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Unveiling the active sites of graphene-catalyzed peroxymonosulfate activation

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ABSTRACT

Graphene-based materials have emerged as novel and green alternatives to metals/oxides for environmental catalysis. This study integrates deliberate material fabrication with density functional theory (DFT) calculations to probe intrinsic active sites, e.g. the defects and oxygen functionalities on graphene for activating O–O bond in peroxymonosulfate (PMS) toward catalytic oxidation. The reaction rate constants of degradation efficiency were discovered to be closely related with the I_D/I_G values of thermally annealed reduced graphene oxides (rGOs). Three rGOs (rGO-CM, rGO-HH, and rGO-HT) with a similar oxygen level by different reduction methods were utilized to investigate the effect of different oxygen groups. The results indicate that rGO-HT with the highest contents of ketonic group (C=O) presented the best activity. The theoretical calculations were applied to simulate the PMS chemisorption with all the possible active sites on rGO. The DFT results suggest that vacancies and defective edges are more reactive than the graphene basal plane with prolonged O–O bond in PMS molecules, greater adsorption energy, and more electron transfer. Besides, the electron-rich ketonic groups may be the major active species among the oxygen functionalities. The findings will contribute to new insights in reaction mechanism and material design in heterogeneous carbocatalysis.

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1. Introduction

Metal-free carbon materials, such as graphene and carbon nanotubes, have achieved a great success as promising alternatives to toxic and/or expensive metals and oxides for various heterogeneous catalysis [1,2]. Perfect monolayer graphene with an intact honeycomb network and sp²-hybridized structure has been demonstrated as a superb semiconductor for electronic devices, yet

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chemically inert for catalytic reactions [3]. Graphene oxide and its reduced derivatives can be synthesized, intentionally or unintentionally, with various structural defects and heteroatom functionalities for emerging catalysis due to the modulated physical, chemical, and electronic properties. Generally, the catalytic properties of metal-based catalysts are very sensitive to the size and shape of the metal crystal, because the specifically exposed crystal facets and ill-defined surface with edges, corners exhibit better excess and lower binding energy for adsorption with the reactants [4]. Meanwhile, the transition metal oxides possess variable valent states, different types of bridging or terminal lattice oxygen, and oxygen vacancies, which play vital roles in interacting with the reactants especially in a redox process [5-7]. Distinctly, it has been widely accepted that pristine carbocatalysis might be originated from the "active sites" such as structure defects, functional groups, or heteroatom-doping induced modulations to the carbon network, which usually exhibit characteristic electronic states and spin





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cultures. However, due to the non-stoichiometric nature and the intricate structure of graphene and the derivatives, it is still elusive to unravel the real active sites and differentiate their unique performances in carbocatalysis [8,9].

Su and co-workers first utilized various small organic molecules to mimic the zigzag/armchair edges and versatile oxygen functional groups in carbon-based catalysts. They applied molecular catalysts and theoretical studies to reveal that armchair defects are the major active sites to activate hydrogen peroxide (H₂O₂) for selective oxidation of benzene to phenol, whereas zigzag configurations play an important role in stabilizing the intermediate of phenoxy radicals in selective oxidation of substituted phenols to p-benzonquinones [10–12]. Loh's group performed in situ Fourier transform infrared (FTIR) and electron spin resonance (ESR) spectroscopies to elucidate that the boundary defects (edges and vacancies) of basetreated graphene oxide (ba-GO) can effectively activate oxygen molecules to generate superoxide radicals, whereas the carboxylic groups functionalized at the edging defects are capable of synergistically trapping the reactants via the localized unpaired electrons [13]. Besides, chemical titration was adopted as a fantastic strategy to selectively block either ketonic carbonyl (C=O), hydroxyl (-OH), or carboxylic groups (-COOH) on the carbon catalysts to probe the effect of the functional groups on catalytic reactions, and kenotic groups were discovered to account for the intrinsic activity of decomposition of H₂O₂ and oxidative dehydrogenation (ODH) reactions [14–16]. Deng et al. synthesized a series of graphene with different sizes and conducted DFT calculation to reveal that the graphene in a smaller crystal size and more zigzag edges present the best activity for oxygen reduction reaction [17]. Heteroatom doping (single-atom doping or co-doping) is widely reported to be able to substantially break the inertness of graphene network and bring about outstanding features for catalytic reactions [18–21].

