Oxygen reduction catalyzed by nanocomposites based on graphene quantum dots-supported copper nanoparticles

Ke Liu, Yang Song, and Shaowei Chen*

*Department of Chemistry and Biochemistry, University of California, 1156 High Street, Santa Cruz, California 95064, USA. * E-mail: shaowei@ucsc.edu*

Abstract

Nanocomposites based on graphene quantum dots (GQDs)-supported copper nanoparticles were prepared by thermal refluxing of copper salts in 1,2-propanediol at 140 °C in the presence of GQDs. Transmission electron microscopic measurements showed that the resulting Cu/GQD nanoparticles increased from 5 to 15 nm in average diameter with increasing metal loadings. Raman spectroscopic measurements showed that all nanocomposites exhibited well-defined D and G vibrational bands. X-ray photoelectron spectroscopic studies indicated the formation of Cu₂O and CuO in the nanocomposite particles, along with various defect concentrations within the GQD graphitic skeletons. Electrochemical studies showed that the nanocomposites exhibited apparent electrocatalytic activity in oxygen reduction in alkaline media, and the sample with a Cu/C atomic ratio of 2.88% exhibited the best ORR activity among the series, within the context of onset potential, number of electron transfer and kinetic current density. The performance was further improved by deliberate hydrothermal treatments of the sample, and 160 °C was identified as the optimal temperature, which was ascribed to manipulation of the electronic interactions between copper nanoparticles and oxygen intermediates by the GQD structural defects.

Keywords: *graphene quantum dots; copper nanoparticle; hydrothermal; defect; oxygen reduction*

1. Introduction

Oxygen reduction reactions (ORR) have long been regarded as a major bottleneck of the overall fuel cell performance, due to the sluggish electron-transfer kinetics and complex reaction pathways [1-3]. Therefore, extensive efforts have been devoted to the development of efficient catalysts so that sufficiently high current density can be achieved for practical applications. Towards this end, substrate-supported discrete nanoparticles have attracted particular attention. These include monometallic nanoparticles [4-7], alloy nanoparticles [8-10], metal oxides nanoparticles [11-15], and transition metal chalcogenide nanoparticles [16] that are supported on diverse substrates including metal structures [17], metal oxides [18], or carbon-based materials such as carbon black, standard carbon fibers [19], single- or multi-walled carbon nanotubes [20], and graphene sheets [21-24]. As summarized in several recent reviews [25-27], these supporting materials play important roles in, for instance, preventing nanoparticle aggregation and increasing the corresponding surface areas; manipulating electronic energy of the metal nanoparticles and hence interactions with O₂ molecules via intimate electronic interactions with the supporting substrates; enhancing electronic conductivity and serving as current collectors; as well as improving structural stability of the catalysts in extreme acidic or basic environments.

Among these, Pt nanoparticles (diameter 2 to 4 nm) supported on high-surface-area carbon black have been used extensively [28]. However, the high costs and scarcity of platinum render it necessary to develop cost-effective non-Pt substitutes for fuel cell electrocatalysis. Copper is inexpensive, abundant with excellent electronic conductivity. It has been reported that O₂ molecules can adsorb readily onto and migrate on copper surfaces [29] and the adsorbed oxygen may undergo a two-step hydrogenation process to form gaseous water [30, 31]. ORR activities of bulk copper have also been observed in a borax buffer solution [32, 33] or in sulfuric

