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1 Electron Paramagnetic Resonance Investigation of
2 the Structure of Graphene Oxide: pH dependence of
3 the spectroscopic response

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1 **ABSTRACT**

2 The time dependence of the electron paramagnetic resonance (EPR) signal arising from purified
3 graphene oxide (GO) in various solvents has been investigated. The prepared GO was
4 sequentially base and acid (ba) treated to remove manganese impurities. The EPR signal of ba-
5 GO was found to be pH dependent, when exposed to different aqueous solutions, which is
6 related to the de-carboxylation process the material undergoes in solution. This process involves
7 the fragmentation of the carbonaceous framework, and occurs most rapidly in alkaline conditions.
8 Under acidic conditions, fragmentation is much slower, leading to a gradual increase in the EPR
9 signal from ba-GO in the presence of oxygen. Inferred structural changes were correlated with
10 those deduced from X-ray photoelectron spectroscopy to explain the observed pH and time-
11 dependent effects. Comparative experiments showed that the oxygen molecule was the key to the
12 increase of unpaired electron density. Exposure to superoxide anions *in situ* confirmed the
13 scavenging ability of ba-GO was related to the oxidation of the sp^2 carbon structure, which led to
14 an increase of the EPR signal. Overall, the results demonstrate changes of the structure and
15 stability of GO at different pH values.

16 **KEYWORDS:** Graphene Oxide, Electron Paramagnetic Resonance, Structure, pH dependence

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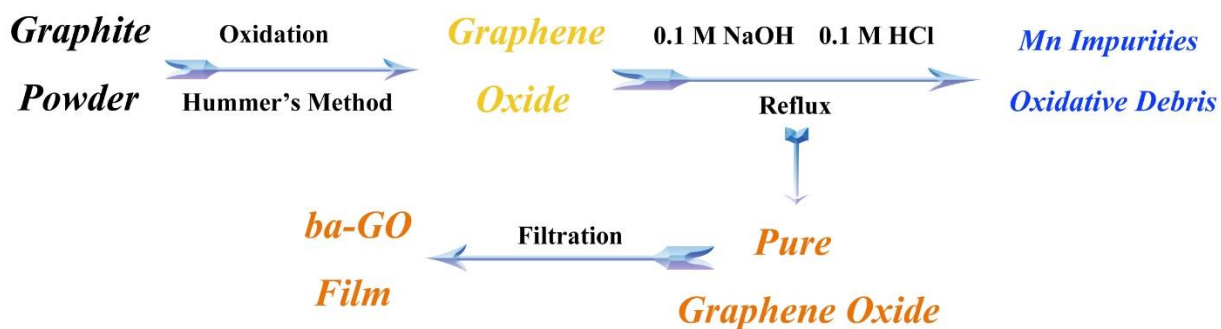
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1 Graphene oxide (GO) is a two-dimensional form of carbon with a high proportion of oxygen
2 functionalized groups on both its basal plane and edges.^{1, 2} Unlike its “parent” material,
3 graphene, the high oxygen content renders it hydrophilic and it is therefore readily dispersed in
4 aqueous solutions. These properties have led to many different applications of this material being
5 proposed. For example, GO can serve both as a supporting framework for various
6 inorganic/organic active species³⁻⁵ as well as a useful material for applications such as drug
7 delivery and for the development of biosensors.⁶⁻⁷ Moreover, GO can be easily transformed into
8 paper-like materials⁸⁻¹¹ with important applications in filtration and separation, and its oxygen
9 functional groups make its use in different fields, such as water treatment,⁸ photoluminescence¹²
10 catalysis,¹³⁻¹⁶ and optoelectronics,¹³ possible. In spite of the plethora of work on the applications
11 of this material, certain properties of GO are still quite poorly understood.¹⁷

12 Much of the structural information on GO is derived from seminal nuclear magnetic resonance
13 (NMR) studies, notably the Lerf-Klinowski model, where the oxygen functionalities of the
14 parent graphite oxide were identified.¹⁸⁻¹⁹ Electron paramagnetic resonance (EPR) spectroscopy
15 is a sensitive method to study carbon-related materials, as it can provide detailed information
16 about the characteristics of different paramagnetic species.²⁰⁻²⁴ Somewhat surprisingly, in view
17 of the importance of NMR in understanding the structure and reactivity of GO, EPR studies of
18 this material are limited. To the best of our knowledge, the first EPR study of GO was carried out
19 by Szabó *et al.*²⁵ and the origin of the spins has often been assigned to localized free radicals
20 associated with lattice defects.²⁶⁻³¹ As well as a narrow signal, Su *et al.*²³ found a broad EPR
21 signal, attributed to the π electrons on the edge states of nanographene, which are believed to
22 play an important role in the generation of superoxide anions during catalytic processes. The
23 broad signal caused by π electrons is also found in reduced GO materials.^{27, 32, 33} Interestingly,

1 Qiu *et al.*³⁴ found that graphene related materials can be used as antioxidants and are highly
2 effective as hydroxyl radical scavengers. They found that few-layer graphene is more active than
3 GO in radical scavenging, which led to the suggestion that the trapping property was linked to
4 the sp^2 -carbon network. Hou *et al.*²⁹ realized control over the radicals species in graphene oxide
5 by photo-irradiation or reduction processes.³⁵ They suggested the formation of radicals was
6 associated with homolytic bond scission of oxygen-containing functional groups.

