Composites of Graphene Quantum Dots and Reduced Graphene Oxide as Catalysts for Nitroarene Reduction

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ABSTRACT: Composites of graphene quantum dots (GQDs) and reduced graphene oxide (rGO) with unique three-dimensional (3D) structure are prepared and their catalytic activities for reduction of nitroarenes are explored. We demonstrate that the 3D GQDs/rGO composites are more active in nitroarene reduction than GQDs and rGO. Some of them are even more active than the Ag-embedded calcium alginate (Ag/CA) or Au-embedded calcium alginate (Au/CA) catalysts. Interestingly, their catalytic property is closely related to the ratio of GQDs to rGO in the 3D GQDs/rGO composites and GQDs-to-rGO mass ratio of 1/4 exhibits the highest catalytic activity. Raman spectra of the composites show that GQDs-to-rGO ratio is related to the number of the surface/edge defects, indicating that the sites of defect and edges are active sites. In addition, the catalytic performance of the 3D GQDs/rGO composites is also contributed by their unique 3D network structures that are beneficial for the reactant adsorption and product diffusion. Given also the long cycling duration and the easy recovery from the reaction system, 3D GQDs/rGO composites are potential applicable metal-free catalytic system for nitroarene reduction.

INTRODUCTION

Aromatic amines have been extensively used as intermediates or precursors for the syntheses of dyes, pigments, agrochemicals, pharmaceuticals, cosmetics, fibers, polymers, and photographic chemicals.1−3 Traditionally, aromatic amines have been obtained through the selective reductions of nitroarenes in the presence of various transition metals or precious metal catalysts.4−6 For instances, Pd,5 Au,6 Pt,7 Ru,8 Ag,9 Cu,10 Fe,11 Ni,12 and some bimetals like AuAg,13 FePd,14 and PdCu15 have been successfully utilized. However, for most aforementioned noble metals, the high price and scarcity greatly limited their practical applications.

Recently, metal-free catalysts, especially the nanostructured carbonaceous materials, have attracted great attention due to their high catalytic activities, low cost, environmental friendliness, and easy availability.16−21 For instance, reduced graphene oxide (rGO) was used in the hydrogenation of nitrobenzene at room temperature, and it was proposed that possibly the zigzag edges of rGO acted as catalytic active sites to facilitate the activation of a reactant molecule based on previous theoretic calculations.22 However, there is no quantitative method to define the number of edges or defect sites on rGO to support the hypothesis. Kong et al. reported that nitrogen-doped graphene (NG) could catalyze the reduction of 4-nitrophenol.23 Yang et al. also found that the graphitic NG exhibited the highest catalytic activity in the nitroarene reduction.24 Moreover, boron-doped onion-like carbon and carbon nanotubes (CNTs) also showed admirable catalytic activity and stability in nitroarene reduction.25 Recently, it was reported that the CNTs modified by H2O2 (oCNT) could catalyze nitroarene reduction, and it was proposed that the carbonyl groups in oCNT are of importance for their catalytic activity.26 However, exact catalytic mechanisms for most carbonaceous materials in nitroarene reduction remain unknown.

Previously, our group and others discovered that the nanoarchitectures assembled with GQDs and other materials could significantly enhance the catalytic activity and stability of the metal catalysts owing to the excellent electron transportation capability and good chemical/physical stabilities of GQDs.27,28 For example, we have found that GQDs/Au system could efficiently catalyze the oxidation of aromatic alcohols because they were intimately absorbed on the catalyst.29 Additionally, as aforementioned, the surface/edge defects of GO and rGO sheets may determine their catalytic activities;28,29 thus, the hypothesis here is that the GQDs should have even larger periphery area than GO and rGO sheets. To this end, in this work, we designed and prepared composites of...
GQDs and hydrothermally reduced graphene oxide (GQDs/rGO), and explored their catalytic activity in nitroarene reduction. As will be shown, the GQDs/rGO composites assume a unique three-dimensional (3D) structure with rGO sheets as structural (networks) matrices, and GQDs are anchored on them; under moderate conditions, the reduction of nitroarene can be preceded with 3D GQDs/rGO composites as catalysts, and the composites exhibited overall higher catalytic activity than individual GQDs and rGO.

