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Electronic Supplementary Information

Flawed MoO_2 on Graphene Template Transformed from MoO_3 towards Hydrogen Evolution Reaction

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Experimental section

Preparation of MoO_3 belts: MoO_3 belts were prepared by a previously reported method.[1] Briefly, 4.839 g $NaMoO_4 \cdot 2H_2O$ was dissolved in 10 ml deionized water under sonication, the as-prepared solution was added to 16 ml perchloric acid (4 M) by a speed of 20 s per drop. The mixed solution was added into Teflon autoclave (45 ml) and reacted at 180 ℃ for 12 h. The obtained products were washed with ample water and dried in vacuum oven at 60 ℃.

Preparation of MoO_3/rGO and MoO_2/rGO composite: Graphene oxide (GO) was prepared according to the Hummer's method.[2,3] GO was further reduced by $NaBH_4$-hydrazine to obtain reduced graphene oxide (rGO). Briefly, 100 mg GO was dispersed in 100 ml deionized water by sonication for 20 min, and 600 mg $NaBH_4$ was added and reacted at 80 ℃ for 1 h. After filtering and washing the excess reductant, the mixture was re-dispersed in water and sonicated for 20 min, then 1 ml hydrazine was added and reacted at 100 ℃ (reflux) for 24 h. After filtering and washing with ample water, the mixture was dried in vacuum oven at 30 ℃ for 12 h to obtain rGO.

40 mg of the as-prepared rGO was dispersed in 80 ml water, then 800 μL 0.1 wt% Poly(diallyldimethylammonium chloride) (PDDA) was added and sonicated for 2 h. After that, 80 ml MoO_3 solution (0.5 mg/ml, dispersed in ethanol) was added and stirred for 2h, afterwards, the mixture was filtered and dried to obtain MoO_3/rGO composite, Fig. S1 shows the TEM image of MoO_3/rGO.

10 mg MoO_3/rGO was evenly dispersed on porcelain boat, then the boat was put in tube furnace. After ventilation of H_2/Ar flow for 15 min in advance, the tube was heated to 450 ℃

with a heating rate of 10 ℃ per min and kept for 30 min, finally, reduced molybdenum oxide/rGO hybrid was obtained.

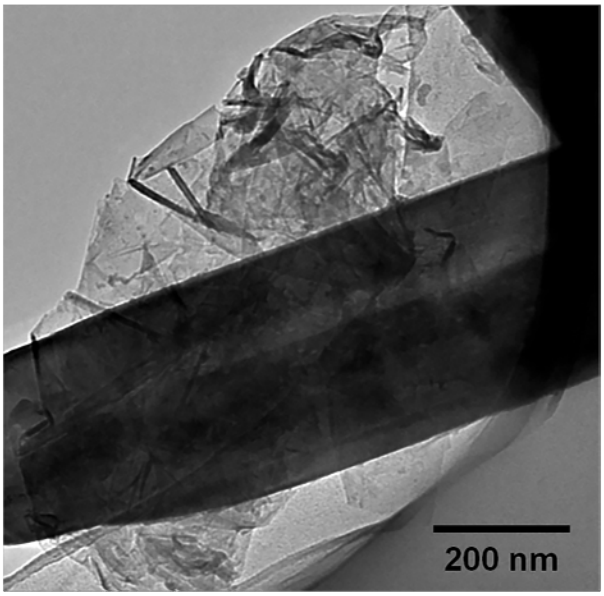


Fig. S1 TEM image of the resulting MoO_3/graphene composites.

Characterization: Both MoO_3/rGO and MoO_2/rGO were characterized by transmission electron microscope (TEM, H-7650B) at 80 kV. The microscopic features of the samples were observed by high-revolution transmission electron microscope (HRTEM, JEOL, JEM-2010) operated at 120 kV. X-ray diffraction (XRD) characterization was carried out on a Bruker D8-Advance using Cu-Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantera Scanning X-ray Microprobe using a monochromic Al-Kα (λ = 1486.7 eV) (Binding energy is calibrated with C 1s - 284.8 eV).

