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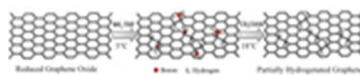
A facile route which opened a narrow band gap to hydrogenate reduced graphene oxide (RGO) with borane was reported.
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Reduction of RGO by BH₃: Facile Route to Partially Hydrogenated RGO Preparation

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**We demonstrated a facile borane hydrogenation route to hydrogenate reduced graphene oxide (RGO). This strategy is simple and might be scaleable for mass production of partially hydrogenated RGO with a band gap of ~1.8 eV.**

Graphene, with two-dimensional structure and unique electronic properties, is considered to be a promising material for next-generation electronic devices.[1] However, the applications of graphene in many semiconductor devices have been hampered by its inherent zero band gap. As one of the effective methods[2, 3] on electronic modification, hydrogenation is an elegant strategy to introduce a band gap into graphene. In theory, by changing the hybridization of all the carbon atoms from sp² to sp³ and removing the conducting π-bands, fully hydrogenated graphene (i.e. *graphane*) with a band gap of ~3.5 eV can be obtained.[4] Of particular interest is that the band gap will decrease with H coverage, and a tunable band gap may be observed in partially hydrogenated or polyhydrogenated graphene.[5, 6] The first experimental attempt was carried out by Geim et al in 2009 with hydrogen and dc plasma excited between two electrodes, and control of the electronic properties by hydrogenation was also revealed.[7] Later, catalytic hydrogenation of graphene over Ni/Al₂O₃ catalysts[8] and Birch reduction with lithium−liquid ammonia[9] have been demonstrated to be efficient methods to hydrogenate graphene. However, more accommodating, efficient, and scaleable approaches for hydrogenated graphene preparation are still highly desirable.

In this study, we report that RGO could be readily reduced by BH₃, and partially hydrogenated RGO with a band gap of ~1.8 eV could be readily obtained after hydrolysis reaction (Scheme 1).

The reduced graphene oxide used here was prepared by exposing the graphene oxide to a sudden thermal shock at 300 ℃ to remove most of the oxide functional groups.[10] The reaction between BH₃ (~40 mL, 1M inTHF) and RGO (~50 mg) was carried out at 5 ℃ for 3 h under an atmosphere of nitrogen. Then, acetic acid (~40 mL) was added to the mixture at 18 ℃ for the hydrolysis reaction.[11] Three hours later, the hydrogenated graphene (HG) was isolated and purified by intensively washing with ethanol and deionized water, and followed by drying in a vacuum freezing dryer.
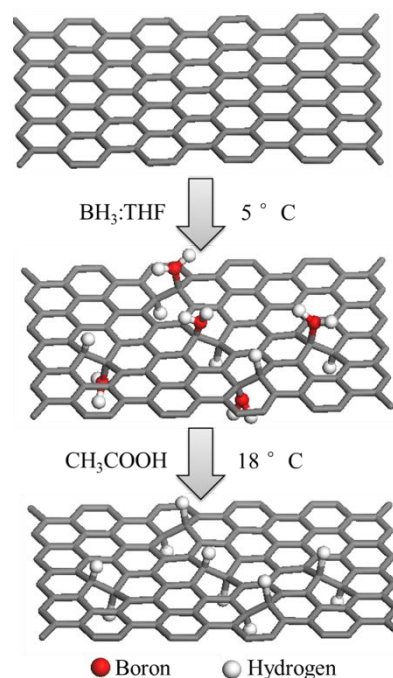
Scheme 1 Illustration for the partially hydrogenated graphene preparation.

