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Title: Effect of pH on the Reduction of Graphene Oxide on its Structure and Oxygen Reduction Capabilities in the Alkaline Media

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Abstract

The reduction of many catalysts in aqueous media is usually carried out in a basic environment using most reducing agents. Graphene oxide (GO) was synthesized and reduced by sodium borohydride in aqueous solution over a wide spectrum of pH values ranging from 1 to 13. X-ray diffraction (XRD) and infrared spectroscopy (FTIR) confirmed the reduction of the graphene oxide at each respective pH value. Raman and X-Ray photoelectron spectroscopy (XPS) spectra displayed an increased repair in the graphitic sp^2 domain of the catalysts as the pH value of the solution was increased. Half-cell electrochemical testing in basic media showed higher oxygen reduction capabilities in the catalysts that were reduced at higher pH values. The onset potential of the oxygen reduction reaction (ORR) also increased as the pH of the solution increased overall due to the increased repair in the graphitic domain of the catalysts reduced at higher pH values.

Keywords: acidity, basicity, graphene, oxygen reduction, sodium borohydride

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1. Introduction

Over the past decade, graphene has attracted much attention in the scientific and industrial communities. Due to its high surface area,^[1] charge carrier mobility,^[2] capacitance,^[3] functionalization ability,^[4] and other aspects, graphene has been sought after for use in batteries,^[5,6] capacitors,^[7,8] sensors,^[9,10] and many other devices. Graphene is a relatively versatile material that can be synthesized via multiple routes from graphene oxide (GO), graphite, and other small organic molecules. A few of these routes include hydrothermal,^[11] microwave,^[12] ultraviolet radiation,^[13] and electrochemical.^[14] Each synthetic route affects the size and morphology, which impacts certain chemical and electrical properties of graphene. In the hydrothermal route, GO is usually dispersed in an aqueous solution or other solvents such as ethylene glycol. A reducing agent is then used to remove the oxygen functional groups such as epoxides, carboxylic acids and hydroxides while regenerating the sp^2 carbon lattice. Unlike hydrazine, which is toxic, sodium borohydride is one of the most widely used reducing agents due to its strong reducing ability and can be used under a wide range of pH conditions.

The oxygen reduction reaction (ORR) has been extensively investigated and is used for many applications, specifically for the cathode reaction in

many types of proton exchange membrane (PEM) based fuel cells. The kinetics of this process, however, is sluggish mainly due to the difficulty in breaking of the oxygen double bond^[15] leading to lower onset potentials, current densities, and decreased fuel cell performance.^[16,17] The step wise formula for the four electron transfer in O_2 reduction in the alkaline media is:^[18]

Where * denotes the adsorption to the active catalyst site. This gives an overall four electron reduction reaction of:

There is also a two electron reduction of oxygen to the peroxide anion in the alkaline media.^[19]

Much work has been carried out to both enhance the ORR kinetics as well as to eliminate the use of noble metal catalysts such as platinum. Recently, graphene and its derivatives have shown great promise as substitutes for noble metal catalysts for ORR especially in the alkaline medium.^[20] Much research has been carried out on graphene to enhance its ORR capabilities such as doping p-block elements into the structure,^[21–23] graphene quantum dots,^[24] graphene flakes,^[25] and other moieties as both stand-alone catalysts and support for other metal catalysts.

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In many of the studies involving the hydrothermal reduction of GO, the pH of the solution is usually adjusted to around 9-10 before adding the reducing agent.^[26-28] This is also the case with many metal salts impregnated onto supports with sodium borohydride.^[29] There have been other studies, where graphene oxide has been reduced in an autoclave at different pH levels. However, different compounds were used for the particular reduction.^[30] In the present study, a facile reduction of GO by sodium borohydride was carried out in aqueous solutions at several pH values ranging from 1 to 13 in order to analyse the effects on the structure and catalytic properties towards ORR in the alkaline medium.

2. Experimental

2.1. GO Synthesis

GO was synthesized via the modified Hummer's method.^[31] Briefly, 2.0 g of graphite powder (325 mesh, 99.8%, Alfa Aesar) was added to 50 mL anhydrous sulfuric acid (H_2SO_4 , Macron) in an ice bath and stirred for 30 minutes. 5.0 g of potassium permanganate (KMnO_4 , EMD) was added and the solution was stirred in the ice bath for 1 hour and then transferred to an oil bath at 40 °C for another hour. The solution was then diluted with 50 mL of Millipore water (Direct-Q UV, 18.2 M Ω), where 15 mL of 30% hydrogen peroxide (H_2O_2 , Macron) was added to terminate the reaction. The GO was vacuum filtered and washed 3 times with a 10% HCl solution and then 5 times with Millipore water before being dried in an oven at 80 °C.