Electrochemical experiments

Cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed by means of a CHI 1030B Instrument (CH Instruments, Inc., USA) and a SP-150 (Bio-logic SAS) Advanced Electrochemical System respectively. EIS tests were conducted in 5.0 mM $Fe(CN)_6^{3-/4-}$ in 0.5 M KCl with a three-electrode system (KCl saturated Ag/AgCl as the reference electrode, Pt as the counter electrode) connected to an electrochemical analyzer. Samples were prepared by dispersing 4 mg composite in 1 ml ethanol-water mixed solution (H_2O:C_2H_5OH=4:1), and drop-casting of 10 μL samples over glassy carbon electrodes (with diameter of 3 mm).

For HER tests, saturated calomel electrode (SCE) was used at the reference electrode (RE), graphite rod as the counter electrode (CE), glassy carbon electrode (GCE) as the working electrode (WE). To convert potential vs. SCE to that vs. RHE, calibration should be done with SCE, Pt electrode, Pt wire as CE, WE, and CE respectively.[4] Briefly, CVs were measured in H_2 saturated 0.5 M H_2SO_4 solution, defined the mean value of two potentials where electrical current became zero as M, therefore, E(RHE)=E(SCE)+M+0.059×pH, as shown in Fig. S2. For our experiments, the formula became E(RHE)=E(SCE)+0.270 (pH for 0.5 M H_2SO_4 solution can be regarded as zero).[4]

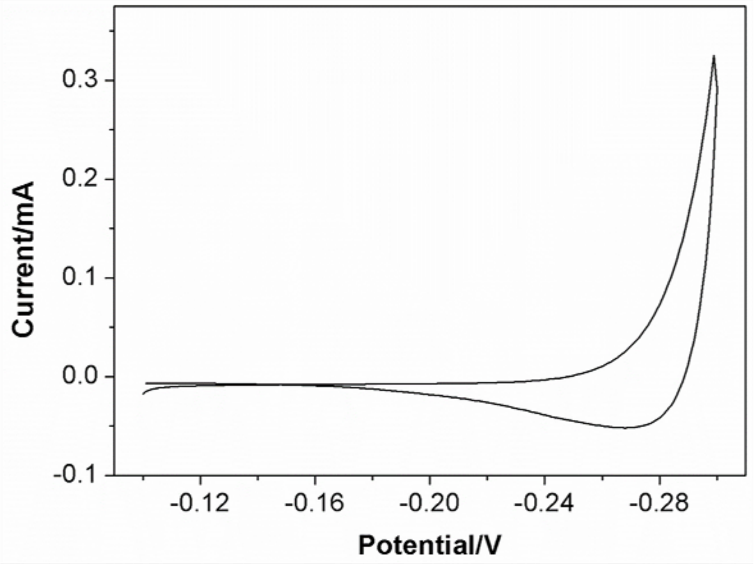


Fig. S2 Calibration curve with respect to reversible hydrogen electrode (RHE). The calibration was performed in the high purity H_2 saturated 0.5 M H_2SO_4 with Pt as the working electrode, Saturated Calomel Electrode (SCE) as the reference electrode,Pt wire as the counter electrode. Scan rate, 1 mV S^{-1}.

Supplementary Results

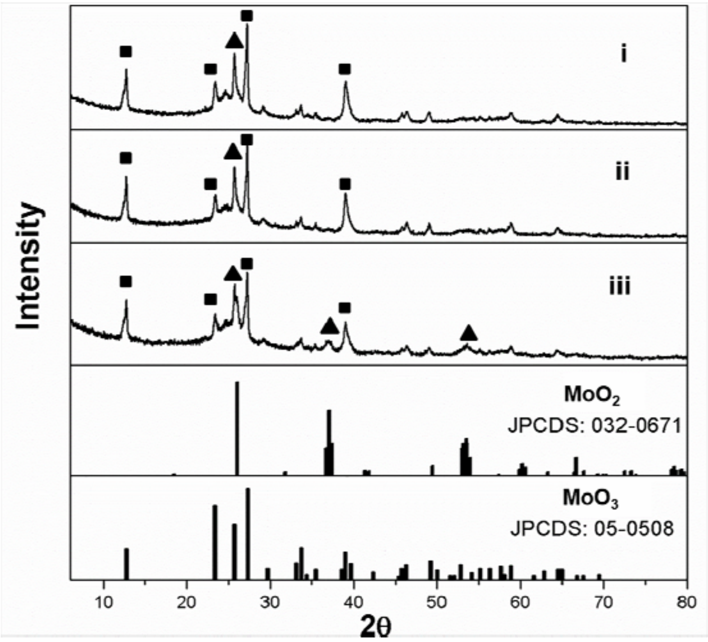


Fig. S3 XRD patterns of MoO_3/rGO annealed at 350 ℃ with H_2 flow of 20 (i), 40 (ii) and 60 (iii) sccm. (■ MoO_3, ▲ MoO_2)