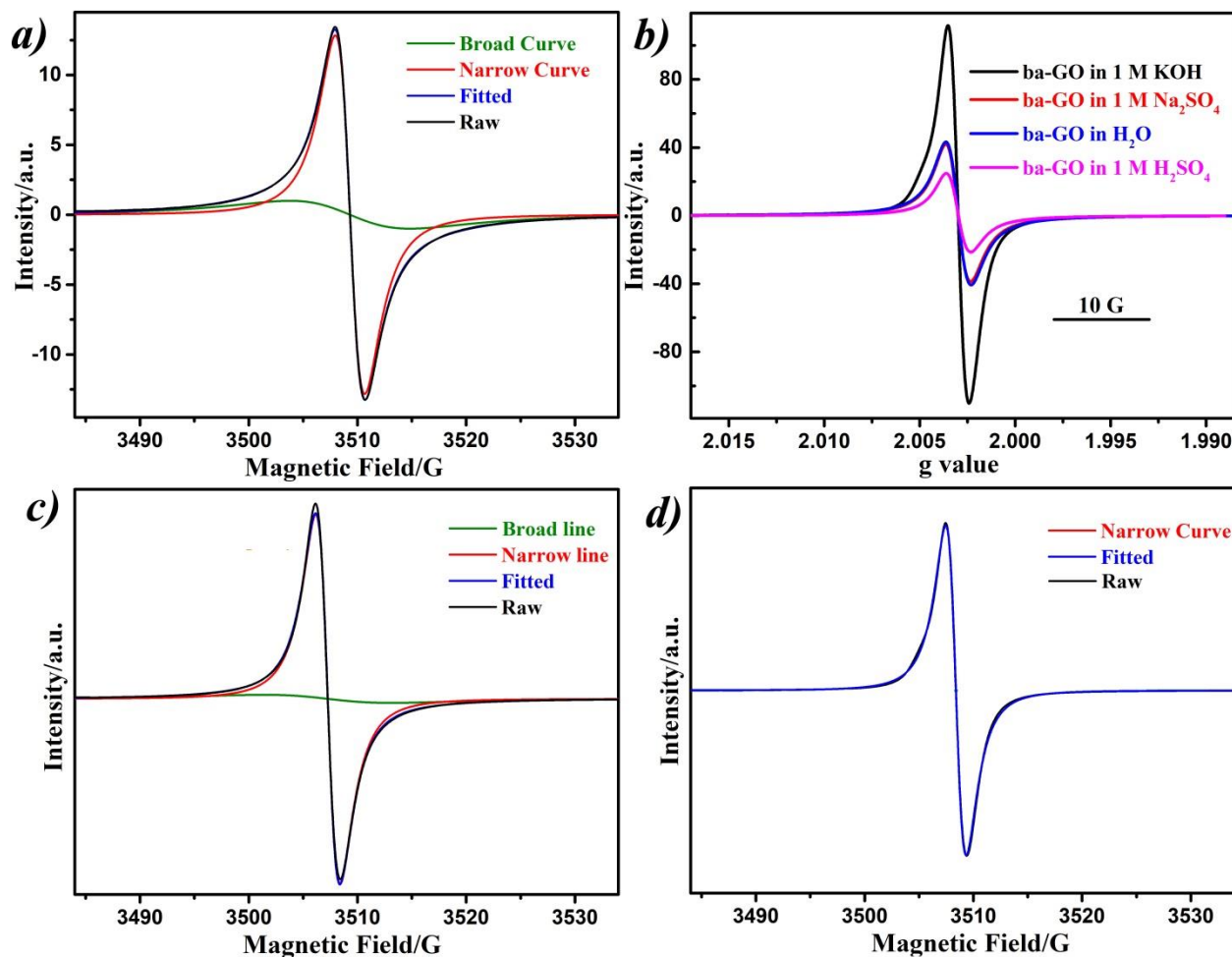
7 Herein, the time-dependent EPR behaviour of the ba-GO film has been studied in both acidic
8 and basic aqueous media. The purpose of giving GO the sequential base and acid wash was to
9 separate oxidative debris and metallic contamination (see Scheme 1 and Figure S1 in Supporting
10 Information), which could otherwise interfere with the EPR response due to their high unpaired
11 electron content, not least because of the transition metals used as oxidizing agents in the
12 preparation of GO.³⁶ In order to avoid the non-resonant microwave absorption caused by the
13 aqueous solution, the rolled ba-GO membrane was put in a capillary to monitor the EPR
14 behaviour in different solution environments. Markedly different behavior was found when ba-
15 GO was exposed to aqueous solutions of different pH. Spectral simulation and XPS analysis
16 were used to rationalize the observations. Finally, the spin trapping ability of ba-GO was found
17 to increase the spin concentration of GO.



18
19 **Scheme 1.** Preparation of ba-GO film with the base and acid wash to remove impurities.

