Graphene Oxide-Facilitated Reduction of Nitrobenzene in Sulfide-Containing Aqueous Solutions

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Supporting Information

ABSTRACT: The main objective of this study was to test the possibility that graphene-based nanomaterials can mediate environmentally relevant abiotic redox reactions of organic contaminants. We investigated the effect of graphene oxide (GO) on the reduction of nitrobenzene by Na₂S in aqueous solutions. With the presence of GO (typically 5 mg/L), the observed pseudofirst-order rate constant \( k_{obs} \) for the reduction of nitrobenzene was raised by nearly 2 orders of magnitude (from \( 7.83 \times 10^{-5} \) h⁻¹ to \( 7.77 \times 10^{-3} \) h⁻¹), strongly suggesting reaction mediation by GO. As reflected by the combined spectroscopic analyses, GO was reduced in the beginning of the reaction, and hence the reduced GO (RGO) mediated the reduction of nitrobenzene. It was proposed that the zigzag edges of RGO acted as the catalytic active sites, while the basal plane of RGO served as the conductor for the electron transfer during the catalytic process. Furthermore, changing the pH (5.9–9.1) and the presence of dissolved humic acid (10 mg TOC/L) were found to greatly influence the catalytic activity of RGO. The results imply that graphene-based nanomaterials may effectively mediate the reductive transformation of nitroaromatic compounds and can contribute to the natural attenuation and remediation of these chemicals.

INTRODUCTION

Carbon nanomaterials are produced and used in increasingly large quantities. According to a recent research report from Innovative Research and Products (iRAP), Inc., the annual production of carbon nanomaterials has increased from 996 tons in 2008 to 4065 tons in 2010, and is expected to exceed 12 300 tons in 2015.¹ Such large-quantity production and use will inevitably lead to the release of carbon nanomaterials into the environment from various sources, including factories, landfills, and attrition from products containing these materials.²–⁵

Due to the very large surface area and high surface hydrophobicity, carbon nanomaterials can strongly adsorb hydrophobic organic contaminants, in particular those \( \pi \)-electron bearing compounds that are capable of interacting with the polarized graphitic surface of carbon nanomaterials via \( \pi-\pi \) electron coupling.⁶,⁷ Thus, carbon nanomaterials released into the environment may play an important role in the fate of organic contaminants. Numerous studies have been devoted to the effects of carbon nanomaterials on the distribution, transport, and bioaccumulation of organic contaminants.⁵,⁸,⁹ However, little effort has been made to understand how carbon nanomaterials may affect the chemical transformation of organic contaminants in the environment.

As an emerging class of carbon nanomaterials, graphenes have in recent years received increasing attention, due to many new fields of application, such as next-generation transistors, sensors, and adsorbents for hydrogen storage.¹⁰–¹² Graphene-based nanomaterials possess distinct open edges (including zigzag edges and armchair edges) around their peripheries.¹³ It has been theoretically proved that the zigzag edges have very high chemical reactivity due to their special edge states (nonbonding \( \pi \)-electrons) near the Fermi level,¹³–¹⁷ and hence render the graphene-based nanomaterials unique catalytic activities. Consistent with this prediction, Gao et al. recently reported that owing to the presence of zigzag edges reduced graphene oxide could catalyze the hydrogenation of nitrobenzene by hydrazine with an efficiency much higher than other test carbonaceous materials, and even comparable with noble metal.¹⁸ Thus, it seems that the graphene-based nanomaterials could also mediate environmentally relevant abiotic reactions. Nonetheless, to the best of our knowledge, there is no report in the literature on the role of carbon nanomaterials in mediation of abiotic transformation of organic contaminants in environmentally relevant aqueous systems.

Nitroaromatic compounds (NACs) are widely manufactured and used as explosives, pesticides, solvents, and organic synthesis intermediates as well, and are frequently detected in surface and subsurface environments.¹⁹–²¹ Understanding pathways to reduce the nitro group(s) of NACs in the environment is of particular concern, because the reduced...
intermediates and products (such as amino- and hydroxylamino aromatic compounds) often have greater toxicity and/or aqueous solubility than their parent compounds. It is worth noting that the reduction of NACs in natural environments can occur not only biotically but also abiotically. Additionally, the reduction reactions of NACs could be significantly accelerated in the presence of iron porphyrins and quinoid-like structures that serve as electron shuttles.