acid solution [34], where the surface redox chemistry of $\text{Cu}_2\text{O}/\text{CuO}$ plays an important role in the reduction of oxygen molecules. In a more recent study, reduced graphene oxide (RGO)-supported cuprous oxide nanoparticles were found to serve as efficient catalysts for ORR where the mobile electrons in the graphene network can be supplied to Cu_2O nanoparticles and then donated to oxygen [35]. However, graphene sheets usually exhibit irregular shapes and are prone to folding and wrinkling because of strong π - π interactions leading to a loss of the surface area [36]. Such an issue may be minimized by using nanosized GQDs. For instance, platinum nanoparticles supported on GQDs (in the range of 1 to 4 nm) have been reported to exhibit significantly enhanced catalytic activity towards ORR as compared to commercial Pt/C catalysts [37, 38]. This was accounted for by the large surface-to-volume ratio and abundant structural defects of GQDs that manipulate the binding interactions of oxygen on Pt and hence facilitate the corresponding charge transfer process. Such a fundamental principle may be exploited for the design and engineering of effective ORR catalysts based on GQD-supported metal nanocomposites. This is the primary motivation of the present study.

Herein, we prepared GQD-supported copper nanoparticle composites and examined the ORR activity in alkaline media. Experimentally, the submicrometer domains of traditional pitch-based carbon fibers were broken down by acid treatments and chemical exfoliation, yielding nanometer-sized GQDs [39]. The GQDs were then used to prepare a series of Cu/GQD nanocomposites at controlled copper loadings by thermolytic reduction of copper salts in 1,2-propanediol, followed by hydrothermal treatments at various temperatures. The structural characteristics of the Cu/GQD nanocomposites were carefully examined by transmission electron microscopic, Raman, and X-ray photoelectron measurements. Electrocatalytic activities of the nanocomposites were tested by rotating ring-disk electrode (RRDE) voltammetry. The Cu/GQD

nanocomposites at a Cu/C atomic ratio of 2.88 % showed the best performance among the series, which might be further improved by hydrothermal treatment to manipulate the GQD defect concentration, within the context of onset potential, number of electron transfer as well as kinetic current density.

2. Experimental section

2.1 Chemicals.

Cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\geq 98.0\%$, Fisher Scientific), sodium acetate trihydrate ($\text{NaOAc} \cdot 3\text{H}_2\text{O}$, MC&B), 1,2-propanediol (ACROS), pitch carbon fibers (Fiber Glast Development Corporation), sodium carbonate (Na_2CO_3 , $\geq 99.5\%$, Sigma-Aldrich), sulfuric acid (H_2SO_4 , Fisher Scientific), and nitric acid (HNO_3 , Fisher Scientific) were all used as received without any further purification. Solvents were purchased at the highest purity available from typical commercial sources and also used as received. Water was deionized with a Barnstead Nanopure Water System ($18.3 \text{ M}\Omega \cdot \text{cm}$).

2.2 Preparation of GQD-supported Cu nanoparticles

The procedure for the preparation of GQDs has been detailed previously [37-39]. Note that low-frequency high-energy sonication is a powerful technology in surface cleaning as well as de-agglomeration and dispersion of bulk materials [40, 41]. Therefore, experimentally, concentrated H_2SO_4 and HNO_3 were mixed with carbon fibers, and the mixture was subject to sonication for 2 h in order to separate those carbon fibers and then continuous stirring at 120°C for 24 h. The sonication was carried out with a VWR B1500A-MTH sonicator with a power of 143 W and a frequency of 40 kHz. The mixture was then cooled down to room temperature and diluted with Nanopure water with the pH adjusted to 8 by Na_2CO_3 . Then the solution was dialyzed in a dialysis bag, affording purified GQDs.

The GQDs prepared above were then used for the preparation of Cu/GQD nanocomposites. In a typical reaction, a calculated amount of CuSO₄ and NaOAc (at a 1:6 molar feed ratio) were dissolved in 50 mL of 1,2-propanediol together with a certain amount of the GQDs prepared above. The mixture was first subject to nitrogen bubbling for 30 min and then thermal refluxing at 140 °C under continuous stirring for 1 h before the solution was cooled down. The black precipitates were collected and purified with a copious amount of acetonitrile and Nanopure water. Four samples were prepared at varied Cu/C atomic ratios (x) and denoted as #1 to #4.