1 **Results**

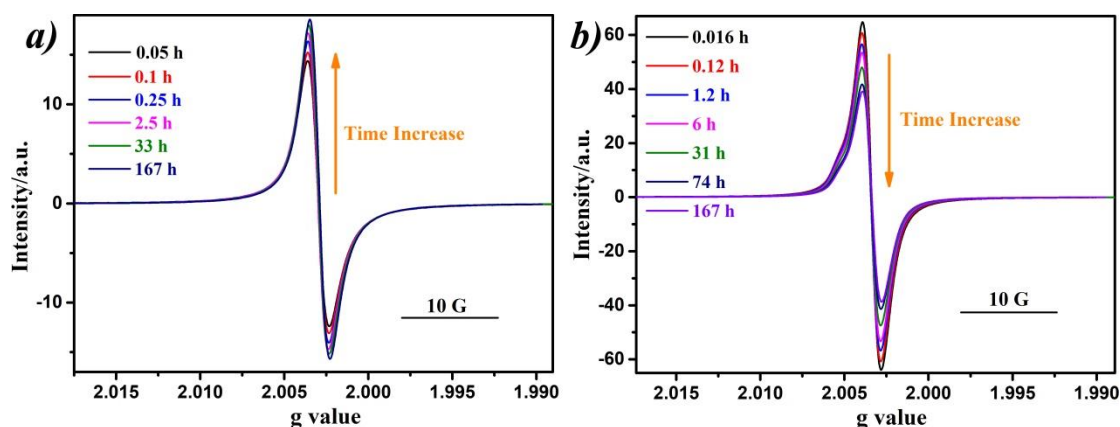
2 As shown in Figure 1a, the EPR signal of solid ba-GO can be fitted to two curves both with g
3 values around 2.0028: a narrow Lorentzian curve (linewidth of 2.7 G, 78 %) and a broader
4 Lorentzian curve (linewidth ~11 G, 22 %). The narrow signal has been widely considered to
5 come from localized sigma electrons at defects.^{23, 26-31, 37} The broad signal has been related to
6 conductive π -carriers propagating in the extended aromatic graphite like structure. The fast spin-
7 lattice relaxation through interaction with adjacent π -electron systems leads to a broader line
8 width.^{23, 32, 38, 39} The EPR signal of ba-GO film was found to be pH dependent (Figure 1b) when
9 exposed to different solutions, with the greatest signal observed at pH 14 (1 M KOH solution)
10 and the weakest signal by a factor of four found at pH 0.4 (1 M H₂SO₄ solution). This is in
11 accord with previous literature, which has demonstrated that the EPR signal from GO is
12 markedly increased after exposure to hydroxide solutions.⁴⁰ When the sample was dispersed in
13 H₂SO₄, it is notable that the broad component falls to around 9 % compared to the solid state
14 (Figure 1c), while it was absent in 1 M KOH (Figure 1d). Also, the EPR signal at 9 and 35 GHz
15 from the ba-GO films was found to be isotropic in the aqueous solvents (Figure S2).



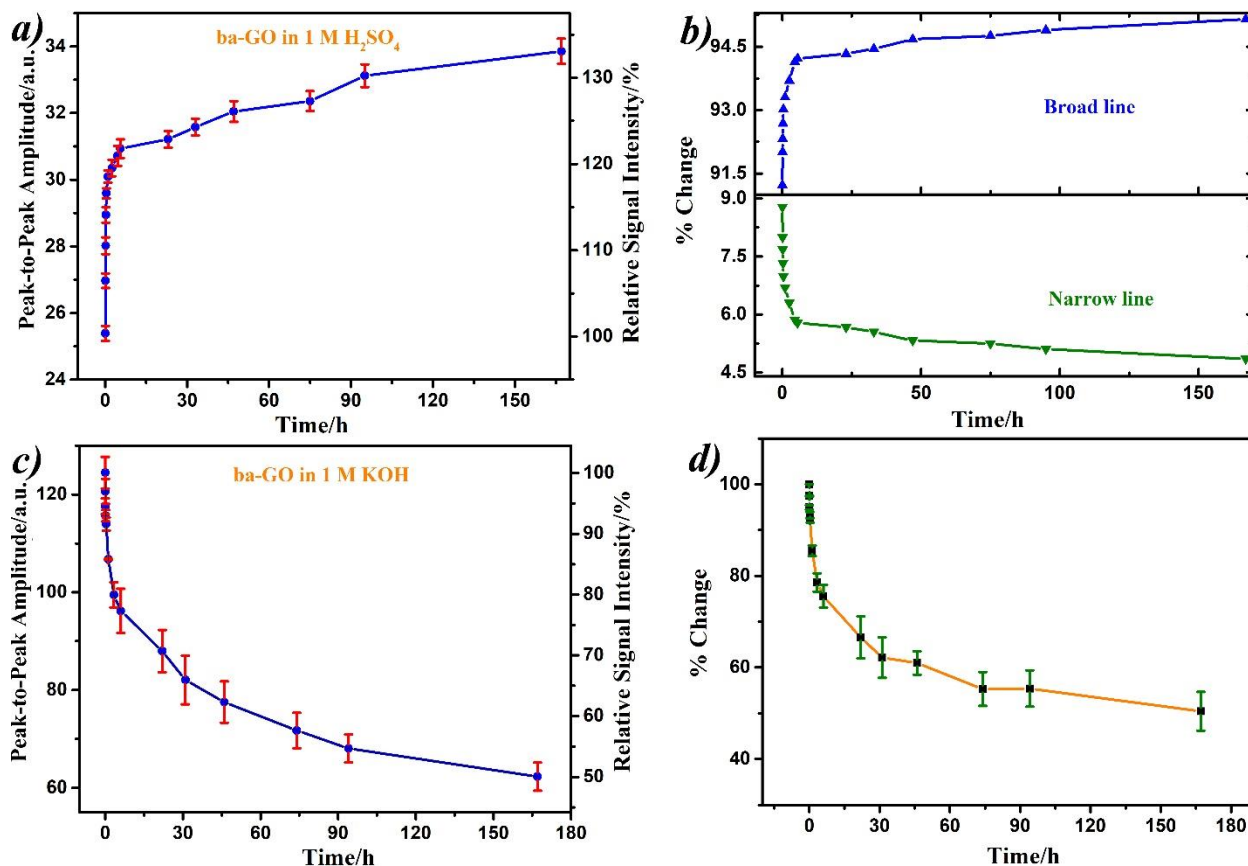
1
 2 **Figure 1.** a) EPR signal and simulation of the ba-GO film; b) EPR signal of the ba-GO film
 3 (1 mg) in different aqueous solutions; c) EPR simulation of ba-GO exposed to 1 M H₂SO₄; d)
 4 EPR simulation of ba-GO exposed to 1 M KOH.