The obtained HG showed no observable difference in morphology when compared with the RGO before the hydrogenation. The scanning electron microscopy (SEM) images of the solid samples (Fig. 1a, b) revealed that both the RGO and HG displayed crumpling features with a clear two-dimensional sheet structure. Transmission electron microscopy (TEM) images (Fig. 1c, d) of RGO and HG on top of the TEM grids showed very small optical contrast. Actually, they appeared transparent under TEM, suggesting their exfoliated natures.
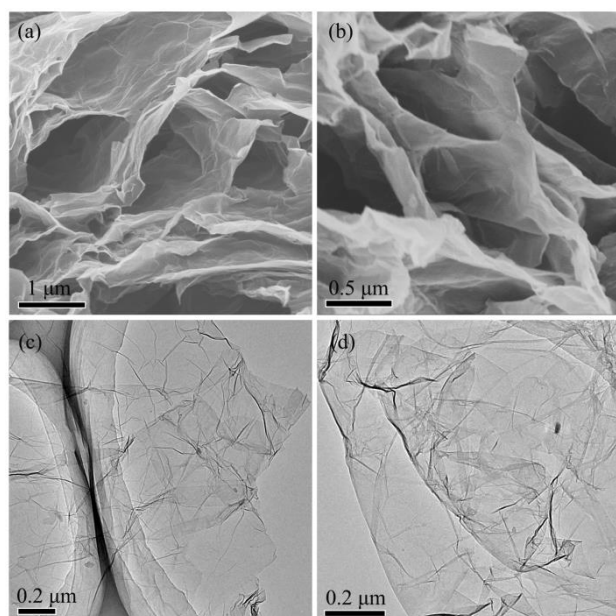
Fig. 1 SEM images of (a) RGO and (b) HG, and TEM images of (c) RGO and (d) HG.

Fourier transform infrared spectroscopy (FTIR) provided a direct evidence for the successful hydrogenation of the graphene sheet. Compared with previous studies on hydrogenated graphene that was prepared by other methods,[8] the obtained HG here showed two prominent bands at 2850 cm^{-1} and 2920 cm^{-1} (Fig. 2), which corresponded to the stretching modes of H bonded to olefinic carbon and the bending modes of H bonded to aromatic carbon.
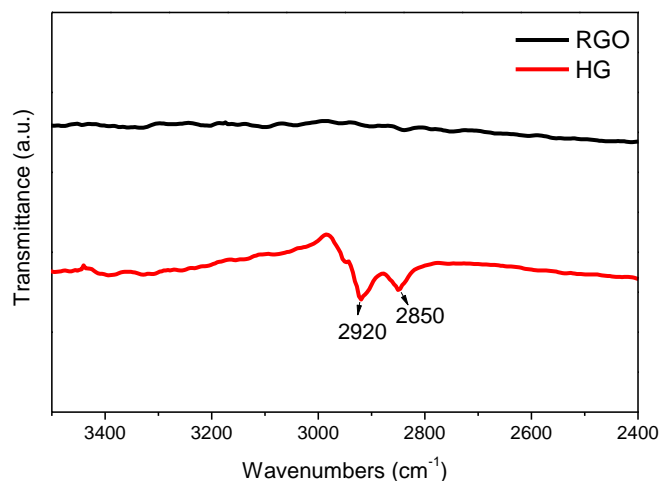

Fig. 2 FTIR spectra of RGO (black) and HG (red).

As shown in Fig. 3 (black), the typical characteristic of reduced graphene oxide was recognized by a sharp π* band (1s-π* transition) at 288.4 eV and a relatively broad 1s-σ* transition starting from 299.8 eV in carbon K-edge region. After the hydrogenation, the σ* band became narrow, and its triquetrous feature suggested the increase of sp^3 hybridization. Quantitative analysis of the sp^2 - and sp^3 -C bonds was given by the double window method (Fig. S2, Supporting Information).[12] The percentage of sp^2 hybridized atoms in RGO converged to a value of 0.124, whereas HG gave a value of only 0.115, supporting the decrease of sp^2 carbon percentage.[13] Another interesting difference in EELS was an obvious shift to lower energy after the hydrogenation, due to a reduction in the density of

the HG.[14] Specifically, Sofo et al had reported that the C–C bond length would stretch from 1.42 Å to 1.52 Å after hydrogenation.[4] And according to our calculations (Supporting Information), this change might result in a decrease of the surface density from 0.76 mg m^{-2} to 0.66 mg m^{-2}. Raman spectra as an aid test also supported this result (Fig. S1, Supporting Information).
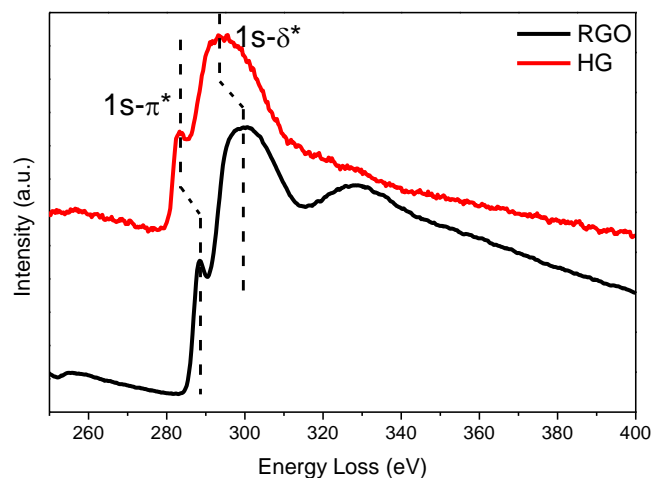

