 shows TEM images of GO-20 and N-rGO-20. It was observed that all graphene-based materials had wrinkled sheet-like structures due to the chemical exfoliation of a graphene sheet and removal of oxygen functional groups. The structure of GO was observed to be plane sheet-like as shown in Figure S2. Furthermore, TEM images of IrO\textsubscript{2} nps deposited on N-rGO sheets showed uniform distribution of these nps (Figure 4).

Figure 4. Large-scale and magnified TEM images of (a,b) IrO\textsubscript{2}-N-rGO-7, (c,d) IrO\textsubscript{2}-N-rGO-20, and (e,f) IrO\textsubscript{2}-N-rGO-125.

The change of interlayer distance between graphene sheets due to the chemical exfoliation of a graphene sheet and removal of oxygen functional groups. The structure of GO was observed to be plane sheet-like as shown in Figure S2. Furthermore, TEM images of IrO\textsubscript{2} nps deposited on N-rGO sheets showed uniform distribution of these nps (Figure 4).

The particle size of the deposited IrO\textsubscript{2} nps was estimated from the TEM images. On all the three doped sheets, the particles were obtained with a similar diameter of ~1.5 nm. This is due to the same amount of solvent as well as the same synthesis temperature and time used during the synthesis of the three catalysts. We further confirmed the uniformity of elemental distribution from SEM–EDX analysis (Figure S4). All the catalysts had a uniform distribution of deposited Ir nps and doped N elements. The doping amount of N was calculated to be 5.7–7.0 wt % with estimated Ir amounts of 9.1, 7.7, and 9.5 wt %, estimated from SEM–EDX for IrO\textsubscript{2}-N-rGO-7, IrO\textsubscript{2}-N-rGO-20, and IrO\textsubscript{2}-N-rGO-125, respectively. The amount of Ir deposited onto the N-rGO supports was further confirmed by MP-AES measurements for the three catalysts (Table S3). The estimated Ir amounts of 8.34, 8.28, and 13.00 wt % for IrO\textsubscript{2}-N-rGO-7, -20, and -125, respectively, from MP-AES, were used for the calculation in electrochemical measurements corresponding to an Ir loading amount of 100 μg cm\textsuperscript{-2} for IrO\textsubscript{2}-N-rGO-7 and -20, and 143 μg cm\textsuperscript{-2} for IrO\textsubscript{2}-N-rGO-125. The difference in the wt % between EDX and MP-AES arose due to the different solubilities of the IrO\textsubscript{2}-based catalysts in an acidic environment.\textsuperscript{12} The values calculated from MP-AES were used for the calculation of np surface area and loading amount of the catalysts in electrochemical measurements. The calculated particle size (nm), mean lattice spacing (nm), and np surface area (m\textsuperscript{2} g\textsuperscript{-1}) of all the catalysts are listed in Table S4. Flake size distribution for GO was studied using AFM (Figure S5) and analyzed by ImageJ software. GO flakes showed a broad distribution in the lateral size ranging from 1.13 ± 0.61, 0.22 ± 0.09, and 1.06 ± 0.05 μm for GO-7, -20, and -125, respectively.

Figure 5a shows the survey spectra of the three IrO\textsubscript{2}-N-rGO catalysts. All the graphene-based materials contained C 1s and O 1s peaks at ~285 and ~530 eV. After nitrogen doping, N 1s peaks at ~398 eV appeared in N-rGO, and with IrO\textsubscript{2} deposition, the peaks appeared at ~61 and ~64 eV for Ir 4f. The N 1s peak can be deconvoluted into four types of N-functionalities, pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen, and N-oxide.\textsuperscript{13} We reported in our previous work that the doping is dependent on the temperature with graphitic
nitrogen stable at 800 °C.13,30 For N-rGO to be highly catalytically active, the presence of pyridinic or graphitic forms of doped N is beneficial.33 We deconvoluted the synthesized N-rGO for the type of doped N-functionalities. The N 1s deconvoluted spectra for N-rGO-7, -20, and -125 are shown in Figure 5b–d, respectively, and the analysis results are listed in Table 1.

