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Transformation of hydroquinone to benzoquinone mediated by reduced graphene oxide in aqueous solution

Chunmei Li ^a, Lingyun Li ^b, Lixiang Sun ^c, Zhiguo Pei ^{a,*}, Jieli Xie ^a, Shuzhen Zhang ^a

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, PO Box 2871, Beijing 100085, China

^b Supervision and Testing Center for Vegetable Quality, Ministry of Agriculture, The Institute of Vegetables and Flowers, Chinese Academy of Agricultural Sciences, Beijing 100081, China

^c College of Chemistry and Materials Science, Ludong University, Yantai 264025, China

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ABSTRACT

The mediation effect of reduced graphene oxide (rGO) on the oxidative transformation of 1,4-hydroquinone (H₂Q) to 1,4-benzoquinone (BQ) in aqueous solution was investigated using a batch method and electron paramagnetic resonance. The results showed that the autoxidation of H₂Q was spin-restricted and extremely slow in acidic and neutral pH range, but this process can be dramatically accelerated when rGO was added. In the presence of 33.3 mg L⁻¹ rGO, more than 76.0% of H₂Q was oxidized to BQ within 36 h. The enhancement effects of rGO were attributed to the combined contribution of the high chemical reactivity of graphenic edges and defects on rGO and the high electron conductivity of graphene basal surface of rGO. It is proposed that dissolved oxygen reacted with graphenic edges and defects of rGO to produce surface-bound oxygen intermediates, which capture H atoms from the phenolic hydroxyl groups of H₂Q and facilitate the generation of semiquinone radical (SQ⁻). The generated SQ⁻ continued to transfer an electron to molecular oxygen to yield superoxide radical (O₂⁻) and BQ. As a chain-carrying radical, O₂⁻ further reacted with H₂Q to produce SQ⁻ and H₂O₂.

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1. Introduction

Graphene is a two-dimensional structure consisting of sp² hybridized carbons that is only one atom thick, and can be regarded as the basic building block of other sp² hybridized carbon materials, such as graphite, fullerene, carbon nanotubes, etc [1]. Since its discovery, graphene-based nanomaterials (GBNs) have been demonstrated to have promising applications in diverse disciplines [2]. In environment science

and technology, GBNs are mainly considered as superior adsorbents to remove contaminants from waters and gases due to its large theoretical specific surface area and high ability of modification [3–9]. For example, it was found that sulfonated graphene was one of the best adsorbents for 1-naphthol due to the occurrence of π – π interaction between 1-naphthol and graphene surface [4]. Sun et al. [7] showed that the maximum adsorption capacity of acridine orange on graphene oxide (GO) reached striking 3.3 g g⁻¹. In addition,

* Corresponding author.

E-mail address: peizg@rcees.ac.cn (Z. Pei).

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it is showed that GBNs had high adsorption capacity for other contaminants, such as heavy metals [10,11], antibiotics [8], pesticides [9], polycyclic aromatic hydrocarbons and their derivatives [6].

However, it should be noted that most of previous studies were usually conducted on the modification of pristine graphene, and on the adsorption ability examination of these GBNs. Few people recognized the fact that GBNs can accelerate the transformation or degradation of some organic contaminants in the adsorption process. For example, previous research suggested that 1,4-hydroquinone (H_2Q) had much higher adsorption capacity than phenol because the additional $-OH$ groups on H_2Q facilitated the formation of $\pi-\pi$ interaction and enhanced its adsorption on reduced graphene oxide (rGO) [12]. In the present study we find a different phenomenon, where most of H_2Q is transformed to 1,4-benzoquinone (BQ) in the presence of rGO instead of the strong adsorption on rGO surface. Fu et al. [13,14] showed that rGO significantly facilitated the reduction of nitrobenzene and hexachloroethane by Na_2S in aqueous solutions. Sun et al. [15] found that rGO was able to effectively activate peroxymonosulfate to produce active sulfate radicals, and then accelerated the decomposition of phenol, chlorophenols and dyes. It is well known that the graphitic surfaces of rGO have extraordinarily high electron conductivity, and thus may facilitate the redox reactions by enhancing electron transfer [16,17]. In addition, dissolved oxygen can react with the active sites (defects, heteroatom, or metal impurities) on carbon nanomaterials to form reactive oxygen species [18–21], which have high oxidation activity for coexisting reductants [18]. Therefore, studies on the mediation effects of GBNs on the redox reactions of organic contaminants are necessary due to their inevitable release into the environment. Relative knowledge is very important for the risk assessment of both GBNs and organic contaminants in the environment [22].