5 Figure 2 shows the time-dependence of the EPR spectrum of the ba-GO film when exposed to
 6 1 M H₂SO₄ and 1 M KOH, respectively. All control experiments (such as the response from the
 7 aqueous solvents or PTFE alone, which are shown in Figure S3) were EPR silent. Thus, the
 8 change illustrated in Figure 2 was due to the ba-GO film itself. As with the initial signal, the EPR
 9 spectral change of ba-GO with time was dependent on the pH of the aqueous medium. The peak-
 10 to-peak amplitude changes are shown in Figure 3 and based on the first EPR signal recorded
 11 after an exposure time of 2 minutes. In 1 M H₂SO₄, the EPR signal of ba-GO increased over

1 time, as shown in Figure 3a, the signal increased by 33 % after 170 h with the fastest rate of
2 change at the beginning. During the exposure process, the proportion of broad component
3 decreased, along with the growth of the narrow component (Figure 3b). By contrast, in 1 M
4 KOH, the EPR signal intensity and double integration value of the ba-GO film decayed over
5 time: only 60 % of the spins remained after exposure for 170 h in 1 M KOH. Interestingly, there
6 was no obvious difference of the peak-to-peak width of the EPR signal when ba-GO was
7 exposed to the solutions over time, indicating the nature of the spins kept the same (as shown in
8 S4).



9
10 **Figure 2.** EPR spectrum change over time when the ba-GO film (1 mg) was exposed to 1 M
11 H₂SO₄ (a) and 1 M KOH (b).

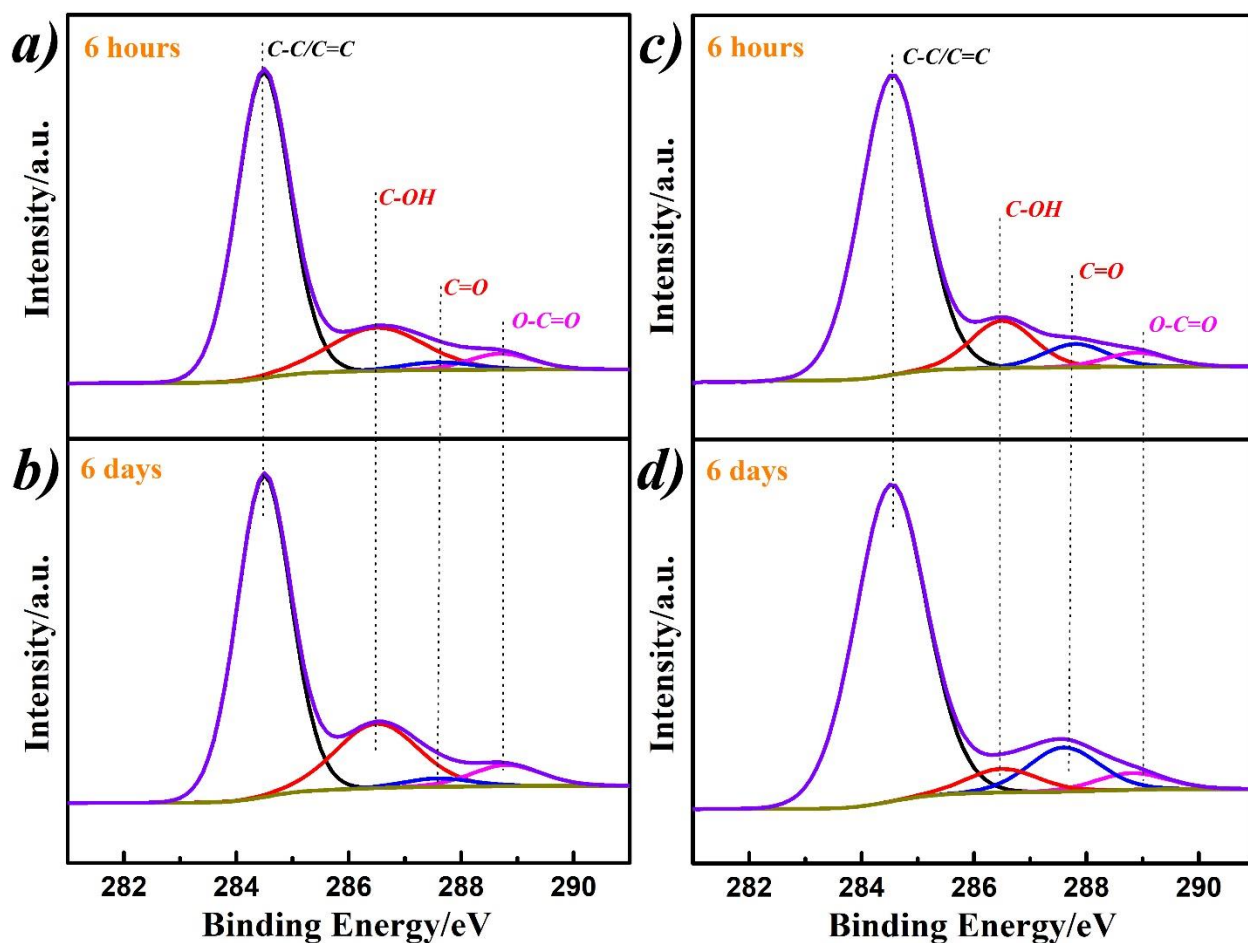


1
2 **Figure 3.** Time-dependent EPR change of ba-GO film in different aqueous solutions. (a) The
3 signal amplitude change and (b) the % change of the broad and the narrow components over time
4 in 1 M H₂SO₄; (c) the signal amplitude change and (d) and the relative percentage change of the
5 double integrated value over time of ba-GO exposed in 1 M KOH.

6 When the time-dependent experiment in 1 M H₂SO₄ was carried out under anaerobic
7 conditions, the EPR signal did not show sustained growth (Figure S5a,b). Both the narrow signal
8 and the broad component decreased over time, indicating that O₂ is responsible for the EPR
9 signal increase in 1 M H₂SO₄ under aerobic conditions.