In environmental catalysis, we first discovered that reduced graphene oxide (rGO) obtained from thermal removal of the excessive oxygen groups and attaining higher defective degrees (I_D) I_G values) can effectively activate potassium peroxymonosulfate (PMS) to generate reactive radicals for aqueous oxidation of organic contaminants [22,23]. Since the derived graphene samples are always simultaneously constructed with defects, oxygen functionalities and mixed sp²-and sp³-hybridized domains, the insightful understanding in identifying the intrinsic active sites has never been achieved. Herein, advanced material design was presented to deliver several rGO samples with different levels of structural defects, oxygen doping, and proportions of varying oxygen groups (C=O, COOH, and -OH/C-O-C). Theoretical calculations were also conducted to mimic all the plausible active sites on graphene clusters for potential PMS activation. This study provides a feasible approach to reveal the genuine active sites for catalytic oxidation in environmental remediation.

2. Experimental section

2.1. Chemicals and materials

The graphite flakes, potassium permanganate (ACS reagent, >99 wt%), potassium peroxymonosulfate (PMS, also known as oxone[®], KHSO₅·0.5KHSO₄·0.5K₂SO₄), and hydrazine hydrate (78–82 wt%) were purchased from Sigma-Aldrich, Australia. Sulfuric acid (98 wt%), ammonia solution (37 wt%), hydrochloric acid (30 wt%), and hydrogen peroxide (30 wt%) were obtained from Thermal Fisher, Australia. The commercial graphene nanoflakes (rGO-CM, obtained via chemical reduction) were purchased from Chengdu Organic Chemical, China.

2.2. Synthesis of reduced graphene oxides

Graphene oxide (GO) was synthesized via a modified Hummers' method and the detailed procedure can be found in our previous study [24,25]. Several approaches were utilized to remove the oxygen groups to obtain reduced graphene oxide (rGO) as illustrated in Fig. 1. With a thermal annealing method. GO was placed in a quartz boat, then transferred to a tube furnace, and annealed under inert atmosphere at set temperatures (300, 500, 700, and 900 °C) for 1 h. The as-made catalysts were denoted as rGO-300, rGO-500, rGO-700, and rGO-900, respectively. A rGO was also synthesized via ultrasonic exfoliation and chemical reduction with hydrazine hydrate at 100 °C for 24 h and marked as rGO-HH [26]. Moreover, a hydrothermal method was also applied to remove the oxygen groups [22]. The GO was well dispersed under basic condition (pH = 10, adjusted by concentrated ammonia solution), stirredovernight, and then sealed in an autoclave and treated at 180 °C for 18 h in an oven. The black suspension (denoted as rGO-HT) was then thoroughly washed with deionized water, filtered and dried. All the obtained carbon materials were washed with 0.5 M hydrochloric acid at 60 °C for 24 h to remove the remaining metal residence before use.

2.3. Sample characterizations

The surface chemistry and chemical states of graphene materials were analyzed on an X-ray photoelectron spectroscopy (XPS) under ultrahigh vacuum conditions with a monochromated Al K α X-ray gun (photon energy 1486.7 eV) with the pass energy high resolution scan at 20 eV and survey scan at 160 eV. Spectra were analyzed with CasaXPS software. All spectra were adjusted to attain the C 1s at 284.5 eV. Component fitting for each element was based on Voigt functions with a 30% Lorentzian component using Shirley background. The Raman spectra of the carbon materials were acquired from the ISA Raman spectrometer equipped with argon ion lasers at 514 nm to estimate the disorder degree of the carbon materials. The Brunauer-Emmett-Teller (BET) surface areas were calculated based on the nitrogen sorption isotherms acquired at -196 °C on a TriStar instrument.