2.2. rGO Synthesis

GO was reduced at various pH values, ranging from 1 to 13. 0.1 g of previously synthesized GO was vigorously stirred and sonicated for 1 hour in 100 mL Millipore water until the slurry was thoroughly dispersed. The pH of the slurry was initially measured at 3.55 and monitored through the adjustment process with a digital pH meter (Mettler Toledo). An appropriate amount of 3.0 M NaOH or 10% HCl solution was then added to adjust the pH of the slurry to 1, 4, 7, 10, or 13. The catalysts will be referenced as "rGO-" followed by the pH of the slurry. The slurry was then heated to 95 °C in an oil bath and a freshly made aqueous sodium borohydride solution was added in three consecutive aliquots each of 10 mM of aqueous sodium borohydride (NaBH_4) to effectively

reduce the GO. The slurry was stirred at 95 °C for 1 hour and then at room temperature overnight. It was then centrifuged and washed with Millipore water until the pH of the supernatant was neutral and no chlorine atoms were detected with the silver nitrate test and the obtained rGO was dried in an oven at 80 °C overnight.

2.3. Catalyst Characterization

Powder X-Ray Diffraction (XRD) measurements were performed on a Rigaku X-Ray diffractometer using $\text{Cu-K}\alpha$ (0.154056 nm) radiation with a scan rate of 6° min⁻¹ from a 2 θ value of 10° to 90°. X-Ray Photoelectron Spectroscopy (XPS) measurements were taken on the Kratos Axis Ultra with a Monochromatic Aluminum X-Ray radiation source. Thermogravimetric analysis (TGA) was performed on a TGA-50 Thermogravimetric Analyzer (Shimadzu) with the catalysts being heated at a rate of 10 °C per minute. Transmission Electron Microscopy (TEM) images were taken on the JEOL JEM 2100F electron microscope with an acceleration voltage of 200 keV. Scanning Electron Microscopy (SEM) images were taken on the JEOL JSM-7001F electron microscope with an acceleration voltage of 10.0 keV. Raman measurements were performed on a Horiba XploRA ONE Raman microscope with a 532 nm wavelength laser excitation. The catalysts also underwent an acid-base potentiometric titration to measure the pK_a values of the surface species. 10 mg of catalyst was sonicated in 10 mL of 0.1 M NaOH solution. The pH of the solution was constantly monitored with a digital pH meter (Mettler Toledo) while 100 μL aliquots of 0.1 M HCl solution were pipetted with the pH equilibrating between each addition. A blank solution of 10 mL 0.1 M NaOH was also titrated for comparison. Surface areas of the catalysts were determined using UV-vis spectroscopy with methylene blue (MB) dye adsorption. 1 mg of the catalysts was stirred in a 5.25 x 10⁻⁵ M aqueous solution of MB for 24 hours. The solution was centrifuged and the supernatant was analyzed by UV-vis spectroscopy at the wavelength peak at $\lambda = 662$ nm.

2.4. Electrochemical Measurements

A standard rotating disk electrode (RDE) was used in a three-cell electrochemical fixture. Measurements were taken on a Solartron SI 1287 Potentiostat using Corware Software for analysis. 1 mg of catalyst was added to a 1 mL solution consisting of 10% isopropyl alcohol, 90% Millipore water, and 10 mg of 5% Nafion® ionomer solution (Ion Power). The solution

was sonicated and 20 μL pipetted onto a glassy carbon electrode with a surface area of 0.195 cm^2 with a catalyst loading of 0.10 mg cm^{-2} . The counter electrode was a platinum wire and the reference electrode a Hg/HgO (MMO) electrode (Koslov, 4.24 M KOH filling solution, 0.98 V vs. RHE).

The cell was purged with ultra pure oxygen (99.994%) for 15 mins before the cyclic voltammetry (CV) scans were performed from -0.5 V to 0.7 V vs. MMO at 20 mV s^{-1} . Linear sweep voltammetry (LSV) measurements were performed by scanning the potential from 0.25 V to -0.75 V vs. MMO at 5 mV s^{-1} with rotations of 100, 400, 700, 1000, 1300, and 1600 RPM. Chronoamperometry measurements were also taken at -0.5 V vs. MMO at 1600 RPM for 3000 seconds.