10 Figure 4 displays the C1s XPS spectra of the ba-GO film with different exposure times in
11 aqueous solvents. C1s spectra present four carbon atom environments corresponding to different
12 functional groups: the non-oxygenated ring C, and the carbon associated with C–O bonds, the

1 carbonyl (C=O), and the carboxylate (O-C=O) groups, respectively.⁴¹⁻⁴³ The change of
2 functional groups under each of the employed conditions is given in Table 1. When exposed to 1
3 M H₂SO₄ (Figure 4a), the ba-GO *sp*² carbon component decreased over time, accompanied with
4 a slight increase in the C-OH/COOH groups. These results are consistent with an increase in
5 oxidation when the carbon material was exposed to acidic conditions.⁴⁴⁻⁴⁶ In contrast, in KOH
6 (Figure 4c,d), both the *sp*² carbon and the carbonyl component increased over time, while the
7 hydroxyl groups (C-OH) decreased over time. This observation is consistent with the mechanism
8 discussed by Tour *et al.*, who proposed that deoxygenation of GO in alkaline conditions could
9 form -C=O groups and, ultimately, decrease the oxygen content of the solid.⁴⁷ The infrared
10 spectroscopy of ba-GO after different exposure times is shown in Figure S6 and supported the
11 XPS results. A slight increase of -COOH and -OH was found in H₂SO₄ over the exposure time,
12 while the decrease of -CO⁻ and -COO⁻ was found when the exposure time in KOH was
13 increased.⁴⁸



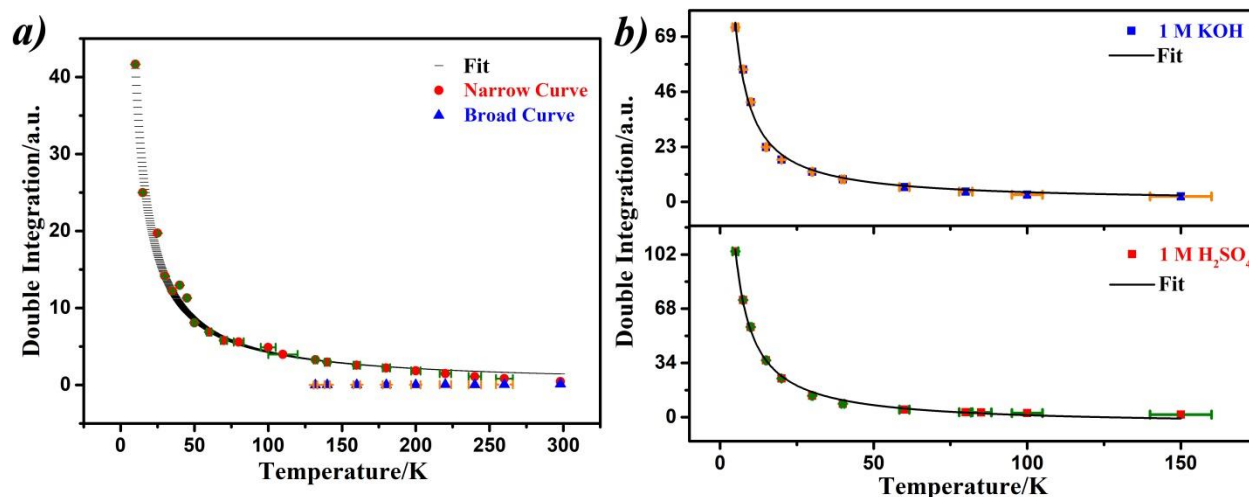
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2 **Figure 4.** Comparison of C(1s) XPS data of the ba-GO film with different exposure times. ba-
3 GO film exposed to 1 M H₂SO₄ for (a) 6 h and (b) 6 days; ba-GO film exposed to 1 M KOH for
4 (c) 6 h and (d) 6 days.

5 **Table 1.** XPS component analysis of the ba-GO film as a function of exposure time.

<i>ba-GO</i>	<i>C content</i>	<i>C=C/C-C</i>	<i>C-O</i>	<i>C=O</i>	<i>OCO</i>	
H ₂ SO ₄ (1 M)	6 h	81.6 %	71.8 %	21.6 %	2.2 %	4.4 %
	6 days	73.4 %	69.0 %	22.5 %	2.1 %	6.4 %
KOH	6 h	85.3 %	77.8 %	12.3 %	6.0 %	3.9 %

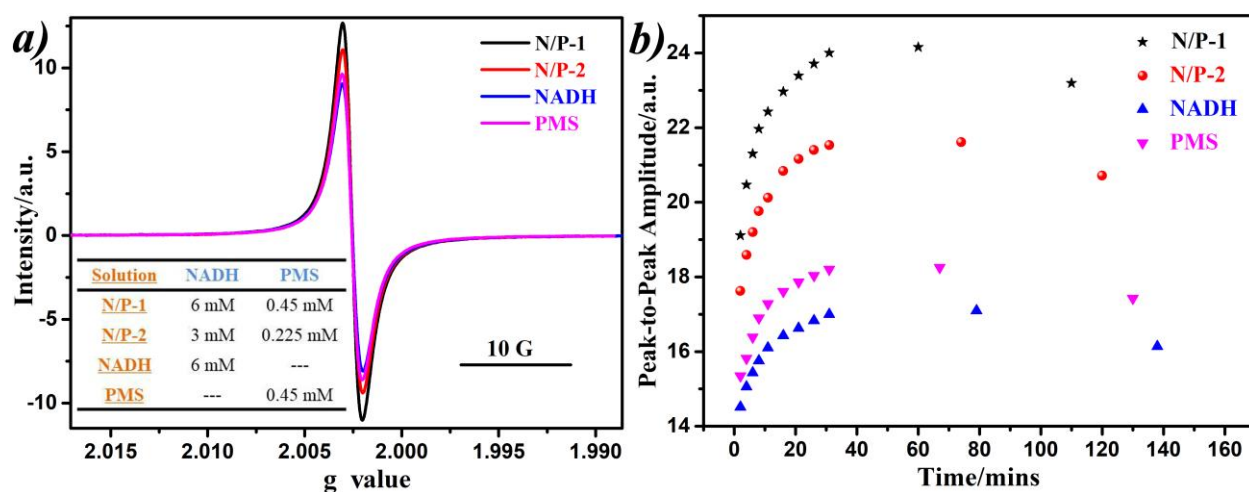
(1 M) 6 days 87.0 % 79.6 % 6.0 % 10.6 % 3.8%