**RESULTS AND DISCUSSION**

**Preparations and Characterizations of 3D GQDs/rGO Composites.** The morphologies of raw GO and GQDs used in the work were characterized by atomic force microscopy (AFM) (Figure S1). The average lateral size of GO sheets reached to a few micrometers, and the average lateral size of GQDs was \( \sim 10 \) nm. GO and GQDs assumed the same planar aromatic carbon backbone structure; therefore, as illustrated in Scheme 1, when GQDs and GO aqueous suspensions were mixed, GQDs would attach to the basal plane of GO through strong \( \pi-\pi \) stacking, and the intensity of such kind of interaction would become stronger when the GO sheets were reduced (rGO) during the hydrothermal treatment. It has been well documented that the hydrothermal treatment of the GO aqueous suspensions with appropriate concentration results in the formation of three-dimensional rGO (3D rGO).\(^{30}\) Figure 1a shows the scanning electron microscopy (SEM) image of the as-prepared GQDs/rGO\(_4\) composite (GQDs-to-Go ratio is 1:4 in weight), which displays a unique 3D network structure similar to the bare 3D rGO (Figure S2). Within the composite, the sheet motif of rGO was maintained well, and GQDs are anchored uniformly on the basal planes of 3D rGO, as shown in Figure 1b,c. The high-resolution transmission electron microscopy (HRTEM) illustrated that the interplane lattice constant of GQDs was around 0.2 nm, as shown in Figure 1d, which is very close to that of the graphite (0.213 nm), corresponding to the (101) facet.\(^{31,32}\) These results indicated clearly that GQDs/rGO composites with a unique 3D structure were prepared with a simple hydrothermal treatment of GQDs and GO.

The reduction of the GO into 3D rGO in the composites was also confirmed by Fourier transform infrared (FT-IR) spectroscopy. As illustrated in Figure S3, the GO showed the vibration and deformation peaks of the \(-\text{OH}\) group at 3395 and 1410 cm\(^{-1}\), the stretching vibration peak of \(-\text{C}==\text{O}\) group at 1730 cm\(^{-1}\) and the stretching vibration peak of \(-\text{C}–\text{O}\) group of epoxy and alkoxy at 1226 and 1052 cm\(^{-1}\), respectively.\(^{33}\) In the IR spectrum of 3D GQDs/rGO, peaks for \(-\text{OH}\) and \(-\text{C}–\text{O}\) group of epoxy and alkoxy disappeared, suggesting that GO was reduced.

**Catalytic Activities of the 3D GQDs/rGO Composites.** The catalytic performance of the 3D GQDs/rGO composites in the reduction of nitroarene with NaBH\(_4\) as a reducing agent was first elaborated using 4-nitrophenol as a model compound, and the reduction process was monitored with UV–vis spectroscopy. As shown in Figure 2a, there are three UV–vis absorption peaks for 4-nitrophenol in the 200–500 nm range,

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Scheme 1. Illustration of the Formation Process of the 3D GQDs/rGO Composites

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Figure 1. SEM (a), TEM (b, c), and HRTEM (d) images of the 3D GQDs/rGO\(_4\) composite.
the intensity of the peak at 400 nm decreased rapidly with the progress in reduction and disappeared after 10 min of reaction. Meanwhile, the appearance of a new absorption peak at 300 nm originating from 4-aminophenol indicated the reduction of 4-nitrophenol to 4-aminophenol.\textsuperscript{23,34} In contrast, NaBH\textsubscript{4} is not able to reduce 4-nitrophenol without a catalyst under the same conditions (Figure S4). The reaction was further evaluated using high-performance liquid chromatography (HPLC) and ultraperformance liquid chromatography quadrupole time-of-flight mass spectrometer (UPLC-Q-TOF-MS) (Figure S5b,c). Only one peak with a retention time of 2.838 min corresponding to the product 4-aminophenol was detected using high-performance liquid chromatography (HPLC) and ultraperformance liquid chromatography quadrupole time-of-flight mass spectrometer (UPLC-Q-TOF-MS) (Figure S5).