3. Results and Discussion

3.1. Catalyst Characterization

In order to confirm the reduction of the catalysts, XRD patterns were obtained and shown in Figure 1a. The GO catalyst displays a sharp peak at a 2θ value of 11.0° signifying the (100) crystallographic orientation of GO with a d-spacing of $8.01\text{ \AA}$. After each reduction, the characteristic peak shifts to a 2θ value of around 23° signifying the (002) crystallographic orientation of the rGO species. The exact 2θ values with the corresponding d-spacings are reported in Table 1. As the pH of the solution decreases, the d-spacing of the catalysts decreased except for the rGO-13 catalyst. This could be due to the lesser concentration of oxygen containing species on the graphitic lattice under more acidic reduction conditions. Peak broadening is also displayed as the pH of the solution decreases from 10 to 1 indicating a smaller overall crystallite size and increase in the defects in the graphitic structure of the catalysts under more acidic reduction conditions.^[32,33]

The FTIR spectra of the catalysts are shown in Figure 1b. The spectrum of the GO has the characteristic peaks at 3342 cm^{-1} and 1414 cm^{-1} representing the OH and C-OH stretching, respectively, 1715 cm^{-1} indicating the carboxyl stretch, 1612 cm^{-1} denoting the aromatic sp^2 carbon stretch, 1218 cm^{-1} representing the C-O epoxy stretch, and 1026 cm^{-1} corresponding to the alkoxy C-O stretch.^[34,35] These major peak intensities are greatly reduced in the rGO catalysts signifying the loss of many of the functional groups after the reduction.^[36]

In the rGO-13 and rGO-10 catalysts, there is a slight presence of the hydroxide stretching peaks at 3342 cm^{-1} and the C-OH stretching at 1414 cm^{-1} and 1419 cm^{-1} , most likely due to the basic environment that the GO was reduced in.

Raman spectroscopy plays a vital role in the relative characterization and disorder of the graphitic plane in both GO and rGO catalysts. Figure 1c shows the Raman spectra of the catalysts. There are two characteristic peaks in the spectra, one at around 1370 cm^{-1} signifying the D-band and the other at around 1580 cm^{-1} signifying the G-band. The D-band measures the lattice distortion of the graphene from various functional groups and defects, while the G-band measures the first order scattering of the E_{2g} phonon from the sp^2 hybridized carbon lattice.^[37] The I_D/I_G ratio reveals the extent of defects and size of the sp^2 graphitic domain of the catalyst.^[38] A summary of the I_D/I_G ratios is reported in Table 1. After the reduction, the I_D/I_G ratios of the rGO catalysts increase due to the smaller overall graphitic domain size compared to GO. The ratios for the rGO catalysts also increase as the pH of the solution decreases due to the unpaired defects in the graphite lattice from the removal of some of the oxygen groups.^[39] This could be due to the harsher acidic environment of the reduction for sodium borohydride where many of the oxygen groups are removed but the sp^2 domain is not restored. Another aspect of the I_D/I_G ratio is the calculation of the in-plane sp^2 grain size of the rGO catalyst particles from the equation:^[40]

$$L_a = C(\lambda) * (I_D/I_G)^{-1} \quad (8)$$

where L_a is the in-plane grain size (in nm) and $C(\lambda)$ is the incident wavelength (532 nm) corresponding to a value of 4.4 nm . The in-plane grain sizes of the rGO catalysts are shown in Table 1. As the pH of the solution increases, the in-plane grain size of the catalyst increases. This can be viewed as the better restoration of the sp^2 graphitic lattice from the sodium borohydride. Another aspect from the Raman spectra is the shifting

Fig. 1. Characterization of the catalysts: a) XRD patterns; b) FTIR spectra and; c) Raman spectra.