1
2 In order to understand further the nature of the spin environment, the temperature dependent
3 EPR behavior of the ba-GO film with, and without, solution exposure treatment was investigated
4 (Figure 5). For ba-GO in the solid state (Figure 5a), the narrow component obeys the Curie-Weiss
5 Weiss Law, which is consistent with localized defect states such as sigma dangling spins.^{33, 49}
6 While the broad component was only found at the higher temperature range, and was
7 temperature independent (Pauli Law). This is indicative of delocalized π electrons interacting
8 within the extended π electron system. After the ba-GO film was exposed to different solutions
9 for 24 hours, the EPR signal still obeyed the Curie-Weiss Law (Figure 5b) with little variation
10 between the samples. The line width was also found to be temperature dependent (Figure S7) and
11 decreased on raising the temperature. This has been observed previously and related to a
12 narrowing mechanism associated with edge states.²⁷



13
14 **Figure 5.** Temperature dependence of (a) solid ba-GO film and (b) after 24-hour exposure to
15 different solutions. The data was fit using the Curie-Weiss law as described in the experimental
16 section.

1 The spin behaviour of the GO film was further studied through experiments in the presence of
 2 superoxide. Figure 6a shows the time dependent behaviour of ba-GO film during exposure to
 3 superoxide radicals. Superoxide was generated by using the β nicotinamide adenine dinucleotide
 4 2'-phosphate reduced tetrasodium salt hydrate (NADH) and phenazinemethosulfate (PMS)
 5 reaction system (N/P) in phosphate buffer pH 7.4 (Figure S8).^{34, 50} The narrow component of the
 6 EPR signal of ba-GO film increased on exposure to superoxide-rich solutions (Figure 6b). When
 7 the concentration of superoxide radical was increased, the maximum EPR signal of ba-GO
 8 increased (Figure 6b); indicating the scavenging of superoxide radicals by ba-GO leads to a
 9 higher density of localized sigma unpaired electrons.



10
 11 **Figure 6.** a) Comparison of the EPR signal of the ba-GO film in NADH/PMS reaction system
 12 with different concentrations; b) Time dependent EPR behavior of ba-GO film in NADH/PMS
 13 reaction system with different concentrations.

14 Discussion

15 The graphene oxide material was free from Mn residues derived from the Hummers method of
 16 preparation: in general, EPR is a useful method to detect the presence of manganese impurities.⁵¹
 17 Graphene oxide samples, without the initial base washing procedure, contained a high level of

1 Mn²⁺ impurities, which were easily detected by the EPR method (Figure S1). The EPR signal of
2 GO has been described as a narrow Lorentzian curve, derived from C centered radicals present at
3 defects.^{23, 26-31} However, in the case of the ba-GO studied here, a broader component, which is
4 related to π electrons, was also found. This should be related to the additional purification
5 process. The removal of oxygen-containing functional groups (such as hydroxyl, carboxyl,
6 Figure S9) and the recovery of the sp² structure reconstitutes more aromatic units at the edge,
7 which create favorable conditions for the existence of delocalized π electron density.²³

8 The magnetic property of graphene based materials is strongly related to edge states. Enoki *et*
9 *al.*³⁸ studied activated carbon fibers as model systems for investigating the magnetism of edge-
10 state spins and showed that magnetic properties change as a result of temperature of treatment, as
11 thermal treatment removes functional groups and creates more electron transport path networks.
12 The nature of spins changed from localized states to itinerant ones, as observed through the
13 temperature dependence of the magnetic susceptibility; Curie-Weis behavior from localized
14 edge-state spins to the less temperature dependent susceptibility of conduction electrons. Non-
15 bonding π electrons trapped by the defects such as zigzag edge states and vacancies show a Curie
16 like behavior.³⁷⁻³⁹ GO has similar structure as to nanographene, while the edge state is more
17 complicated than graphene. However, oxidation and reduction of GO coupled with EPR can
18 offer information about the sites of the paramagnetism. Szabó *et al.*²⁵ found that the EPR signal
19 of GO became weaker and even disappeared when the GO was further oxidized. They attributed
20 the EPR signal of GO to arise from mobile π electrons that are stabilized by the resonance
21 energy in the condensed aromatic structure rather than from broken bonds. Zahra *et al.*³¹ found
22 that UVA irradiation and chemical reduction with ascorbic acid produce smaller amounts of
23 radicals on reduced GO nanosheets. Erdem *et al.*²² found that chemical reduction of GO removed

1 most oxygen-containing functionalities restoring the graphene lattice and as a consequence
2 quenched the EPR signal through the reduced the local spin-state density. Residual EPR signal
3 was attributed to defect centers from zigzag edges of graphene planes.