Fig. S3 shows that annealing MoO_3/rGO at lower temperature with the same H_2 flow as that of 450 ℃ could only obtain partially reduced molybdenum oxide/rGO hybrid.

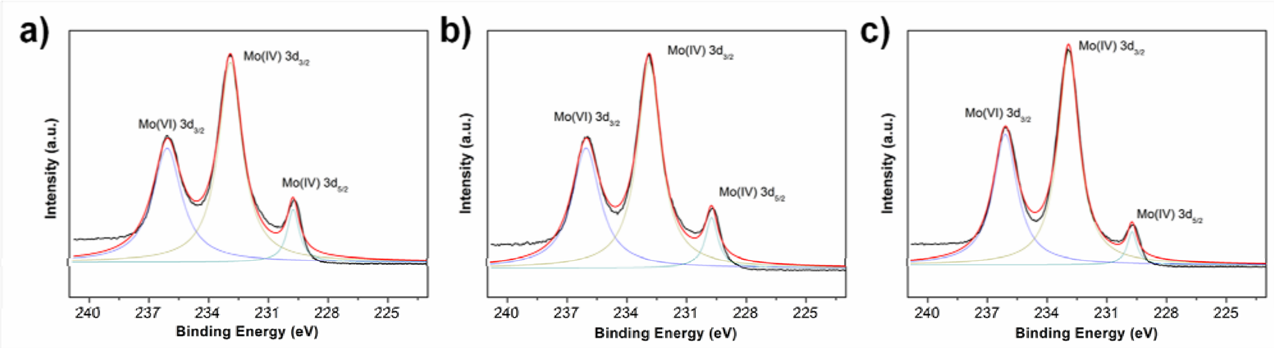
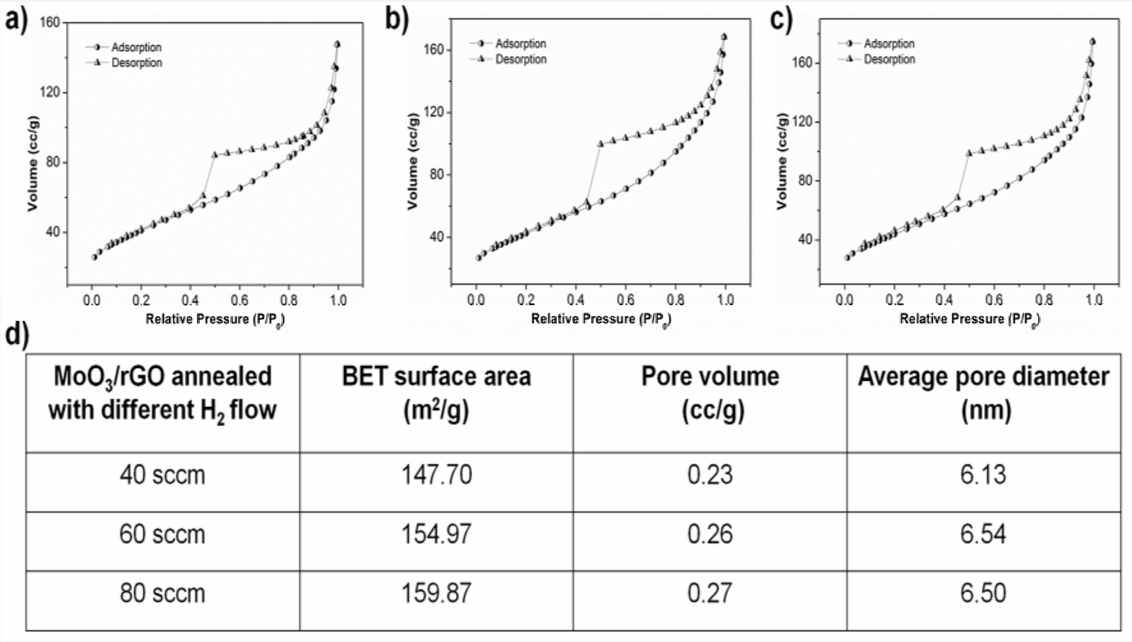


Fig. S4 X-Ray photoemission spectroscopy scans for Mo binding energies of MoO_3/rGO annealed at 450 ℃ with H_2 flow of 40 (a), 60 (b) and 80 (c) sccm.