Figure 2. (a) UV−vis spectra of the reduction of 4-nitrophenol catalyzed by 3D GQDs/rGO at RT, the time interval is 2 min. (b) Time courses of the 4-nitrophenol reduction using GQDs, 3D rGO, GQDs/rGO\textsubscript{1}, GQDs/rGO\textsubscript{2}, GQDs/rGO\textsubscript{4}, and GQDs/rGO\textsubscript{6} composites as catalysts monitored at 400 nm. Reaction condition: 0.048 mg catalyst, 0.5 \( \mu \)mol substrate, and molar ratio of 4-nitrophenol to NaBH\textsubscript{4} is 1:53.

Surface/Edge Defects of the 3D GQDs/rGO Composites Determine Their Catalytic Activities. It was proposed in early works that the surface/edge defects of the rGO might be the catalytic active sites.\textsuperscript{18,22} To illustrate the assumption, the Raman spectra of 3D GQDs/rGO composites with different GQDs-to-rGO ratios were collected and are shown in Figure 3. In principle, the intensity ratios of D and G bands in Raman spectra (\( I_D/I_G \)) of 3D GQDs/rGO composites reflect the amounts of the surface/edge defects of the GQDs and rGO sheets. Actually, as shown in Figure 3, the \( I_D/I_G \) values of GQDs, 3D rGO, 3D GQDs/rGO\textsubscript{1}, 3D GQDs/rGO\textsubscript{2}, 3D GQDs/rGO\textsubscript{4}, and 3D GQDs/rGO\textsubscript{6} and 3D GQDs/rGO\textsubscript{4} composite has the highest \( I_D/I_G \) value, implying that it contained more surface/edge defects than the others. That should be the main reason why the 3D GQDs/rGO\textsubscript{4} has an overall better catalytic performance than bare GQDs, 3D rGO, and other as-studied composites.

The kinetics of the reductions of nitroarenes using 3D GQDs/rGO composites with different GQDs-to-rGO ratios as catalysts was monitored by measuring the UV−vis absorption intensity variation at 400 nm (Figure 2b). Figure S6 shows the linear correlations of \( c_{\text{c}_0} \) versus \( t \) (Figure 3). It is also worth pointing out that all of the composites assumed generally higher catalytic activity than individual 3D rGO or GQDs. The catalyst turnover frequency (TOF), the number of nitroarene molecules that were reduced using 1 g of catalyst per second, was also calculated (Table 1). TOF of the 3D GQDs/rGO is generally much higher than that of Ag/CA and Au/CA.\textsuperscript{36} It was reported that Au nanoparticles decorated on thiol-functionalized reduced graphene oxide (Au/SRG) was a very efficient catalyst for nitroarene reduction.\textsuperscript{37} However, no data of the role of SRG alone were reported; it is not easy to conclude the role of SRG in the Au/SRG composite by comparing the polygonal Au nanoparticles that are in a total different state with the Au modified by SRG. Given that other conditions are the same, the only difference between the composites are the number of GQDs on the basal plane of rGO; we thus conclude that the surface/edge defects within 3D GQDs/rGO act as the active sites. Actually, similar results was observed with native and H\textsubscript{2}O\textsubscript{2}-treated carbon nanotubes CNTs as catalysts, the latter being more active.\textsuperscript{26} It was also reported recently that GQDs...
and graphene nanoribbons (GNRs) composites exhibited ultrahigh electrocatalytic performance for oxygen reduction and were proposed through numerous surface/edge defects in GQD/GNR as active sites.

The high catalytic activity of 3D GQDs/rGO might also be contributed by their unique 3D morphologies. The catalytic activity of chemically reduced GO was much lower than that of 3D rGO we used in this work (Figure S7a,b). The adsorption of reactants on the surface of GO has been identified as one of critical steps for their catalysis. It is possible that the 3D network structural feature is helpful for the substrate adsorption as well as product diffusion. However, the specific surface area of 3D GQDs/rGO (~178 m² g⁻¹) determined by nitrogen adsorption/desorption isotherm curves is lower than that of rGO (~220 m² g⁻¹), and the surface area of 3D GQDs/rGO is quite similar to that of 3D rGO (Figure S8). The difference between the surface areas of rGO and 3D rGO is not unexpected because of their different preparation methods, as described in Experimental Section. In addition, the result further confirms that the catalytic activity of 3D GQDs/rGO is primarily determined by the surface/edge defects within the composites. Taken together, the surface/edge defects combined with the unique 3D structure of 3D GQDs/rGO composites made them active catalysts for nitroarene reduction.