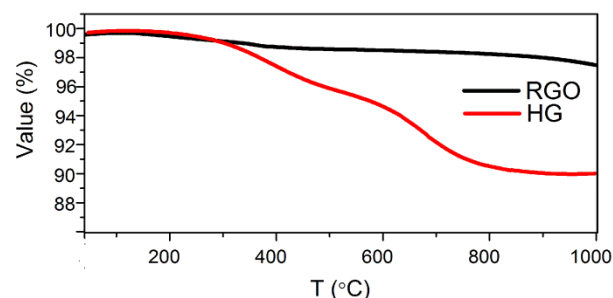**Fig. 3** EELS spectra of RGO (black) and HG (red).

Fig. 4 TGA data of RGO (black) and HG (red).

To evaluate the coverage of H atoms, thermo gravimetric analysis (TGA) was carried out. According to previous studies,[15] the dehydrogenation of hydrogenated graphene starts as low as 75 ℃– 100 ℃ and thus our TGA test started from 40 ℃ and ended in 1000 ℃. As shown in Fig. 4, weight loss of HG ended in ~850 ℃[10] and the difference between RGO and HG is ~7% (weight loss of RGO is ~2%), which could be attributed to the release of hydrogen and the absorbed species. As comparison, release of hydrogen from the sample prepared by Birch reduction was about 6wt%.[9]

As theoretical studies had revealed that the band gap of the partially hydrogenated graphene would be correlated to the H coverage, the HG samples were also characterized by solid–state UV–vis spectroscopy (Fig. 5). Note that the RGO used here showed a small band gap (~0.8 eV), different from the theoretical 0 eV in ideal graphene. After the hydrogenation, however, the band gap of the HG here was opened to be ~1.8 eV according to the method of Tauc's equation.[16, 17] A theoretical study by Jijun Zhao et al reported that the band gap reached ~2 eV with a hydrogen coverage of 85%,[5] while the Birch reduction opened a large band gap close to theoretical maximum (~4 eV)[9]. Considering the relatively lower coverage of H in the HG, the smaller band gap here was reasonable and might be promising in semiconductor devices.
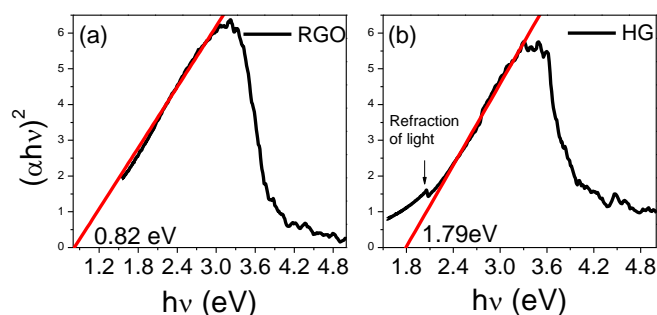
Fig. 5 UV-vis spectra of RGO and HG.

Conclusions

Hydrogenation of reduced graphene oxide is an elegant strategy to introduce a band gap into RGO for its applications in many semiconductor devices. In this study, we reported a facile new route (borane hydrogenation) to hydrogenate RGO. We found that partially hydrogenated graphene (HG) could be readily obtained by the reduction of RGO with BH_3, followed by the hydrolysis reaction in acetic acid. Different from the existing methods, this strategy is simple and might be scaleable for mass production in industry. Notably, UV–vis spectroscopy demonstrated a band gap of ~1.8 eV in the obtained HG, which might find possible applications in many semiconductor devices.

Notes and references

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† Electronic Supplementary Information (ESI) available: The details of Raman spectra, the calculations of EELS analysis and the surface density, and the X-ray Photoelectron Spectroscopy of hydrogenated graphene. See DOI: 10.1039/c000000x/

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