In this work, we study the oxidation reaction of H_2Q mediated by rGO under ambient aerobic aqueous environment. Different factors such as rGO dosage, pH, different mediators and dissolved oxygen are examined. H_2Q is a major environmental pollutant from various industrial processes, such as coke, pesticides and dyes. Exposure to H_2Q residue can cause a variety of adverse consequences, including acute and chronic toxicity. The objectives of this study are (i) to investigate the potential role of rGO in accelerating the oxidation of H_2Q ; (ii) to examine the impact of reaction conditions; and (iii) to provide an insight into the involved reaction mechanisms.

2. Experimental

2.1. Materials

H_2Q (98.0%) and BQ (99.0%) were purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI), and used as-received. HCl, NaOH, 3-(N-Morpholino) propanesulfonic acid sodium salt (MOPS), and other reagents are analytical grade. Methanol is of HPLC grade. GO was prepared by a modified Hummers method [23] from pure graphite (99.9%, Nanjing XFNANO Materials Tech., Jiangsu, China), and rGO was

obtained by thermal exfoliation/reduction using graphite oxide as a precursor [24]. Detailed process has been provided in the “Supplementary data”.

2.2. Characterization of rGO

rGO was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Raman spectroscopy. TEM image was collected with an H-7500 (Hitachi, Japan). SEM image was obtained on a field emission scanning electron microscope (SU-8020). The surface functional groups of rGO were determined by XPS (Perkin-Elmer PHI 550 ESCA/SAM, U.S.). The crystallographic structures of rGO and graphite were determined by XRD patterns on an X' Pert PRO diffractometer (PANalytical, Holland) with $Cu K\alpha$ radiations generated at 40 kV, 40 mA. Scattering angles were ranged from 5° to 40° with a scanning speed at 1° per minute. Raman spectra were recorded with a Renishaw via Raman spectrometer (Renishawplc, UK). The elemental compositions (C, H, O) of rGO were determined with a high-temperature combustion method (PE 2400 SERIES II analyzer, Pekin-Elmer, Inc., USA).

2.3. Batch reaction experiments

The reaction kinetic experiment was carried out by mixing 1.0 mg rGO with 30 mL Milli-Q water (33.3 mg L^{-1}) containing $100 \mu\text{M}$ H_2Q in 50 mL glass flasks. All the solutions were prepared fresh daily. MOPS (2.0 mM) was used to control the solution pH at 6.7 because it was found to have negligible effect on the oxidation reactions of H_2Q . Under such conditions, H_2Q was present in solution as neutral form. The suspension was shaken in dark at 130 rpm at $25 \pm 1^\circ\text{C}$. At different time intervals, the suspension was filtered through $0.22 \mu\text{m}$ membrane to separate liquid and solid phases, and the concentrations of H_2Q and BQ in the filtrate were determined immediately by HPLC (Agilent 1200). Considering the possible adsorption of H_2Q and BQ on rGO, the collected rGO were freeze-dried and eluted with 5.0 mL methanol for twice. The final concentrations of H_2Q and BQ were the sum of those in the filtrate and on rGO. Control was also prepared identically but contained no rGO, which was simultaneously run to assess the loss and the stability of H_2Q . Results show that no significant loss of H_2Q was observed, indicating that microbial degradation, volatilization, or adsorption to the glass walls were negligible during the reaction process.

Separate sets of experiments were carried out to examine the effects of rGO dosages, solution pH, carbonaceous materials and dissolved oxygen on the oxidation reaction of H_2Q . In the rGO dosage experiment, a total of seven rGO dosages, from 0 to 50 mg L^{-1} , were investigated. In the pH experiments, solution pH was adjusted from 3.0 to 10.0 by addition of 0.1 M HCl or NaOH. Initial concentrations of both H_2Q and rGO were $100 \mu\text{M}$ and 33.3 mg L^{-1} , respectively. In order to investigate the structural effects of mediators on the H_2Q oxidation reaction, different carbonaceous materials (rGO, GO and graphite) were chosen. In the dissolved oxygen experiments, the reaction was initiated through mixing 1.0 mg rGO with 30 mL Milli-Q water (33.3 mg L^{-1}) containing $100 \mu\text{M}$ H_2Q in glass

flasks. The Milli-Q water was prepurged with N_2 to remove dissolved oxygen. At different time intervals, the suspension was filtered through 0.22 μm membrane to separate liquid and solid phases for HPLC determination. In comparison, a same reaction was performed using water containing dissolved oxygen. All reaction data were collected in triplicate, and the incubated time of all reactions was 36 h except pH experiment (12 h).