MoO_3/rGO annealed with different H_2 flow	BET surface area (m^2/g)	Pore volume (cc/g)	Average pore diameter (nm)
40 sccm	147.70	0.23	6.13
60 sccm	154.97	0.26	6.54
80 sccm	159.87	0.27	6.50

Fig. S5 Nitrogen adsorption-desorption curves of MoO_3/rGO annealed at 450 ℃ with H_2 flow of 40 (a), 60 (b) and 80 (c) sccm. The BET surface area analysis is summarized in table (d).

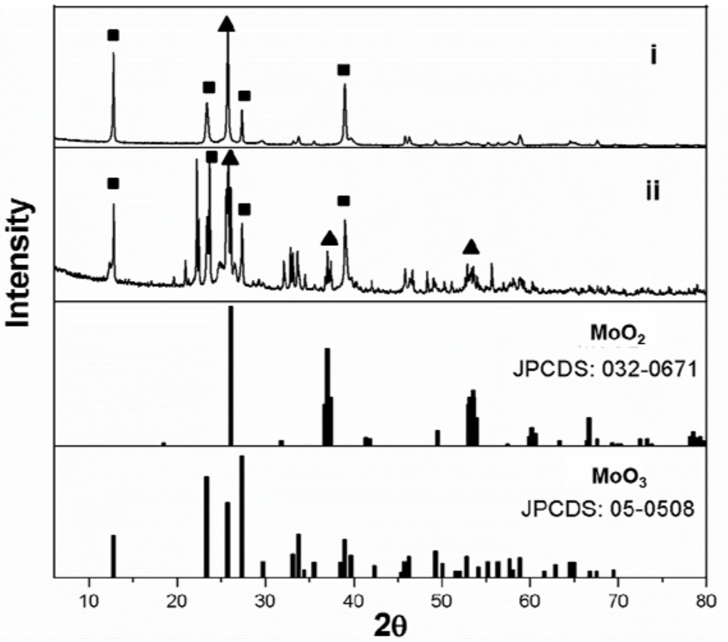


Fig. S6 XRD patterns of pure MoO_3 belts annealed under H_2 flow of 80 sccm at 450 ℃ (i) and 550 ℃ (ii). (■ MoO_3, ▲MoO_2)

We also annealed pure MoO_3 belts under the same or even harsher conditions, and the corresponding XRD patterns (Fig. S4) show that this approach can only result in non-stoichiometric molybdenum oxide. These findings indicate that rGO is necessary to produce MoO_2/rGO hybrid.