4 We now attempt to relate the differing EPR behavior of ba-GO film in aqueous solutions of
5 varying pH to the associated structural changes. The pH dependence of signal intensity (Figure
6 1b) is interpreted as a manifestation of the de-carboxylation in different aqueous solutions. The
7 work of Dimiev *et al.*⁴⁷ indicates that exposure of GO to alkaline solutions effectively leads to a
8 disproportionation with respect to oxidized carbons, with two alcohol groups being converted
9 into half an equivalent C=C unit and a ketone group. Under more extreme (temperature/pH)
10 conditions, this process leads to a loss of carbon dioxide. GO is a relatively acidic material (pKa
11 values: 4.3 for carboxylic groups and 9.8 for phenolic OH).⁴⁸ We therefore attribute the initial
12 high unpaired electron density in KOH solution, as seen in the EPR data of Figures 1, to the
13 generation of carboxyl type radical species, formed from the fragmentation (and associated
14 oxidation) of GO at high pH. As fragmentation proceeds, however, the de-carboxylation of this
15 material removes the sources of stabilized unpaired electron density, and the EPR signal falls
16 rapidly with time (Figure 3). By contrast, under acidic conditions in the presence of oxygen,
17 although the protons can initiate the oxidative degradation of GO, the associated generation of
18 protons on decomposition slows down the cleavage of the material, meaning that simultaneous
19 generation and consumption of “edge” functional groups, which are the locus of unpaired
20 electrons, is slowed down. This means that the initial unpaired density is much lower, but slowly
21 increases, as the oxidative fragmentation of the material proceeds at a much slower rate, in
22 accord with the EPR data of Figures 1-3. The XPS data shown in Table 1 is also consistent with
23 the hypothesized increase in carboxyl functional groups, and associated decrease of hydroxyl

1 groups (see Figure 4c,d). This loss of electron-withdrawing functional groups, which are likely to
2 stabilize unpaired electron density, explains why the signal intensity falls.

3 The radical scavenging ability of ba-GO was verified by the superoxide generation experiment
4 shown in Figure 6a,b. The radical scavenging mainly reflected an increase of the narrow
5 component (Figure 6a), indicating the creation of σ type “dangling bond” spins at defects. The
6 known chemistry of superoxide suggests a mechanism associated with electron transfer or adduct
7 formation.^{34, 52, 53} The oxidation may proceed via an initial abstraction of labile hydrogen atoms
8 by the superoxide radical anion resulting in a radical and HOO^\cdot , which should be more favored
9 in polar solvent.⁵⁴ However, it is not possible to rule out acting as a nucleophile and attacking the
10 activated double bonds of the GO surface to produce a radical adduct stabilized by the
11 conjugation of the GO surface. Itkis *et al.*^{55, 56} recent XPS studies confirmed superoxide species
12 could cause carbon-to-carbonate transformation inside an electrochemical cell.

13

14 **Conclusion**

15 Graphene oxide, prepared the from Hummers’ method, was subjected to a prolonged base and
16 acid wash to remove both magnetic impurities and oxidative debris. The resulting solid, ba-GO,
17 has two EPR components, attributed to localized sigma dangling bond spins and delocalized π
18 electrons which interact with the aromatic structure inside the flake. The narrow EPR signal of
19 ba-GO was found to decrease over time in KOH and increase over time in H_2SO_4 in the presence
20 of oxygen. The radical quench in KOH was related to loss of electron-withdrawing functional
21 groups from the deoxygenation process. Under acidic conditions, this oxidative fragmentation is
22 much slower, leading to a gradual increase in the EPR signal from ba-GO in the presence of
23 oxygen. The comparison to XPS results and the anaerobic control test in H_2SO_4 confirmed the

1 increase of oxygen content. Superoxide radicals were found to cause an increase of the narrow
2 component of the EPR signal, although further experiments (e.g. involving XPS) are needed to
3 confirm the mechanism. Finally, the experiments serve as a useful guide to the stability of ba-GO
4 at different pH values for future application.

6 **MATERIALS & METHODS**

7 All chemicals were of analytical grade and were used without further purification.

8 **ba-GO.** GO was synthesized from graphite flake (~325 mesh, from Sigma-Aldrich) by the
9 modified Hummer's method.⁵⁷ First, graphite powder (5 g) was mixed with concentrated sulfuric
10 acid (115 mL) and then stirred in an ice bath for 50 mins. To keep the temperature below 10 °C,
11 25 g KMnO₄ was slowly added under continued stirring. The mixture was stirred under the ice
12 bath for a further 2.5 h, then the reaction mixture was warmed to 35 °C and the temperature kept
13 constant for 45 mins. Then, 400 mL deionized water was added and the temperature increased to
14 70 °C. After 15 mins, another 300 mL of deionized water was added. Finally, 36 g of 30 % H₂O₂
15 was added to remove excess KMnO₄. The mixture was centrifuged and washed with 5 % HCl
16 and deionized water several times, and further dialysed for more than one month to remove
17 impurities. Physical washing such as filtration and dialysis cannot remove manganese impurities
18 completely.^{21, 22, 50} The as-produced GO was further treated with the base and the acid solution,
19 previously reported in the literature to remove residual manganese ions.^{23, 36} Specifically, GO (1
20 mg/mL) was refluxed at 100 °C in 0.1 M NaOH (aq.) for 1 h, then the treated GO was separated
21 by filtration. The product obtained was dissolved in 0.1 M HCl (aq.) followed by reflux at 100 °C
22 for 1h. The final product, ba-GO, was filtered and washed with H₂O. This base-acid treatment of
23 GO removes manganese impurities/oxidative debris derived from the initial Hummers'

1 oxidation. The EPR signal of the Mn^{2+} in the initially prepared GO could be detected easily
2 (Figure SI-1), whereas after the base-acid wash, no Mn^{2+} signal was found in the EPR signal.
3 Moreover, an inductively coupled plasma mass spectrometry analysis of the sample failed to
4 detect Mn impurities (the manufacturer quoted a detection limit of Mn is $0.07 \mu\text{g/L}$).⁵⁸

5 ***ba-GO Films.*** ba-GO film was prepared by filtration. The ba-GO powder was dispersed in water
6 and sonicated for 2 hours to yield a suspension. Polytetrafluoroethylene (PTFE) membranes (25
7 mm diameter hydrophilic PTFE membrane filter with a $0.1 \mu\text{m}$ pore size and thickness of 140
8 μm , purchased from Merck Millipore) were used as the support to make the film, as they are
9 flexible enough to roll into a columnar-like shape.