2.4. Analysis

H_2Q and BQ were determined by an Agilent 1200 reversed-phase HPLC (Atlantis-dC18 ODS HPLC column, 4.6 i.d. $\times$ 150 mm, 5 μm) equipped with UV detector. The determination wavelengths were set at 290 nm for H_2Q and 246 nm for BQ, respectively. The mobile phases were methanol:water (10:90, v:v, pH 3.0, adjusted with acetic acid) at a flow rate of 1.0 mL min^{-1} . Chromatograms and UV spectra of H_2Q standard, BQ standard and the oxidized product in the HPLC analysis are shown in Fig. S1. Both the retention time and UV spectra verify that the oxidized product of H_2Q is BQ. The concentrations of H_2Q and BQ were measured according to calibration curves prepared by corresponding standard compounds. All calibration curves included at least six concentration levels over the test concentration range with linear correlation coefficients (R^2) of at least 0.999. H_2O_2 was measured using the Amplex Red method [25].

2.5. Electron paramagnetic resonance (EPR) spectroscopy

Samples for EPR analyses were prepared in the same manner as that described in the batch reaction experiment except the initial solution concentration H_2Q was 10.0 mM. After reaction, the suspended solutions were used immediately for EPR measurement without filtration.

EPR spectroscopy was done using an EMX Plus EPR spectrometer (Bruker, USA) equipped with a high-sensitivity cavity and an Aqua-X sample holder. Spectra were obtained at room temperature. Typical EPR parameters were as follows: 3500 G center field; 80 G sweep width; 9.85 GHz microwave frequency; 10.0 mW power; 30 dB receiver gain; modulation frequency of 100 kHz; modulation amplitude of 1.0 G; with the time constant being 164 ms with one X-scan for each 1024 point spectrum.

2.6. Data analysis

All data were analyzed using Origin 8.0. One-way analysis of variance was used to assess the significant difference between groups at $p < 0.05$ level of significance.

3. Results and discussion

3.1. Characterization of rGO

Selected physical and chemical properties of rGO are given in Table S1. The BET specific surface area of rGO is found to be 300 $m^2 g^{-1}$. Elemental analysis result suggests that the prepared rGO includes about 86.59% carbon content and 10.51%

oxygen content. The results of TEM and SEM of the prepared rGO are shown in Fig. S2. It was found that rGO is closely agglomerated together in the form of thin and randomly aggregated nanosheets (Fig. S2a), and has typically wrinkled, sheet-like structure (Fig. S2b). Using the scaling law: layer number = $2600/A_{BET}$, we estimated the average layer number of rGO is ~ 8 layers, belonging to multilayer graphene [26].

Fig. 1a shows the XRD patterns of graphite and rGO. The very intense and narrow peak at 26.5° corresponds to the graphite spacing (002) of graphite plane. After exfoliation, it is found that the peak of graphite (002) broadens and the intensity of this peak decreases significantly, suggesting the appearance of the distorted graphite structure. This is also an indication that the prepared sample comprises largely free graphene sheets.

Fig. 1b shows Raman spectra of graphite and rGO, which are used to monitor the structural changes during the preparation of rGO from graphite. Raman spectrum of graphite displays two prominent peaks at 1328 and 1574 cm^{-1} , which correspond to the documented D band and G band, respectively. It is well known that the G band corresponds to the in-plane vibrations of the graphitic structure, and the D band is related to structural defects, amorphous carbon, or edges that can break symmetry and selection rule. When graphite is exfoliated to rGO, it is found that the D band and G band broaden and the intensity of D band increases. Defect content is given by the ratio of D band to G band intensity (ID/IG). Compared with graphite, the ID/IG of rGO increases from 0.29 to 0.87, indicating the increase of amorphous carbon and structural defects.

XPS provides useful information on the nature of functional groups and on the defects on rGO. In Fig. 1c, the C 1s XPS spectrum of rGO can be deconvoluted into four components. The dominant peak of $sp^2 C=C$ at 284.6 eV is attributed to the graphitic structure. Several small peaks of C–O at 286.0 eV, C=O at 288.2 eV, and O–C=O at 290.0 eV are assigned to carbon atoms attached to different oxygen-containing moieties.

