

## Understanding the reaction mechanism of the reactivity of free radicals with graphene oxide



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### ABSTRACT

On pulse irradiation of an aqueous solution containing graphene oxide (GO), hydrated electrons ( $e_{aq}^-$ ) are captured by GO in microsecond time scales as suggested recently (ref. 26). We have observed low reactivity of  $e_{aq}^-$  towards GO as compared to the reported value. It is shown here that the effect of pH (6.8 - 9.2) on the reactivity of  $e_{aq}^-$  with GO is not significant. The effect of solvent on the reactivity of GO towards free radical was also studied. No significant change in the decay kinetics of  $MV^{+•}$  radical in the presence of GO was observed under our experimental conditions. Quenching of  $e_{aq}^-$  or solvated electron ( $e_{sol}^-$ ) in aqueous solution and ethanol, respectively, by GO is confirmed by decrease in the yield of  $MV^{+•}$  radical in its presence. In ethanol suspension, the decrease in the rate of formation of  $MV^{+•}$  was also observed. It appears that ethanol radicals also transfer electron to  $MV^{2+}$  and GO. Further, to substantiate the formation mechanism of reduced graphene oxide by phenols and amino acids, the pulse radiolysis experiments were carried out and it was observed that phenoxy radicals as well as tryptophan radicals do not react with GO.

### Introduction

In recent years 2D carbon materials, such as graphene oxide (GO) and reduced graphene oxide (RGO) have gained lot of importance because of their potential in various applications [1–4]. Apart from the interest generated in GO and RGO, its composites with metal nanoparticles (NPs) have also drawn much more attention due to their lightweight mass, large surface area (theoretical value up to  $2600 \text{ m}^2 \text{ g}^{-1}$ ) and high electron mobility ( $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) [5–10]. Further, the graphene based nanomaterials have also attracted much attention for bio-applications.

It is known that during oxidation process, GO suffers with poor conductivity due to low quality of  $sp^2$  carbon framework and the presence of oxygen containing groups on its backbone such as  $-\text{COOH}$ ,  $-\text{OH}$ ,  $\text{C}=\text{O}$ , etc. [11] It has been reported that the conductivity of GO can be restored by its reduction. Chemical reduction of GO using various reductants such as hydrazine,  $\text{NaBH}_4$ , etc., have been mentioned in many reports [11–13]. As most of the chemicals used are harsh and toxic, hence, chemists have initiated to explore bio-compatible reductants for the reduction of GO. Many natural reductants such as melatonin, vitamin-C, bovine serum albumin, tannin tea polyphenol, etc., have been explored [15–22]. In this context, radiolytic and photolytic reduction methods have also been explored as no external reducing agent needs to be added [23–27]. As the reduction process/

methods employed were carried out in solvents, it is imperative to determine the reactivity of electron and solvent radicals, if any, towards GO. It is known that on GO surface various groups such as carboxyl, epoxides, etc. exist which have a tendency to react with electron. As electron transfer processes occurs at fast time scales hence, there exists a possibility of quenching of electron by such groups. Thus, it is necessary to determine the concentration of GO at which quenching of electron occurs if GO has to be used as support material for electron transfer reactions. Very recently to shed some light on electron transfer reactions, reactivity of hydrated electron towards GO was shown using laser and pulse radiolysis techniques [25–27]. None of the above studies have mentioned about the pH of the solution. Recent attempts have shown that GO and RGO can form stable aqueous colloids through electrostatic repulsion as they contain ionisable groups with a single  $pK_a$  value at 4.3 and 8.0, respectively [14]. To the best of our knowledge, only a few studies are reported about detailed mechanistic and kinetic aspects of reduction of GO [23,26,27].

As mentioned above reduction of GO by bio-compounds is also being explored [15–22]. Mostly reduction of GO by phenols is reported at high temperature without any reference to the pH of the solution. The formation scheme proposed for the formation of RGO is via one-electron transfer process without any detailed kinetic evidence to authenticate the proposed mechanism. In addition, the effect of increasing amount of GO on primary and secondary radicals in solution remained

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elusive. We have made an attempt to answer the above questions using pulse radiolysis kinetic spectrophotometric technique. The reduction dynamics, if any, is probed by monitoring transient absorption kinetics.