10 ***Characterization methods.*** X-ray photoelectron spectroscopy (XPS) measurements were
11 performed on an ESCALAB 250Xi spectrometer (ThermoFisher-VG Scientific) using a
12 monochromated Al Ka X-ray source (1486.6 eV). Transmission electron microscopy (TEM)
13 measurements were carried out using Thermo Scientific (FEI) Talos F200X instrument. The
14 average flake size of GO sheets was $1\text{-}5 \mu\text{m}^2$.

15 ***Time-dependent EPR behaviour.*** The EPR signal arising from the ba-GO film in aqueous
16 solutions was recorded in continuous-wave (CW) at 9 GHz (X-band) using a Bruker Micro
17 spectrometer. The ba-GO film (*ca.* 1 mg) was rolled into a cylindrical shape and then plugged
18 into a capillary (1 mm) filled with aqueous solution. Triplicate samples were made. All EPR
19 experiments were carried out at room temperature with a modulation amplitude of 1 G ,
20 microwave power of 2 mW , and the spectra reported herein were typically the average of 20
21 scans. Q band (35 GHz) EPR experiments were carried using a Bruker EMX spectrometer at
22 room temperature. DPPH radical was used as a magnetic field standard. All EPR experiments
23 were measured under unsaturated conditions as shown in Figure SI-10.

1 The experiments to study the influence of oxygen in acidic solution was carried out as follows:
2 The solution was bubbled with Argon gas for more than 1 hour, and then the film was left under
3 vacuum (relative vacuum: -30 kPa) for 24 hours. The sample was placed into a capillary inside a
4 glove box, and then the capillary was sealed with glue.

5 The formula of the Lorentzian absorption lineshape used to simulate the spectra was:

$$6 \quad f_L(x) = \frac{2}{\pi\sqrt{3}} \frac{1}{\Gamma} \left[1 + \frac{4}{3} \left(\frac{x - x_0}{\Gamma} \right)^2 \right]^{-1}$$

7 where x_0 is the center, Γ is related to the FWHM (full width at half height): $\text{FWHM} = \Gamma/\sqrt{3}$.

8 The temperature dependent data (Figure 5) was fitted by using the Curie-Weiss law:

9 $X_{EPR} = C/(T-T_0)$. X_{EPR} stands for the spin susceptibility, and here we use the double integration
10 value of the EPR signal; C is the Curie constant; T is the measured temperature and T_0 is the
11 Curie-Weiss temperature ($T_0 = -6.97$ K).

12 ***Superoxide radical capture experiment.*** The generation of superoxide anions used an
13 NADH/PMS solution.^{34, 49} Typically, NADH and PMS were both dissolved in phosphate
14 buffered saline (PBS) (pH 7.4). The operation and the testing conditions were the same as
15 described above. The amount of superoxide anions was adjusted by changing the concentration
16 of the NADH/PMS solution. The generation mechanism of superoxide radical production is
17 shown in Figure S7.

18

19 **Associated Content**

20 **Supporting Information.**

21 EPR detection of Mn impurities; Multifrequency EPR measurements; EPR background
22 measurements; EPR spectral change over time and temperature in acidic and alkaline aqueous;

1 Mechanism of superoxide generation; Comparison of C 1s XPS of GO and ba-GO. This is
2 available free of charge on the ACS publications website at... .

3 **Acknowledgement**

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7 from Mr. Adam Brookfield and the useful mechanism discussion with Jiangan Li.

8 **Competing Interests**

9 The authors declare no competing interests.

10

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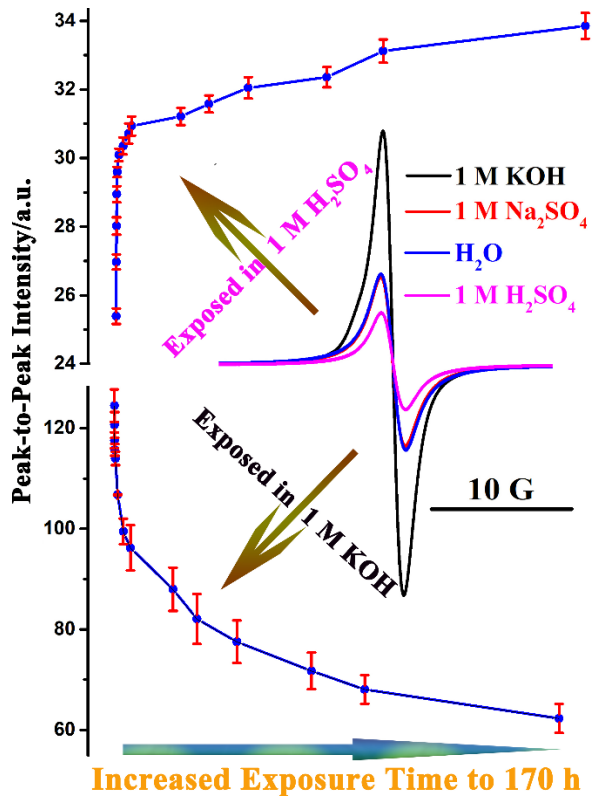
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