2.3 Hydrothermal treatment of Cu/GQD composites

A calculated amount of the Cu/GQD ($x = 2.88\%$) composites prepared above was dispersed in water in a Teflon-lined stainless autoclave, which was then placed in a Thermolyne Type F1500 muffle furnace. The hydrothermal treatment was carried out for 12 h at four different temperatures (140 °C, 160 °C, 180 °C, and 200 °C).

2.4 Characterization

The morphology and size of the Cu/GQD nanoparticles were characterized by transmission electron microscopic studies (TEM, Philips CM300 at 300kV). Raman spectroscopic measurements were carried out with a Delta NU 532 nm Raman spectrometer. X-ray photoelectron spectra (XPS) were recorded with a PHI 5400/XPS instrument equipped with an Al K α source operated at 350 W and 10^{-9} Torr. Silicon wafers were sputtered by argon ions to remove carbon from the background and used as substrates. Deconvolution of the XPS spectra was carried out by using XPSPEAK 4.1 with a Shirley-type background.

2.5 Electrochemistry

Electrochemical tests were carried out in a standard three-electrode cell connected to a CHI 710C electrochemical workstation, with a Pt foil counter electrode and a reversible hydrogen reference electrode (RHE). The working electrode is a rotating platinum ring/glassy-carbon disk electrode (RRDE). A calculated amount of the Cu/GQD nanocomposites prepared above was dispersed in water to prepare a catalyst ink which was then slowly dropcast onto the glassy-carbon disk electrode surface of the RRDE and dried under gentle N₂ in order to minimize the so-called “coffee ring” effects [42]. The catalyst films were then coated with 3 μ L of a dilute Nafion solution (0.1 wt.%) and dried in air. The catalyst loadings were 15 μ g for all Cu/GQD samples.

3. Results and discussion

The chemical compositions and valence states of the Cu/GQD nanocomposites were first evaluated by XPS measurements. Figure 1 (A) depicts the survey spectra of the series of samples where the C1s electrons can be readily identified at ca. 284 eV, and the O1s and Auger peaks at 532 eV and 980 eV are also very prominent (the Si2p peaks are from the Si substrate) [43]. The Cu2p electrons are expected to be found at around 934 eV. Yet the peak is visible only for the sample with the highest Cu loading (sample #4) and becomes increasingly difficult to identify with decreasing copper concentration (#1 – #3). In high-resolution scans, however, both C1s and Cu2p electrons can be easily resolved. For all samples, deconvolution of the C1s spectra in panel (B) yields three major components [44]. The first is sp² C (green curves) which exhibited a rather consistent binding energy among the samples within the narrow range of 284.7 – 285.0 eV. The second is carbon in C–OH (yellow curves) with the peak binding energy between 285.5 and 286.2 eV. The third is C=O/COOH (blue curves) where the binding energy exhibited a rather apparent disparity among the samples, (#1) 287.11 eV, (#2) 289.06 eV, (#3) 287.67 eV, and (#4)

288.22 eV, likely due to a different combination of C=O and COOH moieties. In addition, based on the integrated peak areas, the fraction of C=O/COOH carbons among the total carbons in each sample was estimated to be (#2) 6.6% < (#4) 13.6% < (#3) 15.5% < (#1) 24.8%. That is, sample #2 exhibited the least amount of defective carbons in the series. Additionally, in samples (#1), (#3) and (#4) the primary form was carbonyl carbon (C=O) whereas in sample (#2), carboxylic carbon (COOH) [44].