In this report, to understand the ability of GO to accept electrons from other radicals, reduction of  $MV^{2+}$  was studied in presence of different concentrations of GO using pulse radiolysis studies. The work was carried out in aqueous as well as in ethanol medium. Interestingly, the results found were very different in both the medium. This provides an insight into the effect of solvent on the reactivity of electron/free radicals with GO. In ethanol medium, decrease in the formation rate of  $MV^{2+}$  in the presence of GO as compared to neat water was observed. This could be due to the reaction of radicals generated from ethanol radiolysis with  $MV^{2+}$ . From this, it also appears that ethanol radical reaction rate with GO is low. Further, the work was extended to study the reduction mechanism of GO using bio compounds at fast time scales.

## Experimental section

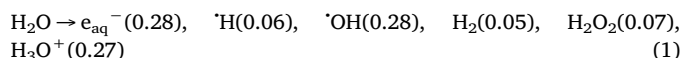
### Materials and methods

Natural flake graphite (Loba Chem. Pvt. Ltd.),  $NaNO_3$  (Ranbaxy Fine Chem. Ltd.),  $KMnO_4$  (Merck), 1'-dimethyl-4,4'-bipyridinium dichloride (methyl viologen,  $MV^{2+}(2Cl^-)$ ; (Sigma-Aldrich), tert-butanol (Sisco, India),  $AgClO_4$  (Fluka), tryptophan (Fluka), hydroquinone (Aldrich), catechol (Fluka), KSCN (BDH, India) and spectrograde ethanol (Spectrochem, India) were used as received. All other reagents were of analytical grade and used without further purification. All solutions were freshly prepared in water purified using Millipore (Milli-Q) system having resistivity of 18.2 M $\Omega$  cm. The total sample volume was 4.0 mL. Solutions were sparged with high purity IOLAR grade nitrogen gas (purity  $\geq 99.99\%$ ) for 5 min prior to pulse irradiation. All stock solutions were prepared just before the experiments, wrapped with aluminium foil and kept in dark to avoid any photochemical reactions. Phosphate or borate buffers were used and the pH of the solutions was kept either 6.8 or 9.2. Graphene oxide was synthesized from natural flake graphite by Hummers method [28] as reported earlier [29]. The stock dispersions of GO were prepared in Millipore water or ethanol by agitating (0.17 g/l) in ultrasonic bath for 10 min.

Pulse radiolysis experiments were performed using a 7 MeV linear electron accelerator as described elsewhere [30]. Electron pulses of 50 ns (400 mA current) were used to generate free radicals by irradiating aqueous or ethanol solutions. Pulse radiolysis measurements were performed using a 450 W Xe lamp that produced the analyzing light. To minimize photo-effects, a cut off filter to cut all the wavelengths below 350 nm was positioned between the lamp and the cuvette. Measurements were done in 1 cm x 1 cm suprasil quartz cuvette kept at a distance of approximately 12 cm from the electron beam window, where, the beam diameter was approximately 1 cm. The dose was determined using the thiocyanate dosimeter [31]. An aerated  $10^{-2}$  M KSCN solution was used for dosimetry, and the  $(SCN)_2^{\cdot-}$  radical was monitored at 475 nm. The absorbed dose per pulse was calculated [32] assuming  $G_e [(SCN)_2^{\cdot-}] = 2.6 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$  at 475 nm. In general, the absorbed doses per pulse were of the order of 14–16 Gy (1 Gy = 1 J kg $^{-1}$ , for aqueous solution 1 Gy corresponds to 1 J L $^{-1}$ ) [33]. All experiments were carried out at room temperature. The Raman spectrum was recorded using 633 nm excitation from the He-Ne laser. The laser power used to record the Raman spectrum was 50 mW. The spot size on the sample was  $\sim 0.5$  mm. The Raman scattered light from the sample on the glass slide was collected at 180 $^\circ$  scattering geometry with a 50X LWD (long working distance) objective by keeping the glass slide under the Raman microscope. The scattered light was detected using a CCD (Synapse, Horiba Jobin Yvon) based monochromator (LabRAM HR800, Horiba Jobin Yvon, France).

