

DOMINO-LIKE SELF-PROPAGATING SOLID STATE REACTIONS IN GRAPHITE OXIDE

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Introduction

Graphite oxide (GO) has gained extensive interest as a precursor for bulk production of graphene based materials. Here we explore the highly energetic nature of GO, noted from the self-propagating thermal deoxygenating reaction observed in solid state. Although the resulting graphene product is quite stable against combustion even in a natural gas flame, its thermal stability was significantly reduced when contaminated with the potassium salt by-products from GO synthesis. In particular, contaminated GO becomes highly flammable. A gentle touch with a hot soldering iron can trigger violent, catastrophic, total combustion of such GO films, which poses a serious fire hazard. While this is alarming for the safety in large scale manufacturing, processing, and storage of GO materials, the released energy can be harnessed to drive new reactions for creating graphene-based hybrid materials. Through such domino-like reactions, graphene sheets decorated with metal and metal oxide particles were synthesized using GO as the in-situ power source. Enhanced electrochemical capacitance was observed for graphene sheets loaded with RuO₂ nanoparticles [1].

Experimental

Graphite oxide (GO) was synthesized using a modified Hummers method with a pre-oxidation treatment [2]. Pristine graphite is oxidized by KMnO₄ in concentrated sulfuric acid, during which the graphitic layers are rendered with various oxygen-containing functional groups. Filtration was used for removing by-products. After rinsing, the solid product was dried and stored in ambient conditions without showing any visible degradation for weeks. The final product can be easily re-dispersed in water, or in various organic solvent/water mixtures. GO film was prepared by pouring GO dispersion into a PTFE dish and letting it dry under ambient condition. GO films blended with metal precursors such as HAuCl₄ and RuCl₃ were prepared in a similar method. Solution of the salts were prepared in 1:10 = DI:MeOH mixture (10 mg/ml). The GO film was cut into small pieces using a scissor, and then used for self-propagating reactions. Reactions were initiated by gently tapping a film with a hot soldering iron tip, which was measured to be around 400 °C using an IR-thermometer. Reactions was done in both N₂ and air atmosphere.

The electrochemical behavior of r-GO and RuO₂/r-GO was characterized by cyclic voltammetry (CV) measurement. Working electrode was prepared by mixing 90 wt.% active material and 10 wt.% PTFE as binder, and pressing the slurry into a thin sheet of uniform thickness loaded on a stainless steel mesh support which served as current collector. The

typical mass load of electrode material was 3 mg. H₂SO₄ solution (1 M) was used as the electrolyte. Experiments were carried out in a three-electrode glass cell. Platinum foil (Alfa Aeser) was used as a counter electrode, and Ag/AgCl electrode (0.199 V vs. NHE) as the reference electrode. Scan speed of 2 mV/s was used.

Results and Discussion

GO can be reduced through methods such as chemical and thermal reduction. Recently it was shown that ordinary camera flashes were capable of triggering the reduction, implying this process can be easily triggered. The highly exothermic thermal deoxygenation of GO is illustrated in the differential scanning calorimetry (DSC) heating curve in Figure 1a. The heat output due to the energy released during the reduction is typically 6 – 8 kJ/g. This is roughly 10 times of the heat needed to trigger the deoxygenating reaction. If the heat released from one reaction site can be fed back to the material, it should be able to drive the reduction of neighboring sites, such as illustrated in the schematics of Figure 1b. Indeed, we have observed such solid state reduction in GO films Figure 1c shows a set of snapshots taken during a self-propagating reduction of GO. The reaction was initiated by gently tapping one end of the strip with a hot soldering iron heated at about 400 °C. Deoxygenation was triggered on the spot and then rapidly propagated (~ 4 cm/s) across the entire film. The color of the film changed from shiny dark brown (GO) to black (reduced GO, abbreviated as r-GO) as the reaction front swiped through the sample.

We observed that its graphene product, r-GO was remarkably stable against combustion. However, the thermal stability of r-GO can be significantly reduced by potassium salts. The synthesis of GO typically involves potassium salts such as KMnO₄ and K₂S₂O₈, which may turn into various forms of potassium compounds. Although graphene nanoplatelets and even GO have been demonstrated to have flame retarding properties, we observe that GO solids containing potassium salt by-products are highly flammable. An accidental spark or hot spot can trigger rapid, catastrophic total combustion, which poses a serious fire hazard. This is particularly alarming for the fire safety in large scale production, processing, and storage of GO materials, especially in solid state. Our discoveries also emphasize the need to improve the processing and purification of GO, especially in scaled-up reactions.

Although the rapid reduction-combustion reactions of GO pose potential safety hazards, one can actually take advantage of the stored chemical energy for synthesizing graphene-based composites. One type of such reactions would be the thermal decomposition of salts for making metal nanoparticles. GO could thus serve as an effective *in-situ* power source to drive these reactions. As a proof-of-concept, we prepared a GO film mixed with HAuCl₄ (10 wt %). Then the “GO reduction + metal formation” domino-like reactions were triggered by a hot soldering iron. The reduction of GO propagated in a similar manner as that shown in Figure 1. Indeed, Au

nanoparticle decorated graphene sheets were successfully obtained. TEM images (Figure 2a) of the product reveal that the r-GO sheets are uniformly loaded with Au nanoparticles with average diameter of 5.0 ± 1.3 nm. Other metal nanoparticles, such as platinum (Figure 2b) and palladium can also be prepared in the same way.