of the D and G band peaks. The red shift in the G-band from the GO to rGO catalysts can be attributed to a more ordered aggregation of the sp^2 hybridized carbons from the reduction.^[41] The rGO-13, rGO-10, and rGO-1 catalysts all display the same amount of redshifting for both the D and G bands of the Raman spectra. The red shift in the D band signifies the amount of strain induced on the graphitic lattice.^[42,43] The rGO-7 and rGO-4 catalysts display a higher red shift in the D and G bands indicating more strain in the graphitic lattice. It is unclear why the rGO-1 catalyst exhibits the same red shift for the D and G bands as the rGO-13 and rGO-10 catalysts instead of the rGO-7 and rGO-4 catalysts. One possible explanation could be the addition of the HCl in the aqueous solution has an effect on the graphitic structure. The shift in the G band could also be due to the presence of a second peak, the D' band, at 1620 cm^{-1} .^[44] However, the presence of the D' band is evident in all of the rGO catalysts as well as the GO catalyst and does not explain why some of the peaks are more red shifted than others.

TEM images were obtained and shown in Figure 2. The rGO catalysts display more crinkles and ridges than for the GO catalyst due to the reduction and removal of functional groups in the graphitic lattice. SEM images were also taken and shown in Figure S1.

The images are all similar showing thin sheets of GO and rGO catalysts with little macro-size differences overall.

XPS is also a powerful technique for characterizing the different functional groups and structures of graphene compounds. XPS C1s spectra were obtained and the deconvoluted spectra are shown in Figure 3a-f with the deconvoluted peak results shown in Table S1. The spectrum for GO in Figure 3a displays two peaks: one comprised of the sp^2 and sp^3 hybridized carbon regions of the graphitic lattice at 284.4 eV and 284.8 eV , respectively and the other at 286.8 eV for the epoxide C-O peak. The size of the C-O peak is greatly reduced in each of the rGO catalysts showing an effective reduction of GO across the pH spectrum. The C=O peak showed little decrease in area due to sodium borohydride's relative inability to reduce the carbonyl groups.^[45] Another aspect worth noting is the ratio of the size of the sp^2 and sp^3 deconvoluted peaks in the spectra shown in Table 1. As the pH of the solution increases, the ratio in size between sp^2 and sp^3 hybridized carbon increases. This can be seen as the effective repairing of the graphitic lattice in the reduction process^[46] as the solution becomes more alkaline. This concurs with the I_D/I_G ratios from the Raman spectra where the ratio decreases as pH increases showing larger graphitic sp^2 domains and less disorder in more basic pH reduction environments. Overall, the sodium borohydride is successful at removing much of the C-O groups during the reduction at all pH values in the solution, however, it seems that the acidity of the solution hinders the ability to repair the sp^2 lattice resulting in smaller overall graphitic domains.

Acid base potentiometric titrations were also performed to analyze the pKa of the ionic species on the rGO catalysts. The titration curves of the catalysts and the blank are shown in Figure S2a. Figure S2b was derived by subtracting the difference in HCl solution added at each given pH value (Δx). Figure S3 was derived from differentiating the curves in Figure 2b with the changing pH values and were deconvoluted from Gaussian distributions to show the pKa values of the acid groups on the catalyst surface.^[47] In all studied catalysts, except for rGO-13, three pKa peaks arise at around 4.0,

Fig. 2. TEM images of the catalysts: a) GO; b) rGO-1; c) rGO-4; d) rGO-7; e) rGO-10; and f) rGO-13. The measuring bar indicates 100 nm.

6.2, and 10, signifying two carboxylic acid groups and one hydroxide group, respectively.^[48] The hydroxide group arises from the rGO in the alkaline solution.^[49] In rGO-13, a fourth peak arises at around 7.4 most likely signifying a carboxylate ion present.^[50] This can also be seen in the XPS spectra where the C=O peak increases with the increasing pH of the reducing solution. This shows that the acidity of the ionized species from the functional groups on the graphene lattice of the catalysts is minimally affected at the different pH values in the reduction process. Surface area determination of the catalysts was also carried out using aqueous Methylene Blue (MB)

Fig. 3. C1s XPS Spectra of: a) GO; b) rGO-1; c) rGO-4; d) rGO-7; e) rGO-10 and; f) rGO-13.

solutions to adsorb onto the surface of the catalysts^[51,52] and are reported in Table 1. The rGO-10 catalyst displayed the highest surface area whereas the surface area decreases as the pH of the reduction solution decreases. This trend closely mimics the D-spacing trend of the catalysts determined from the XRD patterns in Figure 1a. The surface area of the rGO-13 is lower than the rGO-10 catalysts probably due to the increase in ripples in the catalyst sheet as seen in the microscopy images in Figures 2 and S2. This could slightly decrease the MB adsorption and subsequent surface area as well as the increase in defects and lack of repair of the graphitic lattice.