3.2. Reaction kinetics of H_2Q mediated by rGO

The oxidation reaction of H_2Q in aqueous solution mediated by rGO is presented in Fig. 2. All reaction kinetics data fitted the pseudo-first-order kinetic model well (Eq. (1)), suggesting that the oxidation reaction is first-order with respect to the concentrations of H_2Q .

$$C_t = C_0 \times e^{-k_{obs}t} \quad (1)$$

where k_{obs} is the pseudo-first order rate constant, C_t and C_0 are the concentrations of H_2Q at a given time t and time zero, respectively. The corresponding fitting parameters are listed in Table 1. In the absence of rGO, it is found that H_2Q is rather stable at the examined time range and no significant reaction occurs. When rGO is added to the reaction system, more than 76.0% of H_2Q is oxidized within 36 h, suggesting the mediation effect of rGO on H_2Q oxidation. The corresponding k_{obs} are $9.41 \times 10^{-2} h^{-1}$ for H_2Q and $10.2 \times 10^{-2} h^{-1}$ for BQ (Table 1). BQ is identified as the only oxidation product in the reaction system (Fig. S1). The good mass balance ($>95.0\%$) calculated by summing up H_2Q and BQ indicates the negligible occurrence of other reaction products.

Fig. 1 – Structural characterization of rGO and graphite. (a) XRD pattern of rGO and graphite, (b) Raman spectra of rGO and graphite, (c) XPS C1s spectrum of rGO.

Fig. 2 – Oxidation transformation of H₂Q to BQ in the absence and presence of rGO. (■) H₂Q in the absence of rGO; (●) H₂Q in the presence of rGO; (▲) produced BQ mediated by rGO. Reaction conditions: [H₂Q]₀ = 100 μM, [rGO]₀ = 33.3 mg L^{−1}, pH = 6.7. Curve lines for H₂Q and BQ in the presence of rGO are modeled by the pseudo-first order kinetic.

To further assess the role of rGO in promoting H₂Q transformation, the effect of rGO concentrations is evaluated. As shown in Fig. S3, the transformation of H₂Q mediated by rGO is acutely sensitive to the concentrations of rGO in

solution. Increasing the rGO dosage from 0 to 50.0 mg L^{−1}, the concentrations of H₂Q decreased from initial 100 to 4.8 μM after 36 h, and concurrently, the concentrations of BQ also increases from 0 to 95.9 μM. There exists a good linear relationship ($R^2 = 0.992$) between rGO dosages and the concentrations of H₂Q/BQ, suggesting the marked mediation ability of rGO on the oxidation of H₂Q.

3.3. Effects of solution pH

Since the chemical species of H₂Q in solution are likely related to its transformation, the oxidation reaction of H₂Q in the absence and presence of rGO as a function of solution pH is examined (Fig. S4). In the absence of rGO, it is found that H₂Q is stable in aqueous solution at pH 3.0–7.0, but the concentrations of H₂Q start to decrease at pH > 7.0. Considering the pK_a of H₂Q (pK_{a1} = 10.16, and pK_{a2} = 12.02), it is possible that the oxidation reaction of H₂Q is due to the dissociation of H₂Q [27]. According to Yuan et al. [28], the autoxidation of H₂Q is spin-restricted and extremely slow at acidic and neutral pH, but this process can be significantly accelerated when the phenolic OH groups ionize, which overcomes the spin restriction. At pH < 7.0, H₂Q mainly exists in the undissociated form (H₂Q⁰). With an increase of solution pH above

Table 1 – Fitting parameters for H₂Q and BQ by pseudo-first-order model in the presence of rGO.

Compounds	Fitting equations	k_{obs} (h ^{−1})	R^2
H ₂ Q	$y = 23.07 + 61.60 \times e^{-0.09413t}$	9.41×10^{-2}	0.97
BQ	$y = 70.34 - 57.61 \times e^{-0.1021t}$	10.2×10^{-2}	0.99

pH 7.0, the monodissociated (HQ^-) and/or doubly dissociated (Q^{2-}) anions will appear in succession, which are more readily oxidized than H_2Q^0 [28].

When rGO is added to the aqueous solution, it is seen that the oxidation reaction of H_2Q is accelerated at $\text{pH} < 9.0$. For example, approximately 31.1–47.4% H_2Q is oxidized over the pH range of 3.0–7.0 within 12 h. An increase of solution pH from 3.0 to 7.0 causes the oxidation efficiency of H_2Q slow increase. When solution pH is increased further, the concentrations of H_2Q have an abrupt decrease and two curves tend to be close. In alkaline pH range, the decreased mediation efficiency of rGO can be attributed to the presence of monodissociated HQ^- and/or doubly dissociated Q^{2-} . As described above, they have higher activity than H_2Q^0 , thus their autoxidation are rapid and become the main reaction process in high pH range.