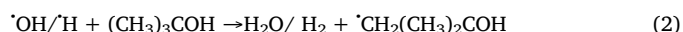
## Results and discussion

The radiolysis of water produces free radicals according to the stoichiometry [31,32] shown in reaction (1)

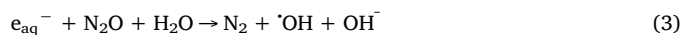


where, the numbers in parentheses represent the radiolytic yields, G-values, the quantity of radicals formed per Joule of energy deposited at pH 7 in  $\mu\text{mol J}^{-1}$ . Total radical concentrations in this study were  $\sim 4 \mu\text{M}$  per pulse.

The hydrated electrons and hydrogen atoms so formed are strong reducing agents while  $\cdot OH$  radicals are oxidizing in nature [31,32]. Depending on the experimental conditions, one can get exclusively either reducing or oxidizing conditions by purging the solution either with  $N_2$  or  $N_2O$  gas, respectively. In general, alcohols are added to the  $N_2$ -bubbled media to scavenge  $\cdot OH$  radicals and  $\cdot H$  atoms to get the reducing conditions. In the present study to obtain reducing conditions, tert-butanol was used in aqueous solution to scavenge  $\cdot OH$  radicals and  $\cdot H$  atoms. The tert-butanol radical so produced is inert (reaction 2) and reduction proceeds via  $e_{aq}^-$  reaction.



The reactions of  $\cdot OH$  radicals were studied by purging with  $N_2O$ , which quantitatively converts the hydrated electron,  $e_{aq}^-$  to  $\cdot OH$  radical



For studying reactions with secondary radicals,  $(SCN)_2^{\cdot-}$  radical was generated (reactions 4 and 5)



### Quenching of electrons by GO in aqueous and ethanol solutions

It is known that  $e_{aq}^-$  shows absorption maximum at  $\sim 700$  nm. The reactivity of  $e_{aq}^-$  towards GO was studied by monitoring the decay kinetics of  $e_{aq}^-$  at 700 nm in the absence and presence of GO at pH 6.8. Fig. 1 shows the decay profiles of  $e_{aq}^-$  in the absence and presence of different concentrations of GO. It can be noticed that with the increase in concentration of GO, the decay rate of  $e_{aq}^-$  also increased. The

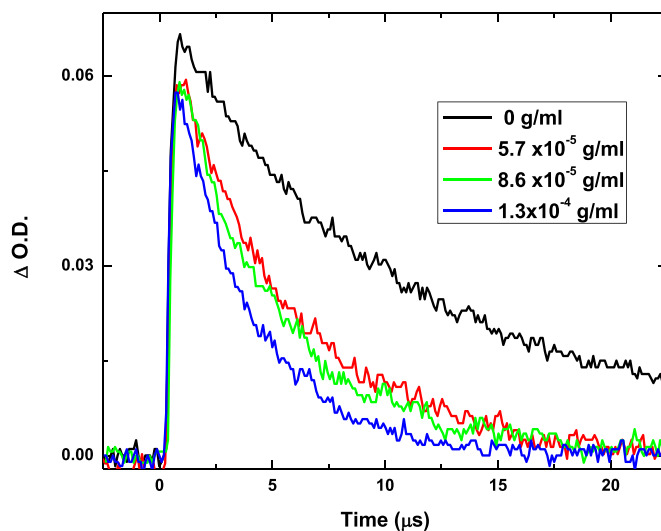


Fig. 1. Decay profiles of  $e_{aq}^-$  in the absence and presence of different concentrations of GO at 700 nm.

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