Table 1. Summary of the characterizations of the catalysts.

Catalyst	Peak (2 θ)	D-spacing (nm)	I _D /I _G	D-band position (cm ⁻¹)	G-band position (cm ⁻¹)	In-plane grain size (nm)	sp ² /sp ³	Surface Area (m ² g ⁻¹)
GO	11	0.801	1	1349.85	1591.27	4.41	0.357	381
rGO-13	23.7	0.375	1.1	1347.34	1578.7	4	1.638	397
rGO-10	22.7	0.391	1.26	1347.34	1578.7	3.5	1.077	418
rGO-7	23.4	0.379	1.29	1344.82	1576.18	3.41	0.891	286
rGO-4	23.5	0.378	1.31	1344.82	1576.18	3.36	0.827	247
rGO-1	24.9	0.357	1.33	1347.34	1578.7	3.31	0.685	117

3.2. Electrochemical Testing

A regular CV of the catalysts under argon at 20 mV s^{-1} in alkaline media is shown in Figure 4. The relative electrochemically active surface area (ECSA) of the catalysts in solution can be found in the double layer capacitance region around -0.1 V to 0.3 V in the CV. This is due to the sorption of the hydroxide groups onto the graphitic carbon lattice edges in the alkaline media.^[49] The active surface area appears to decrease as the pH value of the solution of reduction decreases. This trend mimics the one found with the surface area determinations with the MB adsorption.

Figure 5a shows LSV scans of the catalysts at 1600 RPM in the alkaline media. The current densities at -0.5 V vs. MMO as well as onset potentials are shown in Table 2. The ORR catalytic properties are enhanced from the reduction process when the rGO catalysts are compared to GO. Furthermore, the ORR activity tends to decrease as the pH value of the reduction solution decreases. This could be due to the smaller active surface areas and less ORR active sites on the catalysts as shown in Figure 4. The greater strain in the lattice as shown in the Raman spectra could also play a role leading to lower current densities in the rGO-7 and rGO-4 catalysts. Another trend in the LSV curves among the catalysts is the onset potential of the catalysts increases as the pH of the reducing solution increases. This could also be the result of the increased repair of the rGO catalyst and the increase in surface edges from the higher active surface areas. This could result from the decrease in repair of the sp^2 graphitic lattice as was shown in the XPS and Raman spectra.

There have been conflicting results pertaining to the mechanism and reactive sites for undoped graphene structures for ORR. Some studies have concluded that the sp^2 hybridized carbon edges of the graphene are the most active for oxygen reduction in the alkaline media with zig-zag edges being more ORR active than the armchair region.^[18,53]

Fig. 4. CV scans of the catalysts in 0.1 M KOH under argon.

Other studies have concluded that the functional groups on the graphene sheets such as carbonyl and quinones are actually responsible.^[54,55] From the results of the XPS spectra in Figures 3b-f and Table S1 along with the pH titration results in Figures S4a-e, the trends from our half-cell electrochemical tests would indicate the former explanation to be applicable in this case. The XPS spectra displayed no direct correlation between the pH of the reducing solution and the amount of surface functional groups found on the rGO catalysts. The pKa titration curves also displayed minimal difference in the surface functional groups on the rGO catalysts except for the rGO-13. There seems to be a correlation between the repair of the graphene sheets, which is contrary to the amount of functional groups present and ORR performance. In such a case, the sp^2 carbon edges would seem to be the active sites for ORR. The pH of the solution in the pre-reduction could possibly have an effect of breaking apart the graphene sheets allowing for more edges and increased ORR active sites. Previous studies have shown that the half-life of sodium borohydride decreases in an order of magnitude with each decreasing pH unit from the equation:^[56]

$$\text{Log}_{10}t_{1/2}(\text{mins}) = \text{pH} - (0.034T - 1.92) \quad (9)$$

where $t_{1/2}$ is the half-life of the sodium borohydride in minutes and T is the temperature of the solution in Kelvin. This could be a reason that there is more repair to the graphitic lattice at higher pH values: the sodium

Fig. 5. ORR catalytic tests of the catalysts: a) LSV scans under O_2 at 1600 RPM in 0.1 M KOH and; b) Koutecky-Levich plot of the catalysts at -0.5 V vs. MMO.