2.4. Catalytic oxidation of phenol solution

The activity of the prepared graphene materials were evaluated in catalytic activation of peroxymonosulfate for phenol oxidation. The experiment was carried out in a conical flask with a fixed ratio of catalyst, phenol, and PMS. The batch reactor was maintained in a water bath controlled at a constant temperature. The solution was withdrawn by a syringe and filtered with a 0.45 μ m membrane. The filtrate solution was then transferred into a HPLC vial and mixed with methanol to quench the reactive species and terminate the oxidation reaction. The concentration of the target organic was detected on a UltiMate[®] 3000 Standard LC system equipped with an OA column (150 × 4 mm, 5 μ m) and UV–Vis detector at 270 nm. Parallel tests were performed for each material, and mean value was adopted with standard deviations. A pseudo first-order-kinetic model was utilized to fit the reaction rate.

2.5. Theoretical calculation methods

To understand the effects of graphene sites for the activation of PMS, density functional theory (DFT) calculations were adopted to investigate the chemisorption of PMS on graphene. The spin–unrestricted DFT calculations were carried out by using Dmol³ package [27]. Exchange–correlation functions are taken as generalized gradient approximation (GGA) with



Fig. 1. Illustration of the reduction process from graphene oxide to reduced graphene oxide. (A colour version of this figure can be viewed online.)

Perdew–Burke–Ernzerhof (PBE). Double numerical plus polarization (DNP) is employed as the basis set [28]. The convergence tolerance of energy is 10^{-5} Hartree (1 Hartree = 27.21 eV), and the maximal allowed force and displacement are 0.002 Hartree/Å and 0.005 Å, respectively. In the simulations, a cluster model was used for graphene with dangling bonds passivized by H atoms.

3. Results and discussion

Reduced graphene oxide was synthesized via thermal treatment at a temperature range of 300–900 °C to attain different oxygen contents and structure defects (denoted as rGO-300, -500, -700, and -900, respectively). As indicated in Fig. S1 and Table S1, graphene oxide contains a high oxygen level of 31.35 at.% with various oxygen functional groups such as carboxyl (–COOH), kenotic (C= O), hydroxyl (-OH), lactone (C-O-C=O), and epoxide groups (C-O-C) (Fig. S2). The oxygen level decreased with elevated temperature from 12.35 (rGO-300) to 2.95 at.% (rGO-900) owing to the removal of excessive oxygen groups (Table 1). XPS studies of O1s in Fig. S2 and Table S2 illustrate that most of the carboxyl groups (-COOH) were eliminated at 300 °C, while thermal decomposition of kenotic and hydroxyl groups requires higher annealing temperature (>500 °C) [29]. Owing to the severely stacked sheets resulted from the strong hydrogen bonds among the oxygen groups between the layers, the graphene oxide possesses a low specific surface area (SSA, 29.9 m^2/g) and a small pore volume (0.04 cm^3/g). Thermal annealing not only tuned the oxygen groups but also enabled thermal expansion of graphene layers, giving rise to increased SSAs and enlarged pore volumes of rGOs (shown in Fig. 2a). Meanwhile, the annealing process can modulate and transform the sp³ carbons, leading to the collapse of carbon skeleton and restructure of the defective edges. As a result, rGO can be tailored with more decays, lower crystallinity, and porous structures [30,31]. This was further confirmed by the non-destructive characterization of Raman spectroscopy as indicated in Fig. 2b). Two characteristic peaks were discovered for all the graphene samples. The intensity ratio of D-band/G-band (I_D/I_G) can represent the disorientated degree of graphene arising from the structure defects (e.g. edges, vacancies, and non-hexagonal units) and heteroatom doping [20,32]. Table 1 demonstrates that I_D/I_G values increase gradually with the rising temperatures. Compared with GO ($I_D/I_G = 1.22$) and rGO-300 ($I_D/I_G = 1.24$), high temperature annealing (900 °C) results in a much greater defective degree ($I_D/I_G = 1.69$).

The catalytic performance of the rGOs derived from thermal treatment was evaluated in activating PMS toward phenol oxidation. PMS alone can hardly oxidize the organics (Fig. S3). Phenol adsorption on all the annealed graphene samples was insignificant (Fig. S4). As shown in Fig. 2c, GO only presented little effectiveness for PMS activation. Phenol removal efficiency was enhanced with the elevated treatment temperature in rGO synthesis. More specifically, GO gave only 12.4% phenol removal in 180 min, meanwhile 25.4%, 42.3% and 86.8% phenol oxidation efficiencies were obtained on rGO-300, rGO-500, and rGO-700, respectively. RGO-900 achieved complete phenol oxidation in 150 min with a degradation rate of 0.027 min⁻¹, which is 27 folds faster than that of GO (Fig. S5).

