

Supplementary Material

Reduction of free-standing graphene oxide papers by a hydrothermal process at the solid/gas interface

Hong Chen^{1,3}, Zhanyu Song^{1,3}, Xiaochong Zhao², Xin Li^{1,3}, Hong Lin²

1. MEMS Center, Pen-Tung Sah Institute of Micro-Nano Science and Technology, Xiamen University, Xiamen 361005, China
2. State Key Laboratory of New Ceramics and Fine Structure, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
3. Department of Mechanical and Electrical Engineering, Xiamen University, 361005 Xiamen, China

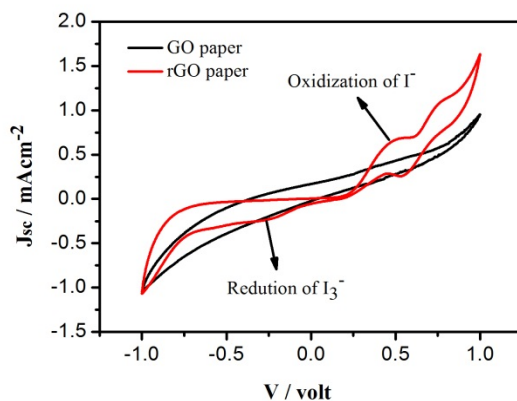


Figure s1. CV curves for GO paper and rGO paper reduced at 220°C. A conventional three-electrode system connected to a CHI 660D electrochemical station (Chenhua Corp., Shanghai, China) was applied to evaluate the electrocatalytic performance of the optimized rGO paper. Electrolyte contained 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄. A calomel electrode was used as reference electrode.

In our study, electro-catalytic performance of rGO papers was also examined. A most popular application of graphene materials is being used in dye-sensitized solar cells for the reduction of iodide.^[1] Hence, the measurement of the GO and rGO papers was conducted in an iodine/tri-iodide solution to simulate the working condition of dye-sensitized solar cell. The rGO paper or GO paper was attached to a FTO substrate to act as an electrode. Pt foil and a calomel electrode were used as working electrode and reference electrode, respectively. Figure s2 showed a C-V curve of typical rGO paper (M 2.0) in a redox solution, and a C-V curve of GO paper was also presented for comparison. The GO-containing electrode exhibited a capacitor behavior which means it has no electrocatalytic properties. The rGO-containing electrode showed good

electrocatalytic property. The peaks in fig. s1 represents the oxidization of I^- and reduction of I_3^- , respectively, which is meaningful for dye-sensitized solar cells. [1]

In our study, although the rGO papers were effectively reduced, the I_D/I_G showed an increased tendency. Such increase may due to an increasing graphene domain which is inversely proportional to the average crystallite size of graphene. The average crystallite sizes of rGO papers reduced with different molar concentration of ammonia in the autoclaves were obtained from x-ray data. Compared figure 6 with figure s3, it can be seen that the change of I_D/I_G is in inverse proportion to that of crystallite sizes. That means the change of grain size resulted in the change of I_D/I_G in figure 6. [2]

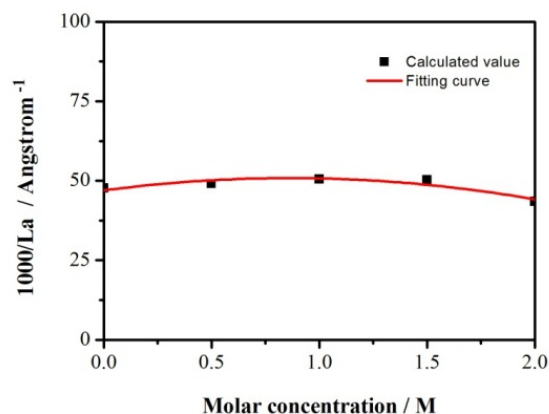


Figure s2. X-ray data of crystallite size versus molar concentration of ammonia in the interface reduction system. The crystallite sizes were obtained by MDI Jade 6.0 (Materials Data, Inc. USA). The fitting residual were kept below 6%.

The elemental analysis results in figure s3, showing that the C/O atom ratios from GO to the rGO papers, are also consistent with the FT-IR results. It proved that our method can effectively reduce the GO papers.

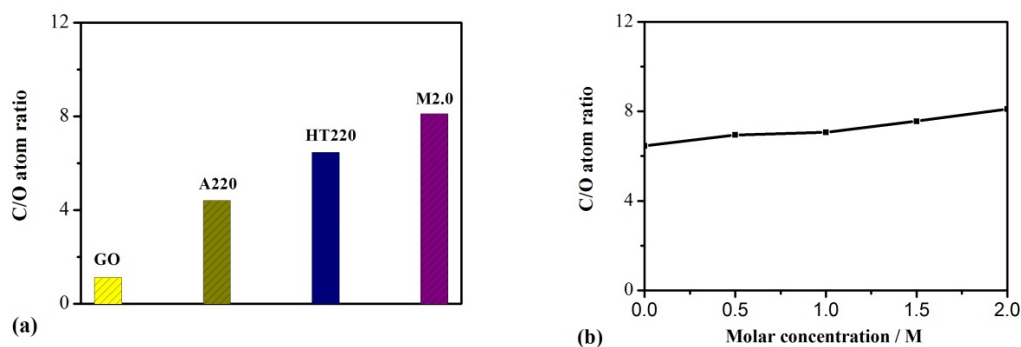


Figure s3. C/O atom ratio of GO and rGO papers reduced under different conditions: a)

annealing under dry air (A220), pure-water hydrothermal reduction (HT220) and ammonia-containing hydrothermal reduction (M 2.0); b) hydrothermal reduction with varied ammonia concentrations by elemental analysis. The elemental analysis was measured on an elemental analyser (CE440, Exeter analytical, Inc., USA).

References

- [1] Veerappan G, Bojan K, Rhee S. Amorphous carbon as a flexible counter electrode for low cost and efficient dye sensitized solar cell. *Renewable Energ* 2012; 41: 383-388.
- [2] Tuinstra F, Koenig JL. Raman spectrum of graphite. *J Chem Phys* 1970; 53: 1126-30.