The N 1s deconvolution of the three N-rGO samples shows that the extent of doping is different for natural (N-rGO-7 and -125) and synthetic graphite (N-rGO-20) samples. The graphitic content is higher for N-rGO derived from natural
graphite, N-rGO-7 and -12S, whereas N-rGO-20 derived from synthetic graphite (N-rGO-20) shows a spectral profile with pyridinic and pyrrolic N domination. For N-rGO-7 and N-rGO-125, the pyridinic component is lower than that of N-rGO derived from synthetic graphite. For N-rGO-7 and -125, the graphitic nitrogen peak appears at 401.08 and 401.25 eV with a negligible shift of 0.13 eV. For N-rGO-20, the peak appears at 400.86, indicating a 0.22 eV shift which can arise due to a change in the local chemical environment of N caused by the initial processing of the synthetic graphite and not due to the flake size. The data is consistent with the fact that the type of nitrogen doping can be controlled with different types of GO and/or their flake sizes in the same N-doping condition. The graphitic N becomes dominant for a bigger flake size when the edge-to-plane ratio is high. The formation of specific dominant functional groups can be a function of the initial processing of the graphite used. It is well known that with the change in the processing method of graphite, the structural properties and hence, the chemical nature of the material changes.

The O 1s deconvoluted data is shown in Figure S6 in the Supporting Information which shows a different ratio of oxygen functional groups for larger-flake-size graphite. The Ir 4f peaks for supported IrO$_2$ nps showed a similar change when supported on N-rGO derived from graphite of different flake sizes. The Ir 4f peaks for the three catalysts were deconvoluted to analyze the change in the oxidation states of Ir. Both ~61 (spin−orbit doublet 4f$^7$/2) and ~64 eV (4f$^6$/2) show a satellite peak at a higher binding energy of ~1 eV. The three catalysts were compared for their Ir 4f peaks, where both IrO$_2$-N-rGO-7 and IrO$_2$-N-rGO-20 showed an Ir 4f$^7$/2 (4f$^6$/2) peak at 60.88 (63.88) eV. IrO$_2$-N-rGO-125 showed that the Ir 4f$^7$/2 (4f$^6$/2) peak shifted by 0.2 eV at 61.02 (64.02) eV (Figures 5e and S7). A difference in the Ir 4f peak positions on the three substrates points toward different electronic states of Ir 4f, causing a varying degree of metal−substrate interactions or charge transfer between IrO$_2$ nps and the supports. The positive shift of 0.2 eV in Ir 4f binding energy to a higher value is attributed to stronger metal−substrate interaction (SMSI) between the IrO$_2$ nps and N-rGO support in case of IrO$_2$-N-rGO-125. Additionally, it is also reported that most N atoms in nitrogen-doped graphene strongly interact with the Ir atoms in the vicinity via electron coordination as they have a higher affinity toward transition metals than the sp$^2$ C atoms of graphene. This shift is expected to result in a stronger attachment of IrO$_2$ nps to the N-rGO surface and, hence, will result in enhancing the durability of the catalyst nps. All the peaks were calibrated keeping the C 1s peak at 284.5 eV corresponding to the C−C sp$^3$ bond.

Electrochemical Characterization. We tested the supports and the IrO$_2$-deposited catalysts for their electrochemical activity toward the OER by LSV in 0.5 M H$_2$SO$_4$. Figure 6a shows the LSV profiles of the three catalysts, tested for their OER activities, and Figure 6b–d shows their durabilities up to 1800 potential cycles between 1.20 and 1.65 V. All the three
catalysts showed optimum current densities. The onset potential was observed to be 1.51, 1.55, and 1.57 V for IrO\textsubscript{2}, N-rGO-7, IrO\textsubscript{2}-N-rGO-20, and IrO\textsubscript{2}-N-rGO-125, respectively. We expect the role of defect sites in controlling the overpotential and durability of these catalysts. We can widely categorize the defect into two groups, (i) functional groups and (ii) lattice defects. The flakes with smaller size are likely to have a high percentage of oxygen functional groups or edge nitrogen groups (pyrrolic, pyridinic, or N-oxide), whereas the flakes with a higher size is expected to have more lattice defects (breaking of the graphene lattice structure and presence of more graphitic nitrogen or defects). The high overpotential for IrO\textsubscript{2}-N-rGO-20 and -125 can be attributed to a contribution of both these defects. In addition, relatively poor distribution and aggregation of IrO\textsubscript{2} nps compared to IrO\textsubscript{2}-N-rGO-7 can also lead to a higher overpotential for these catalysts, as seen in TEM images (Figure 4d,f). A list of the recently published catalysts used for the OER is shown in Table S5. The present catalysts show optimum activities compared to the recently published works.