The main objective of this study is to test the possibility of carbon nanomaterials as mediators for abiotic redox reactions of organic contaminants in natural aquatic environments. We investigated the effect of graphene oxide (a common type of graphene-based nanomaterials) on the reductive reaction of NACs in reducing environments. Nitrobenzene was selected as the model NAC, and sodium sulfide (Na2S) was selected as the reducing agent—sulfide is one of the most abundant reductants typically present in anaerobic aquatic environments. Functionality-free, pure graphene was explored as a comparison to better understand the underlying mechanisms for the graphene oxide-mediated reaction. Influences of solution chemistry parameters (pH and dissolved humic acid) on the reduction of nitrobenzene were also investigated.

**EXPERIMENTAL SECTION**

**Materials.** Nitrobenzene (99.5%, Fluka, Switzerland), N-phenylhydroxylamine (97.0%, Sigma Aldrich, U.S.), and aniline (99.0%, J&K Chemical Ltd., U.S.) were used as received. Stock solutions of individual compounds were prepared in methanol and stored in the dark at appropriate temperatures until use, 4 °C for nitrobenzene and aniline and below −20 °C for N-phenylhydroxylamine (referring to the Material Safety Data Sheet provided by the manufacturer). Analytical-grade Na2S was purchased from Sinopharm Chemical Reagent (Shanghai, P.R. China).

Solid humic acid was purchased from Sigma Aldrich. On the basis of the results of elemental analysis (CHN-O-Rapid, Heraeus, Germany) and Fourier transform infrared (FTIR) analysis (Nexus 870, Nicolet, U.S.), the humic acid was enriched in O-containing functional groups and also contained quinone moieties (see Table S1 and Figure S1, Supporting Information). Pure graphite (99.99%) was purchased from Sigma Aldrich. Well-dispersed water suspension of graphene oxide (GO) at 500 mg/L was obtained from XFNANO Materials Tech (Jiangsu, P.R. China). The suspension appears transparent with yellow-brown color. According to the information provided by the manufacturer (also verified by independent characterizations), GO was composed of nanosheets of 1–5 μm in diameter and 0.8–1.2 nm in thickness.

**Characterization of Graphene Oxides.** Surface elemental compositions of GO were determined by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer PHI 550 ESCA/SAM, U.S.). FTIR analysis was conducted by a Nexus 870 spectrometer (Nicolet, U.S.) on GO mixed with potassium bromide at a ratio of 1 to 100. X-ray diffraction (XRD) pattern of GO was recorded with a D/max-RA powder diffraction meter (Rigaku, Japan) using Cu Kα radiation. UV–vis spectra were performed on a UV-2450 spectrophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM) image of GO was collected on a JEM-200 CX (JEOL, Japan). The reduced counterpart of GO (reduced GO, RGO, collected by washing, filtration, and drying under vacuum at 40 °C after GO reacting with Na2S for 3–18 h) was also characterized using the same techniques as mentioned above. The specific surface areas of RGO and pure graphite were determined by N2 adsorption using the Brunauer–Emmett–Teller (BET) method on a Micrometrics ASAP 2020 (Micromeritics Instrument Co., U.S.).

**Batch Reaction Experiments.** To initiate a reaction kinetic experiment, an aqueous solution of 0.05 M Tris-HCl containing GO at a desired concentration from 0 to 10 mg/L was purged with nitrogen for at least 30 min to remove dissolved oxygen. The pH of the solution was initially adjusted to 7.3 to allow the final pH to be 7.5 after being mixed with Na2S. Then, a full volume of the above solution was added to a 40-mL glass vial equipped with polytetrafluoroethylene (PTFE)-lined screw cap, followed by nitrobenzene in a methanol carrier and Na2S in 0.05 M Tris-HCl prepurged with nitrogen. The initial concentrations were set at 80 μM for nitrobenzene and 8 mM for Na2S. Then the vials were shaken by an orbital shaker incubated at 30.0 ± 0.5 °C, and a subset of vials were sacrificed and sampled at appropriate time intervals. The obtained aliquot was mixed with methanol (1:1, v/v) to extract analytes which might be adsorbed by graphene oxide, filtered through 0.22-μm membrane (Anpel Scientific Instrument, Shanghai, P.R. China) to remove dispersed graphene oxide, and immediately analyzed by high-performance liquid chromatography (HPLC) (see below). Sorption of the analytes to the filter membrane was proved to be negligible by filtration of standard solutions (results presented in Figure S2 of the SI).