Fig. 6. Tafel plots of the catalysts in 0.1 M KOH at 1600 RPM.

borohydride has a greater concentration and time to repair the graphitic lattice before it decomposes. The longer lifetime of the sodium borohydride, the smaller the rGO sheets are with increased surface area as demonstrated from the MB adsorption tests and CVs.

A Koutecky-Levich plot was made from the current densities of the LSVs at a potential of -0.5 V vs MMO and is shown in Figure 5b. The slopes from the plot were taken and the electron transfer values are shown in Table 2, calculated from the Koutecky-Levich equation:^[57]

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} = \frac{1}{I_k} + \frac{1}{0.62 n F A D_{O_2}^{2/3} \nu^{-1/6} c_{O_2}^b \omega^{1/2}} \quad (10)$$

Table 2. Summary of the electrochemical tests for the catalysts.

Catalyst	Onset Potential (V vs. MMO)	Current Density @ -0.5 V ($mA\ cm^{-2}$)	e^- Trans Number @ -0.5 V	Tafel Slope ($mV\ dec^{-1}$)
GO	-0.161±0.054	-0.35±0.09	n/a	102±9
rGO-13	-0.044±0.007	-1.43±0.11	2.34	85±4
rGO-10	-0.064±0.004	-0.94±0.16	2.41	86±1
rGO-7	-0.073±0.003	-0.85±0.07	2.19	81±3
rGO-4	-0.071±0.018	-0.78±0.04	2.21	111±5
rGO-1	-0.103±0.020	-0.79±0.17	2.34	98±15

where I is the measured current, I_k is the kinetic limitation current, I_d is the diffusion limitation current, n is the electron transfer number, F is the Faraday constant, A is the electrode area, D_{O_2} is the diffusion coefficient of oxygen in the bulk phase, ν is the kinematic viscosity of the solution, c_{O_2} is the concentration of oxygen in the bulk phase, and ω is the rotation rate in $rad\ s^{-1}$. The electron transfer numbers of the catalysts were calculated and shown in Table 2. The electron transfer numbers for all the catalysts are all close to 2 signifying a 2 electron transfer process resulting in mainly the peroxide anion being produced as shown in equation (7). This is typical of other undoped, bare rGO catalysts previously studied in an alkaline medium.^[55,58]

Tafel curves of the catalysts were taken and shown in Figure 6 and the Tafel slopes shown in Table 2. There are two main different slope values of the catalysts. For rGO-13, rGO-10, and rGO-7, the slope is in the low to mid 80 $mVs\ dec^{-1}$. These slopes are similar to ones previously reported for doped graphene^[59] and platinum.^[16] For GO, rGO-4, and rGO-1 the slope is in the lower 100 $mVs\ dec^{-1}$ which is similar to other rGO catalysts reported elsewhere.^[60] The overpotentials in the Tafel plots for rGO-13, rGO-10, and rGO-7 display similar value whereas the overpotentials for GO and rGO-4 are similar to one another and the overpotential for rGO-1 is the highest. Chronoamperometry measurements were obtained and are shown in Figure S4. All of the curves have similar slopes signifying similar long-term oxygen reduction stabilities. The current densities resemble the ones shown in the LSVs with GO being the lowest and rGO-13 being the highest.

4. Conclusions

Graphene is a very versatile material that can be easily modified and tuned to serve a wide range of functions. The overall structure and catalytic properties of graphene have been shown to be modified with the varying of pH of aqueous solution in the reduction in this study. The rGO catalysts synthesized in solutions at higher pH values showed a better repair of the sp^2 graphitic lattice from both the Raman and XPS spectra and showed a smaller lattice size with decreasing pH from the XRD pattern. From the electrochemical tests, the ORR capabilities of the catalysts increased as the pH of the reducing solution increased overall. The catalysts synthesized at the lower the pH values displayed less repair of the lattice with defects most likely around the edges, which have been

demonstrated to be unsuitable for effective oxygen reduction. Much work has been carried out to optimize stand-alone graphene for use as an efficient ORR catalyst but still more studies are needed to employ it as a viable alternative to replace many noble metals for use in fuel cells in the future. This technique could possibly be employed for the synthesis of modified rGO materials, particularly heteroatom-doped rGO compounds for metal free ORR catalysis in order to help optimize the ORR kinetics of non-noble metal graphene-based catalysts.

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