**Catalytic Activity of 3D GQDs/rGO in the Reduction of Nitroarene Derivatives.** The catalytic activity of the 3D GQDs/rGO composites was also tested for the reductions of 4-nitrotoluene, 4-nitroanisole, 4-nitrochlorobenzene, 2-nitroaniline, and 1,3-dinitrobenzene under the same reaction conditions, and the results are shown in Figure S9, S10, and Table 2. Generally, all of the derivatives of nitroarene examined could be reduced with 3D GQDs/rGO as a catalyst. As shown in Table 2, the reduction of the nitroarenes containing electron-withdrawing groups was much slower than that of those containing electron-donating groups. It means that electron-donating groups on the aromatic ring do favor for the reduction of nitroarenes. For instance, the reduction yield of 4-nitrophenol is 92.93% (entry 1), whereas the reduction of 4-nitrochlorobenzene was only about 51.67% (entry 4). The lower reduction yield was due to the formation of byproducts, as confirmed by UPLC-Q-TOF-MS (Figure S11). The fast rates and high yields indicated that the 3D GQDs/rGO was an efficient catalyst for the reduction of nitroarenes containing the electron-donating groups, such as −OH, −CH₃, and −OCH₃.

Table 2. Rate Constants and TOF of the Reduction of 4-Nitrophenol with Different Catalysts

| entry | catalyst | k (×10⁻⁷ M s⁻¹) | TOF (×10⁶ molecules g⁻¹ s⁻¹) | ref |
|-------|----------|-----------------|-----------------------------|-----|
| 1     | GQDs     | 2.21            | 0.96                        | this work |
| 2     | 3D rGO   | 2.27            | 1.04                        | this work |
| 3     | 3D GQDs/rGO | 3.28          | 1.42                        | this work |
| 4     | 3D GQDs/rGO | 3.65          | 1.57                        | this work |
| 5     | 3D GQDs/rGO | 4.47          | 1.69                        | this work |
| 6     | 3D GQDs/rGO | 3.04          | 1.28                        | this work |
| 7     | Ag/CA    | 1.72–1.73       | 0.0093                      | 36  |
| 8     | Au/CA    | 0.23–0.33       | 0.0017                      | 36  |
| 9     | none     | 0.73            | 23                          | 23  |
| 10    | Ag/SRG   | 83.3            | 37                          | 37  |

**Table 2. Catalytic Activity of the 3D GQDs/rGO in the Reduction of Various Nitroarenes**

| entry | substrate | product | t (min) | k (×10⁻⁷ M⁻¹ s⁻¹) | conversion (%) | yield (%) |
|-------|-----------|---------|---------|------------------|----------------|-----------|
| 1     | 4-nitrophenol | 4-aminophenol | 10 | 4.47          | >99            | 92.91     |
| 2     | 4-nitrotoluene | 4-aminotoluene | 9  | 4.48          | >99            | 85.73     |
| 3     | 4-nitroanisole | p-anisidine     | 12 | 3.38          | >99            | 84.22     |
| 4     | 4-nitrochlorobenzene | 4-chloroaniline | 18 | 1.95          | >99            | 51.67     |
| 5     | 2-nitroaniline | 2,3-diaminobenzene | 15 | 1.74          | >99            | 66.68     |
| 6     | 1,3-dinitrobenzene | 1,3-diaminobenzene | 15 | 1.26          | >99            | 46.60     |

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stability that should be practically applicable in the reduction of nitroarenes.

**CONCLUSIONS**

Three-dimensional GQDs/rGO composites with different ratios of GQDs versus GO were prepared via one-pot hydrothermal method. The 3D GQDs/rGO composites showed improved catalytic activities for the reduction of nitroarene compared with GQDs, 3D rGO, and some metal catalysts. The high catalytic activity of the 3D GQDs/rGO is directly related to the GQDs-to-rGO ratio, which reflects the content of surface/edge defects within the composites. The catalytic activities of the 3D GQDs/rGO composites are also contributed by their unique structures. The unique 3D structure seems helpful for the absorption of reactants on the surface of 3D GQDs/rGO composites and prompts the product diffusion in the catalyst. It was also found that the 3D GQDs/rGO composites have higher catalytic activities for the nitroarenes with electron-donating groups on their aromatic rings. This, coupled with their high stability and ease of separation and recyclability, indicated that 3D GQDs/rGO could find practical applications in the reductions of nitroarenes.