3.4. Mechanisms of the mediation effect of rGO

3.4.1. Mediation effects of different carbonaceous materials

The comparison of mediation efficiencies among different carbonaceous materials under aerobic conditions are displayed in Fig. 3. As described above, H_2Q is stable in aqueous solution, and little autoxidation is observed in the control experiment (in the absence of any carbonaceous materials). When different carbonaceous materials are added at equal mass dose, it is found from Fig. 3 that rGO exhibited stronger mediation efficiency than GO and graphite. For example, about 76.0% of H_2Q is transformed to BQ in the presence of rGO, in comparison with 8.2% for GO and 3.0% for graphite. Compared to GO, the significant mediation efficiency of rGO can be ascribed to its high electron transfer capacity based on the literature [15,16]. It is well known that graphene basal plane is 2D crystal lattice with sp^2 carbon atoms, which makes each carbon atom have a π orbital that contributes to a delocalized network of electrons [29–33]. Undoubtedly, rGO is a good electron conductor. The electric conductivity of rGO is proportional to its C:O ratio, i. e., the lower C:O ratio means the weaker electron transfer ability [30]. When rGO is oxidized, it is shown that the mediation efficiency of GO decreases significantly with the increase of O content

Fig. 3 – Mediation effects of different carbonaceous materials on the oxidation of H_2Q in aqueous solution. Reaction conditions: $[\text{H}_2\text{Q}]_0 = 100 \mu\text{M}$, $t = 36 \text{ h}$. Initial concentrations of all carbonaceous materials are 33.3 mg L^{-1} . The error bar (some of which are too small to be visible) represents the standard deviations ($n = 3$).

(Fig. 3), suggesting that the oxidation reaction of H_2Q is closely related to the electric conductivity of rGO. In fact, enhancement of electron transfer by graphene surfaces has been proposed to explain the mediation effects of graphite, soot, carbon nanotubes, and active carbon on the degradation reactions of nitroaromatic compounds and phenolics [14,16,17,34–36].

Though graphite is also a good electric conductor, its specific surface area is very small ($5.0 \text{ m}^2 \text{ g}^{-1}$ for graphite and $300 \text{ m}^2 \text{ g}^{-1}$ for rGO), which is unfavorable for the contact of H_2Q with graphite surface and inhibits the oxidation of H_2Q (Fig. 3). In addition, it is found that, even in equal area dose rGO still has higher mediation efficiency than graphite (Fig. 4). This suggests that some active sites on rGO should be responsible for the enhanced mediation effect of rGO. In comparison with graphite, rGO contains many graphenic edges and defects during its preparation process. These sites are reported to be high reaction activity and can react with dissolved oxygen to produce reactive oxygen species by electron transfer from rGO [18,19]. It is significant that these reactive oxygen species are able to react with the coexisting H_2Q and facilitate the oxidation reaction of H_2Q .

3.4.2. Role of dissolved oxygen

To gain some insight into the rapid oxidation of H_2Q in rGO system at neutral pH, the role of dissolved oxygen and the intermediate and terminal products are investigated. As shown in Fig. 5, we examine the effects of dissolved oxygen on the oxidation of H_2Q in the presence of rGO. Consistent with our above results, it is found that H_2Q in rGO suspended solution is transformed to BQ rapidly in the presence of dissolved oxygen, and about 78.9% H_2Q is removed within 36 h. If dissolved oxygen is excluded, interestingly, it is found that the oxidation reaction of H_2Q ceases and H_2Q is stable within the whole time range. This result suggests that dissolved oxygen takes part in the reaction process and plays a vital role in the transformation of H_2Q to BQ.

The reaction of dissolved oxygen with carbon surface had been widely studied [18–20], where dissolved oxygen reacts with active sites on graphenic carbon surface to produce surface-bound oxygen intermediates, such as adsorbed

Fig. 4 – Mediation effects of rGO (■) and graphite (△) on the oxidation of H_2Q as a function of surface area dose. Reaction conditions: $[\text{H}_2\text{Q}]_0 = 100 \mu\text{M}$, $t = 36 \text{ h}$. The error bar (some of which are too small to be visible) represents the standard deviations ($n = 3$).