Despite the high overpotential, the catalyst with the flake size (~12S μm) managed to show higher durability toward the OER. IrO\textsubscript{2} deposited on smaller-size N-rGO showed poor cyclability compared to the IrO\textsubscript{2} deposited on N-rGO of 125 μm size. IrO\textsubscript{2}-N-rGO-125 showed optimum current density with high durability, indicating the fact that the graphene support with higher flake size can improve the durability of the catalyst (Figure 6d). The durability of the catalyst followed the trend IrO\textsubscript{2}-N-rGO-125 > IrO\textsubscript{2}-N-rGO-20 > IrO\textsubscript{2}-N-rGO-7, which stated the fact that a higher size graphene flake can participate in improving the catalyst durability for the OER. This was also expected after the Ir 4f peak shift to higher binding energy in IrO\textsubscript{2}-N-rGO-125. For IrO\textsubscript{2}-N-rGO-7 and -20, no observable shift in the binding energy of the Ir 4f\textsuperscript{5/2} (4f\textsuperscript{7/2}) peak was observed. The higher durability of IrO\textsubscript{2}-N-rGO-20 can be associated with other factors, namely, a differently processed graphite (synthetic graphite) precursor, bigger flake size (20 μm), higher density of defects, and better stability of the intrinsic N-rGO support. Additionally, the intrinsic electrochemical activity of the flakes of higher sizes will be greater due to their enhanced conductivity compared to the flakes of smaller sizes.\textsuperscript{37,38}

For further analysis of OER behavior on the IrO\textsubscript{2} catalysts, the Tafel slopes (b) for the three catalysts were calculated using the Tafel equation \[ \eta = a + b \log j \] where \[ \eta = E - E_0 \] \( (E_0 = 1.23 \text{ vs the RHE}) \) by plotting \( \log j \) versus \( \eta \). The Tafel slopes were ca. 120.5, 115.7, and 101.6 mV dec\textsuperscript{−1} for IrO\textsubscript{2}-N-rGO-7, IrO\textsubscript{2}-N-rGO-20, and IrO\textsubscript{2}-N-rGO-125, respectively. These values of Tafel slopes were similar to that of the one-electron transfer OER, corresponding to a Tafel slope of 120 mV dec\textsuperscript{−1} where the first step acts as the rate-determining step.\textsuperscript{14} The slightly lower value of the Tafel slope for IrO\textsubscript{2}-N-rGO-125 is directed toward the difficulty in the propagation of the reaction as is also indicated by its high overpotential. The estimated Tafel slopes for the three catalysts are also shown in Figure 7. Such variation in the Tafel slope with variable flake size has been demonstrated by other groups for the HER. For nitrogen-doped carbon, variable Tafel slopes have been reported ranging from 35 to 80 mV dec\textsuperscript{−1}.\textsuperscript{39} Kundi et al. reported 3D-IrO\textsubscript{2}/N@C on nitrogen-doped carbon with a Tafel slope of 45 mV dec\textsuperscript{−1}.\textsuperscript{39} In their work, N@C was derived from formamide by the microwave synthesis method. Wang et al. reported a Tafel slope of 35 mVdec\textsuperscript{−1} for Ir/CN where N-doped carbon was used as support in an alkaline medium. The N-doped carbon was obtained after calcination of carbon and urea at 300°C for 2 h.\textsuperscript{44} Tafel slopes of 50 and 83 mV dec\textsuperscript{−1} have also been reported for Ir@N-G\textsuperscript{36} and Ir\textsubscript{0.3}W\textsubscript{0.7}@NC\textsuperscript{41} in an acidic medium. The Tafel slopes vary between 40 and 60 mV dec\textsuperscript{−1} for IrO\textsubscript{2} in acidic solutions on GC and iridium substrates. Moreover, for carbon-based electrocatalysts, the Tafel slopes\textsuperscript{42,43} range from 72 to 140 mV dec\textsuperscript{−1} indicating that the reaction mechanism and kinetics differ based on the nature and/or synthesis method of the support.