The nature of catalytic activation of PMS (O₃SO-OH) lies in the break-up of the superoxide O-O bond and enabling the electrontransfer between the catalyst and PMS molecules. Popular transition metals and metal oxides can effectively activate PMS due to the strong capability for PMS molecules to bond with the empty orbital of transition metals and to interact with the outer-sphere electrons [33]. The polyvalent instinct of metal sites (e.g. Co^{II}/Co^{III}, Mn^{II}/Mn^{III}, Ce^{III}/Ce^{IV}) facilitates the charge-transfer process with PMS to produce free radicals [22,34]. Distinctly, graphene-based materials consist of a honeycomb-like carbon framework with a uniformly sp²-hybridized structure and abundant free-flowing π electrons with a great mobility. In spite of the chemically inert culture of the intact carbon matrix, the carbocatalysis can stem from various active sites such as surface imperfect units and vacancies, zigzag/ armchair edges, substantial heteroatom doping, and functional groups terminated at the flat (001) boundaries, which could be produced during the synthesis and are expected to possess high chemical activities [8,35].

As indicated in Fig. 2d, phenol oxidation rate can be correlated with a positive proportion to the defective degree of the reduced graphene oxides, suggesting that the defective sites and edges are the active sites for PMS activation. Unlike the perfect honeycomb unit, the vacancies and edges at the boundary can generate dangling σ bonds with unconfined π -electron environment.

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Structure and surface chemistry of various nanocarbons.

	O (at.%)	Pore size (nm)	Pore vol (cm ³ /g)	$S_{BET} (m^2/g)$	I_D/I_G	Rate constant (min ⁻¹)
GO	31.35	6.7	0.04	29.9	1.22	0.001
rGO300	12.35	8.5	0.33	118.4	1.24	0.002
rGO500	7.39	8.1	0.43	173.1	1.28	0.004
rGO700	5.29	8.1	0.51	202.8	1.39	0.015
rGO900	2.95	8.2	0.69	286.3	1.69	0.027
rGO900-used	8.90	8.4	0.44	248.8	1.54	0.095



Fig. 2. (a) Nitrogen sorption isotherms of annealed graphene materials. (b) Raman spectra of annealed graphene materials. (c) Phenol oxidative degradation on various nanocarbons. ([Catalyst] = 0.2 g/L; Temp = $25 \degree$ C; [PMS] = 6.5 mM; and [Phenol] = 20 ppm) (d) Correlation between the defective degree (I_D/I_G) and reaction rate of phenol oxidation. (A colour version of this figure can be viewed online.)



Fig. 3. DFT models of favorable adsorption structures of a PMS molecule on different sites of pristine graphene: (a) graphene basal plane, (b) vacancy, (c) zigzag edges, and (d) armchair edges. The grey, white, red and yellow atoms are C, H, O, and S atoms, respectively. (A colour version of this figure can be viewed online.)

Table 2

The adsorption energy (E_{ads}) of PMS on graphene, the electronic transfer (Q) between PMS and graphene, and the O–O bond length $(l_{\rm O}-_{\rm O})$ in PMS (SO₄–OH) in different DFT models shown in Fig. 3.

Configuration	E _{ads} (eV)	Q (e)	l ₀ -0 (Å)
Free PMS	_	_	1.326
(a)	-2.39	-0.684	1.444
(b)	-3.07	-0.635	1.441
(c)	-2.58	-0.782	1.439
(d)	-2.52	-0.725	1.454

Meanwhile the carbon atoms still maintain sp²-hyridized state to present a high chemical potential to conduct a catalytic/redox process [36,37]. The edging sites, with closer Femi level to the bulk structure, unpaired π electrons, and localized spins along the boundaries, are reported to perform as radical-like sites which are able to initialize a radical pathway and facilitate PMS to change into sulfate (SO₄*⁻) and hydroxyl radicals (*OH) via charge transfer [13,38]. Thermal treatment releases oxygen moieties locating at the edges and creates more decays and defective sites during carbon reconstruction under high temperature annealing. The passivated graphene with an oxidized surface and a higher oxygen level

Table 3

Structure and surface chemistry of various reduced graphene oxides.

presented a poorer activity compared with the fresh catalyst (Figs. S1 and S3). Besides, higher temperature annealing endows smaller graphene nanosheets and larger specific surface areas (Table 1 and Fig. 2a), giving rise to the higher catalytic activity due to the exposure of more defective sites and better access to peroxymonosulfate molecules via adsorption and interaction at the interface.