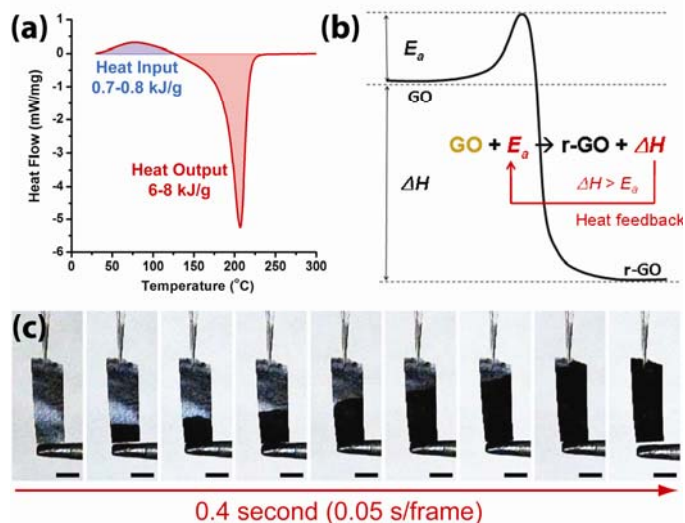


Figure 1. Self-propagating solid state reduction of graphite oxide. (a) DSC analysis of GO in N_2 atmosphere showing that the heat generated by the reaction is roughly 10 times of the heat needed for starting the reaction. (b) Schematic diagram illustrating the energy input and output during the thermal reduction of GO. When heat release is greater than input, the thermal reduction will be self-sustained if the released heat is fed back to the reaction. (c) Snapshots taken by a digital camera during a self-propagating reduction of a GO strip. Reduction was triggered by gentle tapping with a hot solder iron ($\sim 400^\circ C$), and rapidly propagated over the entire film in about 0.4 seconds as noted by the color change. Scale bars = 5 mm.

In addition to metal nanoparticles, metal oxide nanoparticles can also be prepared in similar fashion. Graphene has been shown to be promising for energy storage applications such as ultracapacitors. Therefore, we chose to decorate r-GO sheets with RuO_2 nanoparticles, which have been shown to have a high pseudo-capacitance. To create the composite, a GO film blended with 10 wt% $RuCl_3$ was prepared and reduced. TEM image (Figure 2c) of the resulting product show r-GO sheets decorated with uniformly distributed nanoparticles of 2.4 ± 0.4 nm in diameter. The loading of RuO_2 was estimated to be around 7% wt. The specific capacitance measured for the $RuO_2/r-GO$ composite was 228 F/g, which increased significantly from 162 F/g for r-GO (Figure 2d). The reactions should be a promising, energy-efficient route for synthesizing nanoparticle loaded graphene sheets for energy storage and catalysis applications.

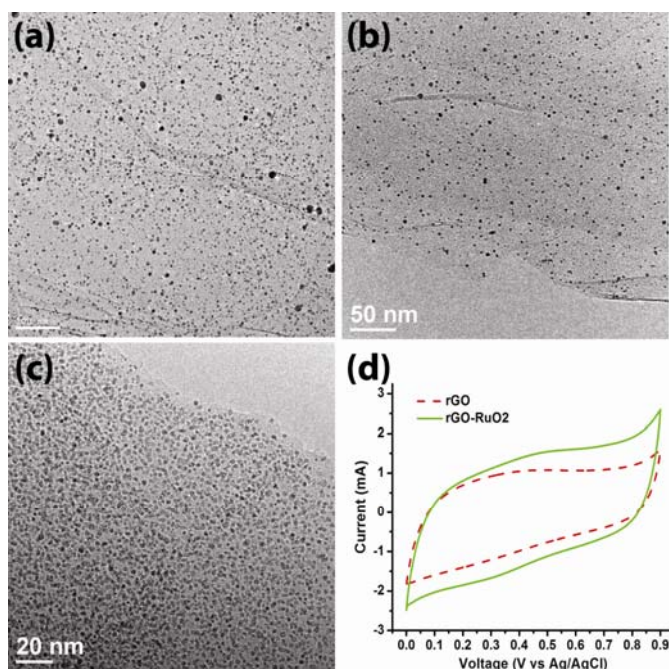


Figure 2. (a – c) TEM images of thus prepared graphene sheets loaded with Au, Pt, and RuO_2 nanoparticles, respectively. CV curves show that the presence of RuO_2 nanoparticles can significantly increase the specific capacitance of graphene based electrochemical double layer capacitors from 162 F/g for r-GO, to 228 F/g for the $RuO_2/r-GO$ composite, respectively. Scan rate was 2 mV/s.

Conclusion

Rapid, self-propagating reduction of GO films can be triggered by a local hot spot. In the presence of potassium salts, violent, catastrophic reduction-combustion domino-like reactions were observed that rapidly burned up the material. The discovery presented here is alarming for the potential fire hazards during the large scale manufacturing and storage of solid GO materials, and emphasizes the need for more efficient sample purification protocols. On the other hand, the domino-like reactions can be guided to produce functional nanoparticle/graphene hybrids using GO as *in-situ* power sources. This could inspire new possibilities for energy-efficient synthesis of graphene based composites.

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- [2] Hummers WS, Offeman RE, Preparation of graphitic oxide. *J. Am. Chem. Soc.* 2010: 80: 1339-1339.