As for the Cu2p electrons in panel (C), three major peaks were identified by spectral deconvolution with the binding energies very consistent among the four samples. Of these, the peaks at ca. 934.5 eV and 954.3 eV are rather consistent with the Cu2p_{3/2} and Cu2p_{1/2} electrons of metallic copper, respectively [45]. Yet, as the binding energy of Cu(I) and Cu(0) is only 0.1 eV apart, the presence of Cu(I) cannot be excluded [46]. In fact, from panel (A), one can see a broad peak at around 570 eV that is consistent with the LMM-2 auger transitions of Cu(I), indicating at least partial oxidation of the nanoparticles into Cu₂O [45]. Additionally, the emergence of a satellite peak at ca. 944 eV between the Cu2p_{3/2} and Cu2p_{1/2} peaks suggested the formation of CuO. Such a satellite feature is typically observed in ions with a partially filled 3d shell (e.g., Cu(II)) but absent in ions with a completely filled 3d shell (e.g., Cu(I) and Cu(0)), and has been largely ascribed to the shake-up effect where the outgoing electron interacts with a valence electron and excites it to a higher energy level [47]. Similar behaviors have been observed in previous studies with alkyne-capped copper nanoparticles [46]. Furthermore, based on the integrated peak areas, the fraction of Cu(II) among the copper species was all around 30%, whereas the atomic ratio of Cu/C in the nanocomposites was estimated to be approximately (#1) 2.34%, (#2), 2.88%, (#3) 3.32% and (#4) 3.54%.

Figure 1. (A) XPS survey spectra and high-resolution scans of (B) C1s and (C) Cu2p electrons of

Cu/GQD nanocomposites at different Cu/C atomic ratios (x). In panels (B) and (C), black curves are experimental data and colored curves are deconvolution fits.

Figure 2. TEM micrographs of Cu/GQD nanocomposites at different Cu/C atomic ratios (x): (A) $x = 3.54\%$, (B) $x = 3.32\%$, (C) $x = 2.88\%$, and (D) $x = 2.34\%$. Scale bars are all 20nm.

The structures of the Cu/GQD nanocomposites were then examined by TEM measurements. Figure 2 shows representative TEM micrographs of Cu/GQD (x) nanocomposites at different Cu/C atomic ratios: (A, #4) $x = 3.54\%$, (B, #3) $x = 3.32\%$, (C, #2) $x = 2.88\%$, and (D, #1) $x = 2.34\%$. The formation of copper nanoparticles was evidenced by the dark-contrast objects (signified by the red arrows), which were embedded within the low-contrast GQDs that showed various degrees of agglomeration in all four samples. Furthermore, one can see that the size of the copper nanoparticles varied rather drastically with the copper loading (Figure S1): ca. 15.1

nm at $x_{\text{Cu}} = 3.54\%$ in panel (A), 14.2 nm at $x_{\text{Cu}} = 3.32\%$ in panel (B), 10.2 nm at $x_{\text{Cu}} = 2.88\%$ in panel (C), and 5.5 nm at $x_{\text{Cu}} = 2.34\%$ in panel (D). Such a variation of the nanoparticle dimensions might be accounted for by the nanoparticle growth dynamics where increasing concentration of capping ligands (i.e., GQDs) is known to lead to enhanced passivation of the nanoparticles and hence diminishing sizes [48].

Figure 3. Raman spectra of Cu/GQD nanocomposites at different Cu/C atomic ratios (x) which are specified in figure legends.

Further structural insights were unraveled by Raman spectroscopic measurements. From Figure 3, one can see two prominent vibrational bands at *ca.* 1370 cm^{-1} and 1615 cm^{-1} for all samples, which might be assigned to the D and G bands of GQDs, respectively. Additionally, the ratio of the D and G band intensity (I_D/I_G) increases in the order of 0.91 (#2, $x = 2.88\%$) $<$ 0.96 (#3, $x = 3.32\%$) $<$ 0.97 (#4, $x = 3.54\%$) $<$ 0.98 (#1, $x = 2.34\%$), suggesting that the Cu/GQD (2.88%) sample exhibited the least amount of structural defects among the series. This is consistent with results from the XPS measurements (Figure 1). Such a correlation between the XPS and Raman characterizations of GQD structural defects has also been observed previously with Pt/GQD nanocomposites [37].