The interactions of PMS molecule (HSO₅) on different positions of pristine graphene were differentiated by density functional theory (DFT) calculations as shown in Fig. 3. As summarized in Table 2, the bond length ($l_{0}-_{0}$) of free PMS molecules (HO–OSO₃) is 1.326 Å, whereas $l_{0}-_{0}$ is remarkably stretched when the PMS is placed with different graphene models, suggesting the great tendency to cleave O–O bond. The adsorption energies of PMS on the vacancy, zigzag edge and armchair edge are -3.07, -2.58, and -2.52 eV, respectively, which are higher than that bonded with graphene basal plane (-2.39 eV). The stronger binding energy indicates that the structural defects and edges are more active than the intact graphene network for PMS adsorption. The electrontransfer capability Q(e) from graphene to PMS also plays a crucial role in generation of active radicals kinetically. In spite of the highest adsorption energy of the vacancy model, the Q(e) is much

	O (at.%)	Oxygen species			$S_{BET}\left(m^2/g ight)$	I_D/I_G	Rate constant (min ⁻¹)	
		C=0 (at.%)	COOH (at.%)	-OH/C-O-C (at.%)	H ₂ O _{ads} (at.%)			
rGO-CM	9.16	16.30	22.02	51.69	9.99	140.3	0.94	0.005
rGO-HH	9.05	28.87	29.97	32.69	8.47	337.6	1.52	0.010
rGO-HT	9.63	32.65	26.01	30.46	7.89	142.3	1.35	0.026



Fig. 4. (a) O 1s high resolution scan and peaking fitting, (b) evaluation of catalytic performance, and (c) Raman spectra of rGO-CM, rGO-HH, and rGO-HT. (A colour version of this figure can be viewed online.)



Fig. 5. DFT models of favorable adsorption structures of PMS molecule on different sites of graphene with oxygen functional groups: (a) PMS on zigzag edge with carbonyl of graphene, (b) PMS on armchair edge with carbonyl, (c) PMS on graphene basal plane with C–O–C, (d) PMS on zigzag edge with –OH, (e) PMS on armchair edge with –OH, (f) PMS on graphene basal plane with –OH, (g) PMS on zigzag edge with –OH, (g) PMS on zigzag edge with –COOH, and (h) PMS on armchair edge with –COOH. The grey, white, red and yellow atoms are C, H, O, and S atoms, respectively. (A colour version of this figure can be viewed online.)

 Table 4

 DFT calculations for the models shown in Fig. 5.

		·	
Configuration	E _{ads} (eV)	Q (e)	l ₀ -0 (Å)
(a)	-2.10	-0.520	1.412
(b)	-2.37	-0.617	1.441
(c)	-2.58	-0.651	1.439
(d)	-3.52	-0.454	1.466
(e)	-2.99	-0.492	1.462
(f)	-2.83	-0.744	1.459
(g)	-2.96	-0.678	1.464
(h)	-2.69	-0.712	1.461

lower than the models of PMS binding to zigzag and armchair edges. This is further verified by the fact that the charge densities of the two oxygen atoms in O–O bond are more negative when adsorbing on the edging sites (Table S4). It should be pointed out that the non-periodic graphene clusters applied in the theoretical calculations were stabilized and passivated with H-terminated edges, thus the edging sites might be expected with a much higher catalytic activity in the real rGO/PMS system.