HPLC analysis was performed on an Agilent 1200 apparatus equipped with a variable wavelength detector (VWD) by a 4.6 × 250 mm Eclipse Plus Phenyl-Hexyl column (Agilent, U.S.). Isocratic elution was performed at 30 °C under the following conditions: 0.05 M ammonium acetate-acetonitrile (70:30, v/v) with a uniform wavelength of 254 nm. Chromatograms of nitrobenzene and its products in the HPLC analysis are shown in Figure S3 of the SI. The concentrations of nitrobenzene and the reduction products (N-phenylhydroxylamine and aniline) in the aliquot were measured according to calibration curves prepared by corresponding standard compounds. Calibration curves were built separately from controls receiving the same treatments as the samples but without GO and Na2S. All calibration curves included at least six concentration levels over the test concentration range with linear correlation coefficients (R2) of at least 0.999. Identifications of reduction products were further verified by gas chromatography–mass spectrometry (GC–MS) analysis of chloroform extract of the aliquot using a Trace GC Ultra coupled to an ISQ mass spectrometer (Thermo Fisher Scientific, U.S.) (results presented in Figure S4 of the SI).

Separate sets of experiments were carried out to examine effects of solution chemistry parameters (pH and presence of dissolved humic acid) on the reaction. The reaction systems consisted of 5 mg/L GO and 0.05 M buffer. In the pH experiments, the pH was set from 5.9 to 9.1 using suitable buffers. In the humic acid experiments, a stock solution of humic acid was prepared by dissolving appropriate amount of solid humic acid in distilled water and then filtering through a 0.45-μm membrane (Anpel). The total organic carbon (TOC) of the stock solution was measured to be 60 mg/L by a TOC analyzer (TOC 5000A, Shimadzu). The stock solution was then diluted to prepare the operational background solution (pH = 7.3) containing 10 mg TOC/L humic acid.

For reactions involved graphite, 48 mg of graphite was directly added to the 40-mL vials (equivalent to a concentration
of 1200 mg/L), followed by a full volume of nitrogen-prepurged background solution (0.05 M buffer with desired pH and concentration of humic acid), and finally by nitrobenzene and Na2S. All kinetic experiments were performed over a time period of at least one half-life of nitrobenzene reduction. All reaction data except the blanks were collected in triplicate. The variance in pH was found to be less than 0.1 pH unit during the reaction process for all experiments.

RESULTS AND DISCUSSION

Reduction of Nitrobenzene. Figure 1 gives an example of the disappearance of nitrobenzene as a function of time in sulfide-containing reducing aqueous solutions. More than 70% of the initial nitrobenzene disappeared within 168 h in the presence of 5 mg/L GO, and the reduced products were identified as N-phenylhydroxylamine and aniline (Figures S3 and S4 of the SI). The good mass balance (95%~101%) calculated by summing up these species indicates negligible or non-existence of other reaction products. Similar observations were obtained in graphite-containing solutions (Figure S5 of the SI).

Figure 1b presents the reaction kinetics plotted as ln (Ct/C0) versus time, where Ct and C0 are the concentrations of nitrobenzene at a given time t and zero, respectively. Reaction conditions: 80 μM nitrobenzene, 8 mM Na2S, and 0~10 mg/L GO at pH 7.5 and 30.0 °C. The blanks (in absence of GO and graphite) were performed in single. Error bars represent standard deviations calculated from triplicate samples.