**EXPERIMENTAL SECTION**

**Materials.** 4-Nitrophenol, 4-nitrotoluene, 4-nitroanisole, 4-nitrochlorobenzene, 2-nitroaniline, 1,3-dinitrobenzene, and sodium borohydride (NaBH₄) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All of the chemicals were used as received. GO and GQDs were prepared following the procedures described in our previous works.33,41

**Preparation of 3D GQDs/rGO Composites.** In a typical experiment, 12 mL, 2 mg/mL aqueous dispersion of GO was added to an 30 mL autoclave, GQDs were then added to get final GQDs/GO ratios of 1:1, 1:2, 1:4, and 1:6 (in weight) and stirred for 10 min. The autoclaves were transferred to an oven and kept at 180 °C for 9 h. During the thermal treatment, GO was reduced and abbreviated as 3D rGO. After cooling down to room temperature, the solid products were separated through centrifuging and washing three times with deionized water. Finally, the composites were dried for 24 h in a vacuum freeze-dryer. The corresponding composites are named as 3D GQDs/rGO, GQDs/rGOₓ, GQDs/rGOᵧ, and GQDs/rGO₂ corresponding to their initial GQDs-to-Go ratios of 1:1, 1:2, 1:4, and 1:6 (in weight). For comparison, 3D rGO was prepared by hydrothermal reaction of the GO without GQDs under similar condition.

**Catalytic Reduction of Nitroarene.** Nitroarene (0.5 mL, 1 mM), NaBH₄ (2 mL, 5 mg/10 mL), and 3D GQDs/rGO (48 μL, 1 mg/mL) were mixed in a UV–vis cuvette. The reduction reaction was followed by monitoring UV–vis absorption of the reaction mixture at λ max at room temperature. The reduction reactions of nitroarene were also conducted with bare rGO and GQDs as catalysts under the same condition as controls.

**Instrumental.** Atomic force microscopic (AFM) images of GQDs and GO were taken on a MultiMode Nanoscope V scanning probe microscopy system (Veeco), and AN-NSC 10AFM cantilever tips (SHNIT Co., Russia) with a force constant of ~37 N/m and resonance vibration frequency of ~330 kHz were used. Samples for AFM were prepared by dropping the aqueous suspension (~0.02 mg/mL) of GO or GQDs on a freshly cleaved mica surface and dried in air. The SEM images were acquired using Ultra 55 field emission scanning electron microscope (Zeiss, Germany) with the working voltage of 10.0 kV. The TEM images were obtained on a JEOl JEM-2100F transmission electron microscope (JEOL, Japan) with the operation voltage of 200 kV. The high-resolution TEM (HRTEM) images were recorded on the same instrument. The TEM specimens were prepared by placing the ethanol suspensions on the copper grids and drying under ambient condition. The FT-IR spectra were acquired on an EQUINOX 55 FT-IR spectrometer (Bruker, Germany). The specimens for FT-IR measurement were prepared by grinding the dried powder of GO, rGO, or GQDs/rGO with KBr together and then compressing it into thin pellets. Raman measurements were performed on a Senterra R200-L Dispersive Raman Microscope (Bruker, Germany) with the excitation laser beam wavelength of 633 nm. The powders of GQDs, rGO, and GQDs/rGO after grinding were used for the Raman measurement. The surface area was determined using the Brunauer–Emmett–Teller (BET) method by ASAP 2000 M (Micromeritics). Catalytic reactions were monitored using a UV-2550 UV–vis spectrometer (Shimadzu, Japan). After the reaction, the conversion of nitroarene and yield of corresponding aniline were analyzed by 1220 HPLC (Agilent Technologies) with phosphate buffer (A) and acetonitrile (B) as mobile phase. The reaction mixture and reaction intermediates were analyzed by ACQUITY UPLC & Q-TOF MS Premier (Waters) with water (A) and acetonitrile (B) as mobile phase under gradient elution conditions.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00908.

Characterization data for GO, GQDs, rGO, 3D rGO, and 3D GQDs/rGO composites and detailed data regarding catalytic experiments (PDF)

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**Author Contributions**

The manuscript was written through contributions of all of the authors. All of the authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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