In addition to defective sites and edges, the versatile oxygen functional groups on graphene were also well demonstrated to serve as the active sites in heterogeneous catalysis [13,15,39]. In preliminary studies, we discovered that graphene oxide with a high oxygen-doping level (over 35 at.%) can hardly activate PMS, whereas the activity was significantly improved after eliminating the excess oxygen functional groups through thermal (or hydrothermal) reduction process [22,23]. A minor amount of electronrich oxygen groups terminated at the defective edges were supposed to be more active than the graphene (001) plane to catalyze PMS activation [22,40,41]. In this study, we prepared another three rGOs derived via different chemical reduction procedures. As presented in Table 3, the three samples of rGO-CM, rGO-HH, and rGO-HT possess similar oxygen levels (9.16-9.63 at.%) with different compositions of C=O, COOH, and -OH/C-O-C (Fig. 4a). The rGO-HT exhibits the best activity (Fig. 4b) among the rGOs in spite of rGO-HH harvesting a higher defective degree (Fig. 4c), larger SSA (Fig. S6), and stronger adsorption capability (Fig. S7). The phenol oxidation efficiency is suggested to be related to the percentage of ketonic groups (C=O) (Figs. S8 and S9). Therefore, the oxygen groups may also play vital roles in PMS activation.

To probe the roles of different oxygen groups, we took into account of PMS adsorption on all the possible adsorption sites on graphene in Fig. 5. The O–O bond was prolonged remarkably when PMS is interacted with oxygen groups as shown in Table 4, implying the potential to be transformed into HO and SO₄. PMS adsorption on graphene with -OH group on the zigzag and armchair edges exhibited the greatest adsorption energy, but the electron transfer tendency is guite low. Besides, the H atom in the -OH group detaches from the O atoms and binds with the PMS molecule, meanwhile the -OH groups on graphene would transfer into C=O groups. This process implies that the PMS activation on -OH is highly infeasible from the thermodynamic perspective. Hereby, the -OH groups could not be the active sites for PMS activation. On the other hand, the oxygen groups such as -COOH (O=C-OH) and C= O possess an oxygen atom with lone-pair electrons presenting high activities to bond with PMS molecule and coordinate an electrontransfer process. Moreover, PMS activation favors at basic conditions due to the stronger oxidative potential of SO_5^{2-} (pKa₁ < 0; $pKa_2 = 9.9$) with a highly asymmetric structure and bare electronrich oxygen atoms. The C=O as a Lewis basic site may perform as the principal reactive site among the oxygen functionalities. We suppose that only minor amount of oxygen functional groups, especially ketonic groups can serve as the active sites and facilitate the binding and adsorption of PMS onto graphene due to inner O–O or H–O bond (SO₄–O–H–O=C). The defective edges and vacancies may still be the dominant active sites for PMS activation. However, excess oxygen doping level (e.g. graphene oxide) would occupy the active edges and prevent the interaction of PMS with defective sites via a stereo-hindrance effect. Moreover, since the electron-mobility between a carbocatalyst and PMS was tailored by the relative redox potential of reactants, the oxygen content remarkably influences the reducibility of graphene sheets, thereby impacting the charge-transport process. Therefore, both the type and doping level of the oxygen groups should be manipulated for fabrication of efficient graphene materials for efficient metal-free carbocatalysis.

4. Conclusions

In summary, we integrated an elaborate material design and DFT calculations to investigate the intrinsic active sites for PMS activation on reduced graphene oxide. Both experimental and theoretical evidences suggest that the defects such as vacancies and zigzag/ armchair edges at the boundaries of graphene can serve as the active sites for cleaving O-O bond in PMS with enhanced adsorption energy, prolonged O-O bond, and more efficient electrontransfer. A proper level of electron-rich ketonic groups may also function as active sites and facilitate the adsorption of PMS molecules onto the defective sites. This study enables insightful understanding on the intrinsic activation of superoxide by graphene toward catalytic oxidation. The findings can be beneficial to identify reaction mechanism of graphene in heterogeneous metal-free catalysis. Considering the relatively high cost of graphene compared with activated carbon and transition metal oxides (Co₃O₄, MnO₂, CuFeO₂ etc.), intensive efforts are still needed to produce cheap, efficient, and large-scale graphene-based materials for practical environmental application. However, the graphenebased catalysis completely prevents the possible metal leaching in aqueous reactions, and more importantly, provides a both structural and surface-chemistry tunable model for the fundamental study of state-of-the-art carbocatalysis.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.06.016.

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