The comparison of mediation efficiency between GO and graphite is displayed in Figure 1b. In the presence of 1200 mg/L graphite, the kobs for nitrobenzene reduction is 5.12 × 10^−3 h^−1, which is lower than the kobs in the presence of 5 mg/L GO (7.77 × 10^−3 h^−1). To better estimate the mediation efficiency of the mediator, the second-order rate constant (kmed) is calculated by normalizing kobs to the mass concentration of the mediator (Table S2 of the SI). The obtained kmed values for systems mediated by GO (in the order 10^−3 L·h^−1·mg^−1) are over 2 orders of magnitude larger than those by graphite (in the order 10^−6 L·h^−1·mg^−1) (see values in Table S2 of the SI). It is noteworthy that under similar reaction conditions the krec values for GO are comparable to or even larger than the literature values reported for quinones (in the order 10^−3~10^−2 L·h^−1·mg^−1), iron porphyrins (in the order 10^−3 L·h^−1·mg^−1), and natural organic matter (in the order 10^−5 L·h^−1·mg TOC^−1)²³,²⁴ These observations further support the prominent mediation effect of GO on nitrobenzene reduction. Negligible reduction of nitrobenzene (less than 2% loss of the initial nitrobenzene added) was observed in the control experiments (in presence of Na2S but absence of GO and graphite).

Mechanisms for GO-Mediated Nitrobenzene Reduction. A number of previous studies reported that carbonaceous materials can mediate reductive reactions of organic compounds via the mechanism of enhanced electron transfer.²⁹~³³ For example, it was proposed that graphite and black carbon could serve as electron conductors to enhance electron transfer, and hence effectively catalyze the reduction of NACs by hydrazine ²⁹ or dithiothreitol.³¹ In parallel, Tang et al. pointed out the electron conductor role of graphitized carbons of
activated carbon in the reductive dechlorination of trichloroethylene by zerovalent iron. Zee et al. also ascribed the activated carbon-mediated bioreduction of azo dyes to enhanced electron transfer, but by a different mechanism—electron shuttling by the quinone moieties on the carbon surface. In addition to enhanced electron transfer, activation of reactants is another widely accepted mediation mechanism for reductive reactions on the surface of carbonaceous materials. Guo et al. reported fullerene-catalyzed reduction of azo dyes by sodium borohydride through activation of the N=N bond by the vacant orbital of fullerene. Likewise, it was proposed that fullerene can activate hydrogen molecules and thus catalyze the hydrogenation of nitrobenzene. More recently, Gao et al. suggested that the zigzag edges of reduced graphene oxide can activate the molecule of nitrobenzene and therefore accelerate its reduction reaction with hydrazine.

On the basis of the literature and the observations made here, the following mechanisms are proposed for the GO-mediated nitrobenzene reduction: (1) reduction of GO to RGO by Na2S; (2) mediated nitrobenzene reduction by RGO. To confirm the reduction of GO to RGO, the chemical structures of GO and its counterparts (RGO) obtained after being mixed with Na2S at desired times were characterized using combined spectroscopic techniques. Table 1 summarizes the surface elemental composition and carbon species distribution determined by XPS (corresponding C1s spectra are presented in Figure S7 of the SI). After mixing with Na2S for 3 h, the C:O ratio of GO increased markedly from 2.0 to 4.3, indicating that GO was indeed reduced. Moreover, the carbon species distribution was significantly changed, in that the carbons in epoxy/ether (C−O−C) disappeared while those in phenolic hydroxyl (C−OH) and carbonyl (C=O) increased dramatically, indicative of production of quinone moieties. Comparison of the FTIR spectra (Figure S8 of the SI) between GO and RGO provided consistent results. The UV-vis spectra and XRD results (Figures S9 and S10 of the SI) further confirm the formation of RGO aggregates. Notably, under the examined conditions GO could be fully reduced to RGO in approximately 3 h (justified by the nearly stable content of O-containing groups, see Table 1), while the reduction of nitrobenzene lasted for at least 168 h, implying that it was RGO, rather than GO, that mediated the reduction of nitrobenzene.