Fig.4. Cyclic voltammograms of a glassy-carbon electrode (dia. 5.61 mm) modified with Cu/GQD nanocomposites in a nitrogen-purged 0.1 M NaOH solution. Potential scan rate 10 mV/s. Catalyst loading 15 μg .

The electrocatalytic activity of the nanocomposite catalysts for ORR was then tested by voltammetric measurements. Figure 4 shows the cyclic voltammograms of a glassy-carbon electrode modified with 15 μg of Cu/GQDs in a nitrogen-purged NaOH solution. It can be seen that the Cu/GQD (3.32%, red curve) sample exhibited two rather prominent anodic peaks at around +0.55 V and +0.84 V (vs RHE), where the former might be ascribed to the formation of a monolayer of Cu_2O while the latter to the formation of a thick multilayer film of CuO, and a cathodic peak at around +0.70 V that is likely to originate from the partial reduction of CuO to Cu_2O [46, 49, 50]. Similar voltammetric features can be seen with other Cu/GQD (2.88%, green curve; 3.54%, black curve) samples. In contrast, for the Cu/GQD (2.34%, blue curve), the voltammogram was largely featureless, possibly because of the encapsulation of the copper nanoparticles by the GQDs (Figure 2). Such encapsulation effects may also account for the apparent variation of the double-layer charging currents and hence the effective electrochemical surface area among the series, which increased in the order of Cu/GQD (#1, 2.34%) < (#4, 3.54%) < (#2, 2.88%) < (#3, 3.32%), despite the same catalyst loading.

Figure 5 shows the RRDE voltammograms of the same electrodes in an oxygen-saturated 0.1 M NaOH solution at the rotation rates of 100 to 2500 rpm. We can see that for all Cu/GQD nanocomposites, non-zero cathodic currents started to emerge at electrode potentials more negative than +0.80 V, and reached a plateau at sufficiently negative potentials (e.g., $E < +0.60$ V), indicating apparent ORR activity. Yet, marked discrepancy can be seen of the electrocatalytic performance. For instance, the onset potential varied with the copper concentration in the nanocomposites, (#2, $x = 2.88\%$) $+0.82$ V $\approx$ (#3, $x = 3.32\%$) $+0.82$ V $>$ (#4, $x = 3.54\%$) $+0.81$ V $>$ (#1, $x = 2.34\%$) $+0.75$ V. A similar variation can be seen with the disk limiting current density (J_{lim}) at +0.40 V at the rotation rate of 1600 rpm, (#2, $x = 2.88\%$) 40.5 A/m² $>$ (#3, $x = 3.32\%$) 39.7 A/m² $>$ (#1, $x = 2.34\%$) 32.4 A/m² $>$ (#4, $x = 3.54\%$) 29.6 A/m².

Figure 5. RRDE voltammograms of a platinum ring-glassy carbon disk electrode with the disk electrode modified with 15 μg of (A) Cu/GQD at different Cu/C atomic ratios (x), (A) 3.54%, (B) 3.32%, (C) 2.88%, and (D) 2.34% in an oxygen-saturated 0.1M NaOH solution. Current density was obtained by normalizing the voltammetric currents to the electrode geometrical surface area (0.247 cm^2). Electrode rotation rates are specified in the figure legends. Ring potential was set at +1.30 V vs RHE.