**Postmortem Analysis.** We further investigated the change in catalyst morphology after electrochemical (EC) analysis using TEM. The post-EC TEM images (Figure 8) show an obvious morphology change of IrO\textsubscript{2} nps on N-rGO. The variation of the IrO\textsubscript{2} np shapes after EC analysis supports the fact that the IrO\textsubscript{2} nps deposited on a bigger flake size N-rGO were more stable than their smaller counterparts. Both the catalysts, IrO\textsubscript{2}-N-rGO-7 and IrO\textsubscript{2}-N-rGO-20, showed a higher degree of degradation of IrO\textsubscript{2} nps after EC analysis. In both cases, the particles underwent shape change/degradation and aggregation after 1800 cycles. The particle diameter changed drastically for IrO\textsubscript{2}-N-rGO-7 after the EC test. A wider range of particle distribution was observed with small and large size particles of diameter 2.1 ± 0.4 and 4.7 ± 1.7 nm. For IrO\textsubscript{2}-N-rGO-20, the particle diameter increased to 1.7 ± 0.4 nm, resulting in its reduced activity. In the case of IrO\textsubscript{2}-N-rGO-125, the IrO\textsubscript{2} nps showed shape distortion; however, the agglomeration of nps was not observed after 1800 cycles. The particle diameter (1.6 ± 0.3 nm) also remained the same as it was before EC analysis (1.6 ± 0.3 nm). The comparison of the np size distribution histogram for the three catalysts before and after EC analysis is shown in Figure S9 and Table S6. The selected-area diffraction (SAED) patterns for the samples after postmortem analysis are shown in Figure S10. The relative carbon content after ADT analysis could not be estimated as, during the OER process, there is a high possibility of a simultaneous carbon oxidation reaction (COR) occurring. In general, the standard potential for oxidation of carbon to CO\textsubscript{2} is 0.207 V versus the RHE,\textsuperscript{44} corresponding to \[ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \]

While the OER advances, there occurs a possibility of OER–carbon corrosion reaction interaction, that is, the OER and COR or carbon corrosion reaction can occur simultaneously.\textsuperscript{45,46} Loss of carbon content due to carbon corrosion

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\text{Figure 7. Tafel plots and calculated Tafel slopes of the OER for IrO}_2\text{-N-rGO-7, -20, and -125 estimated from the LSV profiles in Figure 6a.}
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during this process would alter the relative content of N-rGO. The fact that the effect of the OER and COR process on N-rGO cannot be separated would add to the difficulty of estimating the content change due to the OER.

In conclusion, this research article is the first investigation of the size dependence of the initial precursor of the N-rGO support on the OER activity of deposited IrO$_2$ catalysts. The catalysts showed optimum densities but significantly improved durability with increased flake size. Additionally, the activities were better than the initial activities of the supports. However, the effect of the extent of heteroatom doping amount, varied IrO$_2$ loading, and actual size of the flake after several processing steps on catalytic activity remain unclear. We plan to optimize the synthesis condition of nitrogen-doped reduced GO and the loading of IrO$_2$ to improve the catalytic activity in our future work.

■ CONCLUSIONS

N-rGos were prepared using graphite with various flake sizes as the precursor. The synthesis was done via the combination of pyrolysis in the presence of a N precursor followed by IrO$_2$ np deposition via the hydrothermal method. The N-rGO supports were characterized for their morphology and chemical composition. The XPS spectra indicated that N-rGO-7 and N-rGO-125 (both processed from natural graphite) have a higher ratio of pyrrolic N than N-rGO-20 which is processed from synthetic graphite. On a different note, IrO$_2$-N-rGO-125 (the catalyst from a bigger flake size graphite) shows higher overpotential and better durability compared to the other two catalysts derived from smaller-size graphite, IrO$_2$-N-rGO-7, and IrO$_2$-N-rGO-20. Our XPS results reveal that in IrO$_2$-N-rGO-125, the Ir 4f is shifted 0.2 eV to a higher binding energy compared to Ir 4f peaks in IrO$_2$-N-rGO-7 and IrO$_2$-N-rGO-20. This means that the Ir binding in IrO$_2$-N-rGO-125 is different than that in the other two catalysts. This emphasizes the fact that the interaction between the metal and the support is an important factor in the improvement of the electrocatalytic activity for the OER. Apart from all the other parameters such as loading amount, the surface area of nps, conductivity of the support, and so forth, the structural aspects of initial graphite precursors also play a crucial role in determining the electrocatalytic activity for the OER.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03496.

Materials and methods, TEM, Raman, XRD data, SAED and AFM analysis of GO and rGO, Ir 4f deconvolution data of the catalysts, and size distribution data of nps before and after electrochemical analysis (PDF)

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Figure 8. Postmortem TEM images of (a−c) IrO$_2$-N-rGO-7, (d,e) IrO$_2$-N-rGO-20, and (f,g) IrO$_2$-N-rGO-125.
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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript. P.J.: research, data analysis, and drafting of the manuscript. R.Y. and K.K.H.D.S.: data analysis and synthesis. H.S. and Y.M.: MP-AES analysis. M.H. and M.Y.: supervision and manuscript editing.

Notes

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