The mediation effect of RGO on nitrobenzene reduction can be explained by the combination of enhanced electron transfer and activation of nitrobenzene. It was reported that the graphene basal planes of graphene oxides have very high electric conductivity, while the electric conductivity of graphene oxides is generally proportional to the C:O ratio. The C:O ratio of RGO (see values in Table 1) is comparable to those reported for reduced graphene oxides having satisfactory electric conductivity. Moreover, it can be deduced that RGO (with C:O ratio of 4.3–4.5) has prominently higher electric conductivity than GO (with C:O ratio of 2.0). Notably, the mechanism of enhanced electron transfer is also viable for graphite due to the electric conductivity properties of graphitic carbon surfaces. Additionally, as reflected by the XPS results (Table 1), RGO is rich in quinoid-like groups, which are deemed to assist electron transfer in nitrobenzene reduction. A similar mechanism was also proposed previously to account for the catalytic activity of activated carbon in bioreduction of azo dyes. Quinone moieties in humic substances are known to be able to facilitate the reduction of NACs by sulfides via the electron-shuttle mechanism. Consistently, the reduction of Fe (III) oxides by Fe (III)-reducing microorganisms was found to be remarkably enhanced in the presence of quinone derivatives and humic acid. In summary, the high electric conductivity (with assistance of the quinone moieties) make RGO a superior mediator for electron transfer and hence nitrobenzene reduction.

Activation of nitrobenzene molecules might be an additional factor contributing to the mediation effect of RGO. According to the results of density functional theory (DFT) calculation, the carbon atoms at the zigzag edge of graphenes are partially radicalized due to the existence of localized π-electrons, and therefore are able to interact strongly with the atom/group of H, OH, halogen, or CH3. It was also shown recently by DFT calculation that the zigzag edge carbons of graphenes can interact strongly with the oxygen atoms in the nitro group, resulting in prolonged and weakened N=O bonds. Thus, the nitrobenzene molecule is activated and the reduction reaction is accelerated. The unique role of zigzag edge carbons of RGO in nitrobenzene activation is partially supported by the fact that the kobs is nearly one order of magnitude higher on RGO than on graphite after being normalized on the basis of mediator surface area (4.5 m2/g for graphite and 201.3 m2/g for RGO).

Effects of Solution Chemistry Parameters on Nitrobenzene Reduction. pH. The effects of pH on the reduction efficiency of nitrobenzene are displayed in Figure 3. In the presence of 5 mg/L GO, the reduction efficiency increases as the pH is increased from 5.9 to 7.5, but then decreases as the pH is further increased up to 9.1. The facilitated reduction of nitrobenzene with increasing pH from 5.9 to 7.5 could be explained by the alkaline-enhanced reducing capability of sulfide. However, because proton delivery is required for the reduction of nitro group to (hydroxyl)amino group, the
The reduction of nitrobenzene is disfavored as the pH is further increased from 7.5 to 9.1. Nearly the same trend of pH-dependent responses is shown for graphite. Graphite is functionality-free and is essentially nondispersible due to the coarse particle sizes (in the range of 5−40 μm as determined by scanning electron microscopy); therefore, it is derivable that the observed pH-dependency of RGO-mediated nitrobenzene reduction is not due to changes in dispersal of RGO, which is expected to be affected by the protonation−deprotonation transition of the O-containing groups and hence pH-dependent.

**Presence of Dissolved Humic Acid.** Figure 4 presents the effects of dissolved humic acid on the reaction rate for nitrobenzene reduction. Consistent with previous studies, the dissolved humic acid effectively promoted the reaction on its own ascribable to the role of electron shuttle of the quinone moieties. In the presence of 10 mg TOC/L humic acid only, the \( k_{\text{sec}} \) for nitrobenzene reduction is equal to \( 5.46 \times 10^{-4} \) L·h\(^{-1} \)·mg\(^{-1} \), which is lower than the \( k_{\text{sec}} \) (1.55 \times 10^{-3} L·h\(^{-1} \)·mg\(^{-1} \)) in the presence of 5 mg/L GO only (see the values in Table S2 of the SI). Therefore, GO appears to be a more efficient mediator than humic acid in the reduction of nitrobenzene. Furthermore, it should be emphasized when present together at comparable concentrations GO and RGO would easily outcompete humic acid for nitrobenzene due to the much stronger adsorption affinity and capacity. Within the examined concentration ranges, the adsorption coefficient (\( K_d \)) of nitrobenzene was in the order 10\(^3\) L/kg by GO and 10\(^4\) L/kg by RGO, but was close to zero by the humic acid (details for sorption experiments and the obtained isotherm data are shown in Figure S13 of the SI).