Furthermore, one can see that at the ring potential of +1.30 V, the ring currents were at least one order of magnitude smaller than the disk currents for all four nanocomposites catalysts. Based on the corresponding ring (I_{Ring}) and disk currents (I_{Disk}), the number (n) of electron transfer involved in ORR can be quantitatively estimated by $n = 4I_{\text{Disk}}/(I_{\text{Disk}}+I_{\text{Ring}}/N)$ with N being the collection efficiency (37%) [51]. Figure 6 shows the variation of n with electrode potential. It can be seen that the n values increased rapidly with the electrode potential swept from ca. +0.80 V to +0.75 V in the so-called kinetic-controlled region, and at more negative potentials, the increment remained apparent but slow. Within the potential range of +0.60 to +0.10 V, the n values also exhibited a variation with the copper concentration (x) in the Cu/GQD composites, $(\#4, 3.54\%) < (\#3, 3.32\%) \approx (\#1, 2.34\%) < (\#2, 2.88\%)$. For instance, at +0.40 V, $n = 2.76$ for $x = 3.54\%$, 3.17 for $x = 3.32\%$, 3.20 for $x = 2.34\%$, and 3.42 for $x = 2.88\%$, corresponding to the fraction of peroxide species in the final products of 62%, 41%, 40%, and 29%, respectively. This signifies that ORR took place predominantly by the two-electron pathway at Cu/GQD (#4, 3.54%) whereas four-electron reduction to hydroxide (OH^-) was the primary process at other nanocomposites catalysts, in particular, sample #2 which displayed a highest n value and lowest peroxide yield.

Figure 6. The number of electron transfer (n) in oxygen reduction catalyzed by Cu/GQD at different Cu/C atomic ratios (x) which were specified in the figure legends. Data were calculated from the RRDE voltammograms at 1600 rpm in Figure 5.

Taken together, these results indicate that the Cu/GQD nanocomposites with a Cu/C atomic ratio of 2.88% stood out as the best among the series within the context of limiting currents, onset potential, and number of electron transfer. Importantly, the performance might be further enhanced by hydrothermal treatment of the samples at controlled temperatures. Figure 7 depicts the RDE voltammograms of Cu/GQD-2.88% after hydrothermal treatments at controlled temperatures: (A) 140 °C, (B) 160 °C, (C) 180 °C and (D) 200 °C in oxygen-saturated 0.1 M NaOH. In comparison to the results of the as-prepared Cu-GQD-2.88% sample, one can see that the ORR activity of the Cu/GQD-2.88% nanocomposites treated at 140 °C, 180 °C and 200 °C was almost unchanged; yet, significance improvement can be seen with the sample treated at 160 °C, as manifested by a 30 mV positive shift of the onset potential and an appreciably higher limiting current. For instance, at +0.40 V, the limiting current density at 1600 rpm remained at ca. 40.5 A/m² for the as-prepared Cu/GQD-2/88% sample and after hydrothermal treatment at 140 °C, 180 °C and 200 °C; yet it increased markedly by about 40% to 56.7 A/m² for the sample treated at 160 °C.

In addition, the number of electron transfer in ORR also shows a similar variation (determined from the corresponding RRDE voltammograms, Figure S2). From the figure inset, one can see that within the potential range of +1.0 to +0.2 V, the n values of the 160 °C sample were markedly higher than those of other samples which were almost identical. For instance, the n value at +0.40 V increased from 3.42 to 3.64 after hydrothermal treatment at 160 °C, indicating an increasingly dominant 4e reduction pathway for ORR.

Figure 7. RRDE voltammograms of a glassy-carbon rotating disk electrode modified with 15 μ g of Cu-GQD-2.88% before and after hydrothermal treatment at different temperatures (specified in figure legends) in an oxygen-saturated 0.1 M NaOH solution. Current density was obtained by normalizing the voltammetric currents to the electrode geometrical surface area (0.247 cm²). Electrode rotation rate 1600 RPM. Inset shows the number of electron transfer (n) in oxygen reduction at different electrode potentials. Data were calculated from the RRDE voltammograms in Figure S2.

