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Residual acetone produces explosives during the production of graphite oxide

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ABSTRACT

Chemically modified graphenes (CMGs) are promising candidates for a wide range of applications. Graphite oxide (GO) is most commonly used to produce CMGs. We note that residual acetone can produce dangerous explosives during the synthesis of GO. Addition of acetone produced acetone peroxides *via* a reaction with H_2O_2 and H_2SO_4, which are used in the Hummers/modified Hummers methods of making GO. The use of $Na_2S_2O_3$ instead of H_2O_2 yielded GO without making explosives.

Graphene has excellent mechanical, electrical, thermal, and optical properties, and a high specific surface area [1,2]. Chemically modified graphenes (CMGs) and their colloidal suspensions allow for use of CMG materials in polymer composites, in ultracapacitors, for hydrogen storage materials, in rechargeable batteries, as conducting inks, for thermal management, and in chemical/bio sensors [1–4]. Graphite oxide (GO), produced *via* oxidation of graphite, has been most frequently used as a starting material to generate various CMGs [5]. We have identified a safety concern in the synthesis of GO and present it here.

We accidentally formed white powder during the production of GO using the modified Hummers method and separately, the Hummers method, each a common method to produce GO (Fig. 1) [5–7]. The isolated powders were a strong explosive at high temperature (200–300 °C) and also when 'hammered' on.

We then learned that it was acetone that generated such explosives during the synthesis of GO using the Hummers/modified Hummers methods. Acetone peroxide (dimer, or trimer), a strong explosive [8], has caused lab accidents [9] and is produced by the reaction between H_2O_2 and acetone in an acid-catalyzed nucleophilic addition [10]. H_2O_2 and acid (H_2SO_4) are commonly used in the synthesis of GO using the Hummers/modified Hummers methods. Nuclear magnetic resonance spectroscopy of the isolated powder confirmed the generation of acetone peroxide from the GO preparation (see Supporting Information (SI)).

We found that the addition of H_2O_2 at different processing steps (Fig. 1) to reaction vessels containing residual acetone produced mixtures of graphite/graphite oxide with such explosives, and also caused explosions in the liquid-phase mixtures (see SI for experimental details). We have not attempted to further investigate these explosions because of the obvious dangers.

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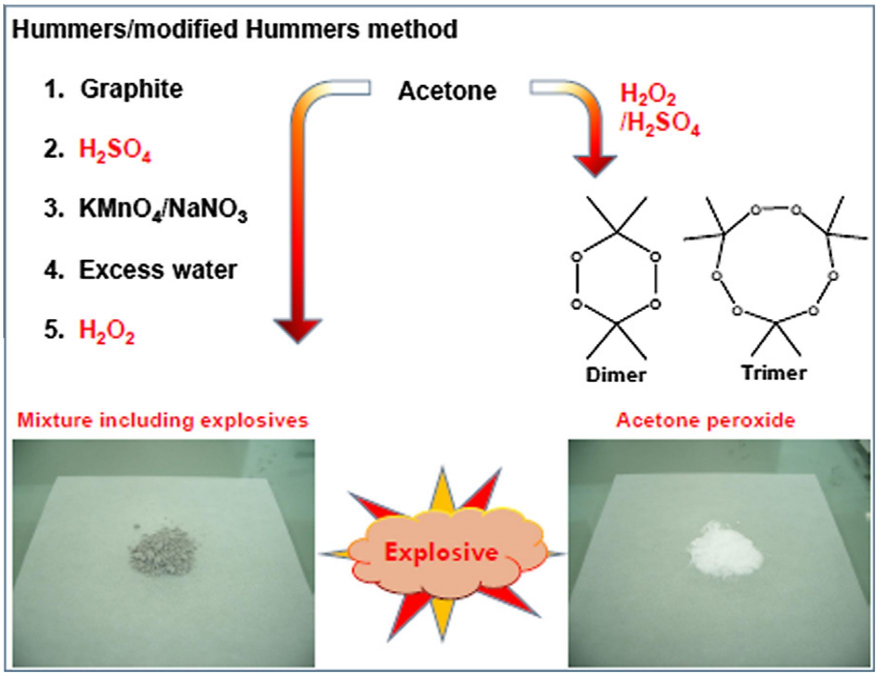

Fig. 1 – A representative scheme of the Hummers/modified Hummers methods. Residual acetone was converted to explosives during the procedure.

Acetone is the most commonly used wash solvent for reaction vessels because of its low boiling point, low cost, excellent solubility for organics, and good miscibility with water or organic solvents. Obviously, the best thing is to ensure that there is no residual acetone in the glassware used to make GO. Care should be taken to avoid that.

In addition, new synthesis procedures that do not present an explosion risk could be important. Among the chemicals (H_2SO_4 and H_2O_2) necessary to produce the explosive in the presence of residual acetone, the acid is essential to oxidize graphite. On the other hand, H_2O_2 terminates active species after oxidation of graphite [5], which suggested to us that it could be replaced.

The use of H_2O_2 has a couple of advantages during the synthesis of GO. First, water insoluble by-products in reaction mixtures are solubilized by adding H_2O_2 [5], and thus, easily removed by rinsing with water. Second, H_2O_2 'decolorizes' reaction mixtures, which makes it possible to see the orange-colored GO particles. We found that $Na_2S_2O_3 \cdot 5H_2O$ (sodium thiosulfate pentahydrate, 'STP') is an effective replacement for H_2O_2 in the modified Hummers method to make GO ('STP–GO') and has the two advantages of H_2O_2 described above (see the SI for synthesis and characterization of STP–GO). Importantly, the use of STP avoided the explosion risk even in the presence of excess acetone. Although the resulting GO (STP–GO) from such new reaction is slightly less oxidized relative to H_2O_2–GO, it shows similar chemical properties and exfoliation behaviors to usual GO materials (see SI for details).

In conclusion, it was found that residual acetone in reaction vessels led to the risk of explosion(s) in the reaction vessels during the production of GO using the Hummers method or the modified Hummers method. The culprit is acetone peroxides generated by a reaction of acetone and H_2O_2 in the presence of H_2SO_4. Acetone residues should be completely removed from reaction vessels and that acetone thus be avoided during the preparation of GO using the Hummers/modified Hummers methods. We introduce use of $Na_2S_2O_3$ instead of H_2O_2 in the modified Hummers method that even in the presence of acetone appears to be safe.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2011.10.045.

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