For the GO (5 mg/L)-humic acid (10 mg TOC/L) binary mediator system, the \( k_{\text{obs}} \) (1.20 × 10\(^{-2}\) h\(^{-1}\)) is higher than the \( k_{\text{obs}} \) (7.77 × 10\(^{-3}\) h\(^{-1}\)) for the single mediator of 5 mg/L GO, but surprisingly lower than the \( k_{\text{obs}} \) (1.42 × 10\(^{-2}\) h\(^{-1}\)) for the single mediator of 10 mg TOC/L humic acid, suggesting the antagonism between GO and humic acid. This can be rationalized by the adsorption of humic acid on graphene oxides. It is well documented in the literature that carbonaceous materials can strongly adsorb humic acids via hydrophobic effect and specific interactions (including \( \pi-\pi \) interaction, electrostatic interaction, and hydrogen bonding). Under the given conditions (10 mg TOC/L dissolved humic acid, 5 mg/L GO, and 8 mM Na\(_2\)S at pH 7.5 and 30.0 °C for 96 h), the \( K_d \) for humic acid adsorption on RGO (GO consequently reduced to RGO) was measured to be 95000 ± 7000 L/kg (standard deviation calculated from three replicate samples), corresponding to a sorption ratio (the ratio of the adsorbed amount of humic acid by RGO to its initially added amount) of 32 ± 2%. The adsorptive interactions of humic acid, in particular the polar interactions would preferentially occur on the edges of RGO that are abundant of O-containing groups and hence pH-dependent.

It is worth noting that the adsorption of humic acid greatly facilitates the dispersal of RGO (see Figure S11 of the SI). However, changes in dispersal of RGO can be ruled out as a main factor responsible for the observed humic acid effects on nitrobenzene reduction. This is because graphite exhibits similar trend of humic acid effects on nitrobenzene reduction (Figure S6 of the SI) while graphite is considered nondispersible regardless of whether humic acid is present or not.

**Implications.** The most striking observation here is that the presence of graphene oxide at concentrations as low as 2 mg/L can greatly facilitate the reduction of nitrobenzene in sulfide-containing reducing aqueous solutions. Combined spectroscopic evidences indicate that GO is reduced to RGO in the beginning of the reaction, and hence RGO mediates the reaction virtually. The mediation capability of RGO is attributed to the graphene basal planes (with assistance of the quinone moieties on the edge) that enhance electron transfer, as well as the zigzag edges that activate the nitrobenzene molecule. It is likely that other carbon nanomaterials (such as...
carbon nanotubes) having the above-mentioned structural characteristics would also mediate the reduction of NACs in similar ways. Additionally, as often functionalized or derivatized for practical use carbon nanomaterials can be well dispersed in an aquifer, particularly in the presence of dissolved humic acids, and hence transport long distances. Thus, it is possible that carbon nanomaterials may adsorb NACs in surface (aerobic) environments and then convey them to other sulfide-containing anaerobic environments where the reduction reaction of NACs can be induced. An important implication of this study is that carbon nanomaterials released to the environment can not only act as superb adsorbents for organic contaminants but also function as efficient mediators to accelerate the redox reaction of the adsorbed chemical.

ASSOCIATED CONTENT

S Supporting Information

Table S1, the elemental composition of humic acid. Table S2, the fitting parameters for reduction kinetics of nitrobenzene by pseudo-first-order model under different conditions. Figure S1, the FTIR spectra of humic acid. Figure S2, the calibration curves built with and without filtration. Figures S3 and S4, the chromatograms of nitrobenzene and its products by HPLC and GC–MS, respectively. Figure S5, the disappearance of nitrobenzene and appearance of its reduction products in solutions containing graphite. Figure S6, the effects of dissolved humic acid on reduction of nitrobenzene in solution containing graphite. Figures S7–S10, comparisons of the C1s XPS spectra, FTIR spectra, UV–vis spectra, and XRD patterns of GO and RGO, respectively. Figure S11, the visual examination of GO reduction by Na2S in the absence and presence of humic acid. Figure S12, the TEM images of GO and RGO. Figure S13, the sorption isotherms for nitrobenzene to GO, RGO, and humic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (Grants 21237002 and 21225729).

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