

Supporting Information for

**The impact of functionalization on the stability,  
work function and photoluminescence of reduced  
graphene oxide**

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**1 Kinetics and structural transformations during thermal  
annealing of GO**

One of the important considerations during realistic rGO structure generation is the inclusion of both kinetic and thermodynamic effects. In our simulations, we assumed a random spatial distribution of epoxies and hydroxyls in the initial GO structures, thereby accounting for kinetic effects. A similar methodology has been followed previously [1]. Thermal annealing of the GO structures using molecular dynamics (MD) allows for thermodynamically-driven structural evolution of GO into rGO. Thus, we expect to get a mixture of kinetic and thermodynamic effects, desirable from an experimental viewpoint. In order to confirm rGO structures generated from MD simulations are physically meaningful, we compared the final morphologies and final oxygen content with previous simulations [2]. We obtain

sufficiently disordered structures with a number of newly-formed defects, consistent with previous simulations.

Our MD simulations also revealed the evolution of  $O_2$  and desorption of hydroxyls via formation of  $H_2O$  molecules. With the release of CO and  $CO_2$  from the basal plane, we observed an increase in carbon vacancies with oxygen content (up to  $\sim 3.5\text{-}5\%$  for GO with 25% oxygen). The reduction efficiency is found to be larger for hydroxyl-rich GO sheets (as reported in Table 1). Although desorption of hydroxyls by the release of  $H_2O$  is easier and happens at a lower temperature [2], this process does not necessarily translate into higher reduction efficiency of hydroxyl-rich GO sheets, since the  $H_2O$  release mechanism requires the presence of two hydroxyl molecules in close proximity. Instead, we explain this observation based on our MD simulations that indicate higher amounts of CO and  $CO_2$  release from the basal plane of epoxy-rich GO structures (0.01-5% for epoxy-rich as compared to 0-3.5% for hydroxyl-rich GO starting from 14.3-25% oxygen). Since carbon is removed from the graphene plane in this reaction, the final atomic concentration of oxygen in the resulting carbonyl-rich rGO structures is observed to be higher than those observed from the reduction of hydroxyl-rich GO. This insight leads to an important implication with respect to the amount of disorder introduced in the rGO sheets that translates into poor sheet properties. Clearly, with higher number of carbon vacancies, rGO structures obtained from epoxy-rich GO have greater disorder and reconstructions along the periphery of the holes, which in turn can significantly alter the optical and electronic properties.

One of the reasons for the thermodynamic stability of hydroxyl-rich rGO can be attributed to the fact that isolated hydroxyl groups are far more favorable than isolated carbonyl and epoxy groups. Our calculations predict that an isolated hydroxyl pair is more stable than an isolated epoxy pair by 60 meV/atom and an isolated carbonyl pair by 55 meV/atom at 1.5% oxygen. At 20% oxygen, the relative stability of a hydroxyl pair

**Table 1:** Reduction efficiency table for GO structures. The final O% is reported with an error of less than 0.2% in all cases.

Initial O% in GO	epoxy:hydroxyl	Final O% in rGO
15.0	3:2	11.4
20.0	3:2	16.1
25.0	3:2	20.0
15.0	2:3	10.4
20.0	2:3	15.1
25.0	2:3	18.2

increases to 270 meV/atom when compared to an epoxy pair and 236 meV/atom when compared to a carbonyl pair. Stability is further derived from hydrogen bonding. From our structures, we estimate the proportion of hydrogen bonds in hydroxyl-rich structures to exceed that of carbonyl-rich structures by a factor of 1.3 to 1.75 within the range of 10-20% oxygen.

## References

- [1] J. T. Paci, T. Belytschko, and G. C. Schatz, “Computational studies of the structure, behavior upon heating, and mechanical properties of graphite oxide,” *Journal of Physical Chemistry B*, vol. 111, no. 49, pp. 18099–18111, 2007.
- [2] A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla, and V. B. Shenoy, “Structural evolution during the reduction of chemically derived graphene oxide.,” *Nature chemistry*, vol. 2, no. 7, pp. 581–587, 2010.
- [3] C.-T. Chien, S.-S. Li, W.-J. Lai, Y.-C. Yeh, H.-A. Chen, I.-S. Chen, L.-C. Chen, K.-H. Chen, T. Nemoto, S. Isoda, and et al., “Tunable photoluminescence from graphene oxide.,” *Angewandte Chemie International Edition*, pp. 1–6, 2012.

- [4] P. Johari and V. B. Shenoy, “Modulating optical properties of graphene oxide: role of prominent functional groups,” *ACS nano*, vol. 5, no. 9, pp. 7640–7, 2011.