pH Dependent Ultrafast Charge Dynamics in Graphene Oxide Dispersions

Georgia Kime^{1,2}

Rahul Raveendran-Nair², Kai-Ge Zhou², Daria Andreeva³, Samantha Hardman⁴, Kostya Novoselov² and David Binks^{1,2}

¹Photon Science Institute, University of Manchester, M13 9PL, UK ²School of Physics and Astronomy, University of Manchester, M13 9PL, UK

³Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, 117546, Singapore

⁴Manchester Institute of Biotechnology, University of Manchester, M13 9PL, UK

david.binks@manchester.ac.uk

The photoluminescence (PL) of graphene oxide (GO) dispersions can be tuned from blue-green to near-infrared by altering their pH, making GO of interest for applications such as in-vivo pH monitoring^[1]. It has been suggested that this effect is due to excited state protonation of functional groups, such as COO⁻, on the GO surface^[2] but so far this effect has only been studied in steady state.

We observe pH-dependent changes in the ultrafast charge dynamics of aqueous GO dispersions using transient PL & ultrafast transient absorption measurements.

Figure 1 shows the steady-state PL spectrum over a range of pH values; the centre of the broad emission band is at ~700 nm for pH < 9.3 but shifts to ~520 nm for pH > 9.3. The corresponding PL transients (see inset of Fig 1) show that the lifetime of the emitting species also increases significantly for pH > 9.3. These results indicate that different species emit above and below a pH of 9.3, consistent with an excited state protonation process that is prevented by highly alkaline conditions. The ultrafast absorption change transients, as seen in Figure 2, show that the final excited state takes ~1 ps longer to form for pH < 9.3, consistent with an additional protonation step.

The results of this study are thus consistent with excited state protonation in GO dispersions for pH < 9.3, and the time-scale of this protonation process is found to be ~1 ps.

References

Figures

- [1] Wang, Y., Li, Z., Wang, J., Li, J. & Lin, Y. Trends Biotechnol. 29 (2011) 205–212
- [2] Galande, C. et al. Sci. Rep. 1:85 (2011) 1-5



Figure 1: pH-dependent photoluminescence spectra of an aqueous GO dispersion for excitation at a wavelength of 400 nm. Inset: pHdependent PL decay transients for excitation at 400 nm and detection at 580 nm