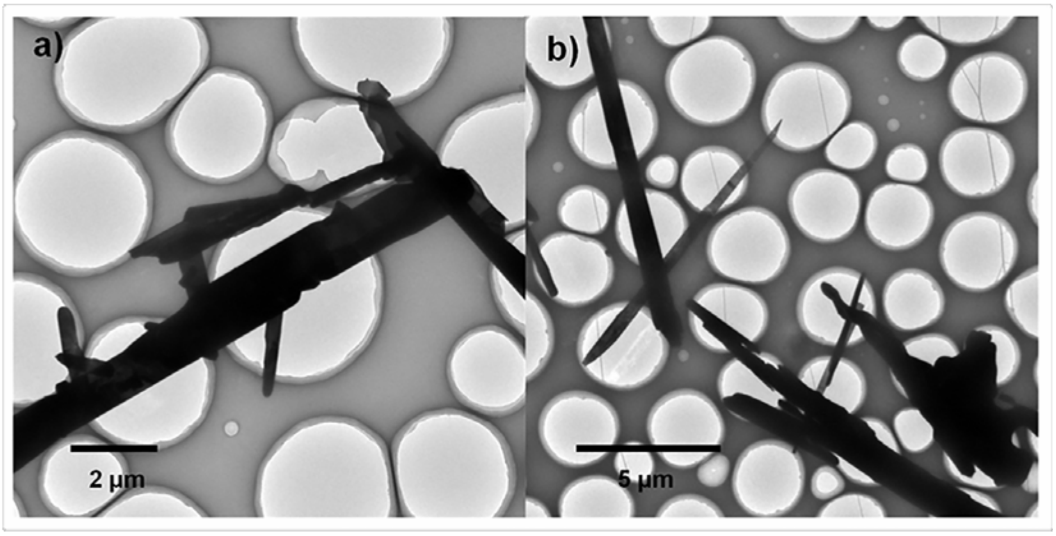


Fig. S7. TEM images of pure MoO_3 belts annealed under H_2 flow of 80 sccm at 450 ℃ (a) and 550 ℃ (b).

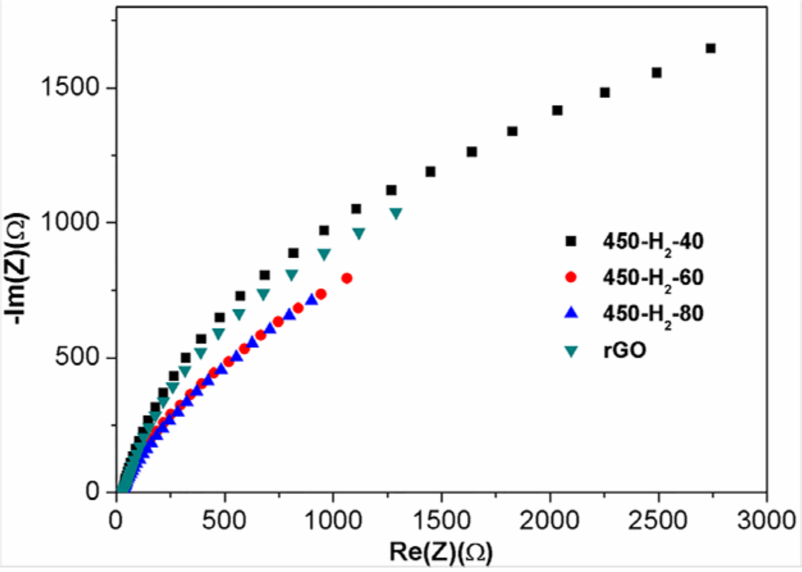


Fig. S8 Impedance spectra of materials modified glassy carbon electrodes in 5.0 mM $Fe(CN)_6^{3-/4-}$ containing 0.5 M KCl at 25 ℃. The frequency range is between 0.1 and 105 Hz with signal amplitude of 10 mV.

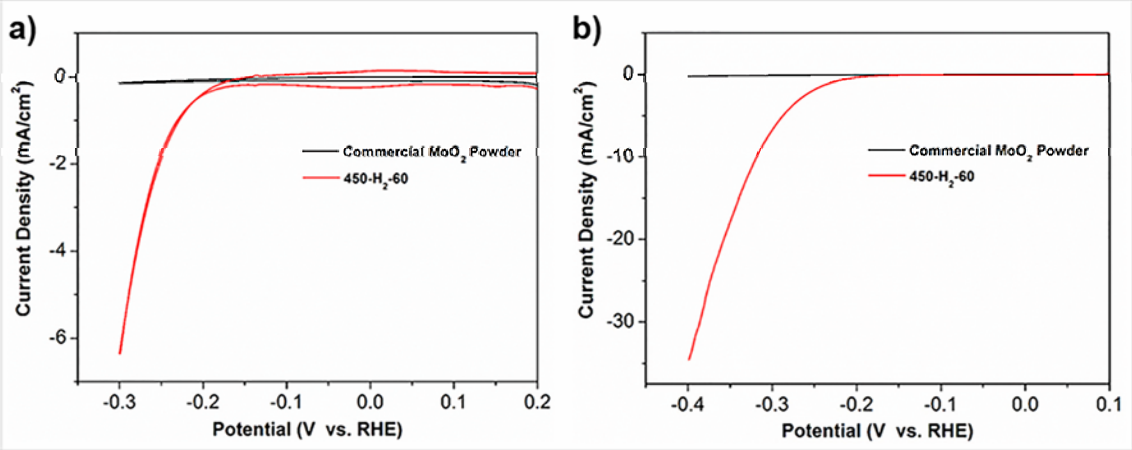


Fig. S9 a) Cyclic voltammograms (CVs) of commercial MoO_2 (black line) and MoO_2/rGO composites (red line) in N_2 saturated 0.5 M H_2SO_4, scan rate, 5 mV/s; b) Polarization curves of the corresponding materials in N_2 saturated 0.5 M H_2SO_4, scan rate, 2 mV/s.