It should be noted that whereas the electrocatalytic performance of the Cu/GQD nanocomposites remains subpar as compared to those of the Pt/GQD counterparts or commercial Pt/C catalysts (Table 1) which typically exhibit an onset potential around +1.0 V and $n \approx 4.0$ [37, 52], the activity is actually better than those of Cu₂O/RGO composites (onset potential $\sim$ +0.80 V and n in range of 3.2-3.6) [53] and alkyne-capped copper nanoparticles supported on carbon black ($n = 2.5 - 2.7$ in the potential range of +0.70 V to +0.40 V) [46]. Furthermore, the

Cu/GQD nanocomposites all exhibit far better catalytic activities than bulk polycrystalline Cu or CuNi electrode (onset potential +0.36 V vs RHE in a borax buffer solution) [54, 55] and single crystalline Cu(100) or Cu(111) electrodes (~0 V vs RHE in H₂SO₄ solution) [56, 57].

This apparent ORR performance might be ascribed to the intimate interactions between the copper nanoparticles and the GQD substrates where the GQD structural defects are known to manipulate the electronic interactions of the metal nanoparticles with oxygen species and hence the ORR activity [58]. It has been long known that there is a volcano-shaped relationship between the ORR activity and the d-band center of transition metals where Pt lies nearest the top of the volcano [17, 59, 60]. To reach the peak performance, it has been argued that the d-band center of Pt needs to be downshifted by 0.1 – 0.2 eV so as to weaken the interactions with oxygen intermediates [61]. In fact, in a prior study [37], we observed that the ORR activity of Pt/GQD nanocomposites reached the maximum with about 20% structural defects of the GQDs. As copper exhibits even stronger affinity to oxygen than Pt and its d-band center lies on the right side of Pt [62], the copper d-band center has to be downshifted even more. This means that a substantially higher defect concentration is needed to enhance the ORR activity of Cu/GQD nanocomposites. In fact, within the present experimental context, XPS measurements (Figure S3) showed that the optimal GQD defect concentration, corresponding to the Cu/GQD-2.88% (160 °C) sample which exhibited the best ORR activity among the series, was about three times higher at 63%. Consistent results were obtained in Raman spectroscopic measurements (Figure S4).

Table 1. Summary of ORR activity of Cu/GQD, Pt/GQD, and Pt/C nanocomposite catalysts.

Catalysts	E _{onset} (V)	n (+ 0.4 V vs RHE)	J _{lim} (A/m ² , at 1600 rpm and +0.40 V vs RHE)
Cu/GQD-3.54%	0.81	2.76	29.6

Cu/GQD-3.32%	0.82	3.17	39.7
Cu/GQD-2.88%	0.82	3.42	40.5
Cu/GQD-2.34%	0.75	3.20	32.4
Cu/GQD-2.88%-160°C	0.85	3.64	56.7
Pt/C [63]	0.98	~ 4.0	51.8
Pt/GQD [52]	1.05	~ 4.0	58.7

4. Conclusions

Cu/GQD nanocomposites were readily prepared by thermolytic reduction of metal salts in the presence of GQDs in 1,2-propanediol. TEM measurements showed that the average diameter of the copper particles ranged from ca. 5 to 15 nm, increasing with increasing Cu/C atomic ratios which were quantitatively determined by XPS measurements. Electrochemical measurements showed that the sample with a Cu/C atomic ratio of 2.88% exhibited the best ORR activity among the series within the context of onset potential, number of electron transfer, and limiting currents. The electrocatalytic performance might be further enhanced by hydrothermal treatment of the Cu/GQD composite catalysts and 160 °C was identified as the optimal temperature where the corresponding sample exhibited the largest improvement of the ORR activity. This was ascribed to the manipulation of the electron density of the copper nanoparticles and hence the interactions with oxygen species by the GQD structural defects. In comparison to the Pt/GQD counterparts, the optimal concentration of the GQD structural defects were almost three times higher, consistent with the greater oxygen affinity of copper to oxygen as manifested in the volcano plot. The results further confirm the significance of metal-support interactions in the manipulation of nanoparticle electrocatalytic activity and might be exploited for the rational design and engineering of effective catalysts for fuel cell electrochemistry.

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