Fig. 5 – Effects of dissolved oxygen on the oxidation of H₂Q in the presence of rGO. (■) H₂Q in the absence of dissolved oxygen; (●) H₂Q in the presence of dissolved oxygen; (Δ) produced BQ in the presence of dissolved oxygen; (▽) produced BQ in the absence of dissolved oxygen. Reaction conditions: [H₂Q]₀ = 100 μM, [rGO]₀ = 33.3 mg L^{−1}, pH = 6.7. The error bar (some of which are too small to be visible) represents the standard deviations (n = 3).

superoxide anion C_s(O₂^{•−}), or hydroperoxide C_s(OOH) [18,19]. In this study, these generated surface-bound oxygen intermediates are thought to capture H atoms from H₂Q molecular and facilitate the generation of semiquinone radical (SQ^{•−}). Using the EPR technique, we determine the signal intensity of SQ^{•−} in solution. As shown in Fig. 6, the signal intensity of SQ^{•−} is weak at pH 6.7 under aerobic environment in the absence of rGO. When rGO is introduced into the reaction system, it is found that the signal intensity of SQ^{•−} has a pronounced increase, suggesting that rGO stimulates the generation of SQ^{•−}. If the dissolved oxygen in rGO system is partially removed, as seen in Fig. 6c, the signal intensity of SQ^{•−} is significantly inhibited under anaerobic condition. The above results imply that rGO and dissolved oxygen are two key factors to produce SQ^{•−}.

However, the formation of SQ^{•−} is only the first stage of the oxidation reaction of H₂Q. The radical continues to transfer an electron to molecular oxygen to generate superoxide radical (O₂^{•−}) and BQ (reaction (2)) [37,38]. Repeated attempt has been made to detect the appearance of O₂^{•−}. Unfortunately,

Fig. 6 – EPR spectra of the generated SQ^{•−} from H₂Q, (a) in the absence of rGO under aerobic condition; (b) in the presence of rGO under aerobic condition; (c) in the presence of rGO under anaerobic condition.

O₂^{•−} is very short-lived, and the production of O₂^{•−} could not be observed using 5,5-dimethyl-1-pyrroline N-oxide as a spin trapping agent due to the possible rapid reaction of O₂^{•−} with H⁺ and/or H₂Q (reactions (3) and (4)) or scavenging by carbon surface [39]. Finally, we determine the possible occurrence of hydrogen peroxide in the reaction solution. Result shows that as H₂Q is oxidized to BQ, the concomitant hydrogen peroxide is formed at the same time (Fig. S5) [40–42]. This result is consistent with the observation of Eyer [43], and indicates the chain-propagating role of O₂^{•−} in the oxidation reaction of H₂Q to some extent:

These observations above demonstrate that dissolved oxygen will be consumed in the oxidation reaction of H₂Q, giving rise to the formation of BQ and hydrogen peroxide, the net reaction being

In addition, we also examine the possible interference of metal impurities in rGO on the oxidation reaction of H₂Q [21]. rGO is washed with 3 M HCl followed by hot water wash as described in Liu et al. [44]. The final result demonstrates that there is no significant difference between the mediation efficiencies of treated and untreated rGO (data not shown). The result suggests that the accelerated oxidation reaction of H₂Q is not due to the metal impurities in rGO.

4. Conclusion

The present study demonstrated a novel role of rGO as redox mediator in accelerating the oxidative transformation of H₂Q to BQ at pH 6.7. It is found that the presence of rGO markedly increases the oxidation rate of H₂Q under ambient aerobic condition. The enhancement effects of rGO are attributed to the combined contribution of the graphenic edges and defects on rGO and the high electron conductivity of rGO. The graphenic edges and defects on rGO can react with dissolved oxygen to form surface-bound oxygen intermediates by electron transfer. Subsequently, these surface-bound oxygen intermediates capture H atoms from the phenolic hydroxyl groups of H₂Q and stimulate the generation of SQ^{•−}. The generated SQ^{•−} transfers an electron to dissolved oxygen to yield O₂^{•−} and BQ. Then O₂^{•−} continues to react with H₂Q or H⁺ to produce SQ^{•−} and H₂O₂. This finding highlights that rGO can not only act as superb adsorbents for organic contaminants but also function as efficient mediators to accelerate the redox reaction of coexisting chemicals. Relevant knowledge provides new information for the risk assessment of both rGO and other coexisting phenolic contaminants in aqueous environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2015.03.027>.

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