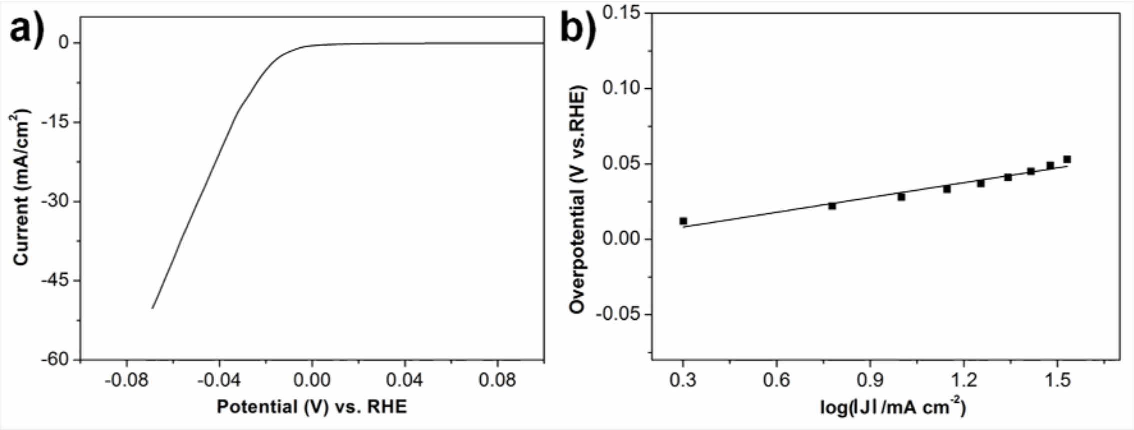


Fig. S10 Polarization curve (a) and Tafel plot (b) of commercial Pt catalyst (20 wt % Pt on Vulcan carbon black) in N_2 saturated 0.5 M H_2SO_4, scan rate, 2 mV/s.

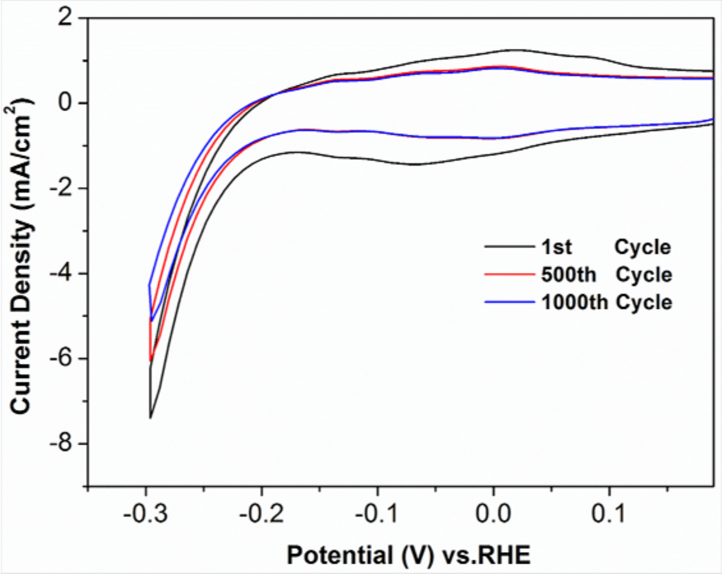


Fig. S11 Durability test for MoO_2/rGO in N_2 saturated 0.5 M H_2SO_4. Scan rate, 50 mV/s.

References

1 X. L. Li, J. F. Liu, Y. D. Li, *Appl. Phys. Lett.*, 2002, **81**, 4832-4834.

2 L. J. Cote, F. Kim and J. X. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 1043-1049.

3 W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.,* 1958, **80***,* 1339-1339.

4 Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *J. Am. Chem. Soc.*, 2011, **133**, 7296-7299.