Lecture 11. Chemical Reactivity of Graphene Oxide. Applications of Graphene and Graphene Oxide

The purpose of the lecture: to provide information on the chemical reactivity and applications of graphene and graphene oxide.

Expected results: to master methods for the chemical reactivity and applications of graphene and graphene oxide.

Graphene oxide is a very versatile material. It is not only an important material for preparation of graphene, but the presence of different oxygen functionalities on its surface make graphene oxide an important precursor for a variety of chemically modified graphenebased materials. The chemical conversion of graphene oxide offers a promising route for processing of graphene-based materials for different applications.

Chemical conversion of graphene oxide to graphene via reduction methods is one of the most desirable routes to large quantities of graphene-like materials. The reduction process is among the most important reactions of graphene oxide because of the similarities between reduced graphene oxide and pristine graphene, in terms of their structural and electrical properties. Unlike graphene, graphene oxide is an electrically insulating, hydrophilic material due to the disruption of its sp2 bonding network and the presence of polar hydroxyl, epoxy, carboxylic acid, and carbonyl groups on its surface. Electrical conductivity of the structure can be recovered by restoring the π-network of graphene by reduction of graphene oxide by removal of oxygen groups. The transformation of sp3 carbons to sp2 by reduction of graphene oxide restores electrical conductivity; thus, conductivity is a valuable qualitative measure of the conversion of graphene oxide to graphene. Strong alkaline agents, such as hydrazine hydrate and sodium borohydride, are effective reducing agents, as the electrical conductivity of reduced graphene oxide is significantly increased after reduction. While graphene oxide is insulating, reduced graphene oxide films are conducting. The electrical conductivity of reduced graphene oxide (~2 Ч 102 S/m) increased by about 5 orders of magnitude in comparison to graphene oxide and closely approached that of pristine graphite by reduction with hydrazine. By using an acidic reducing agent, such as hydroiodic acid, electrical conductivity increases to about 298 S/cm. The reduction with hydroiodic acid maintains good integrity and flexibility, and even improves the strength and ductility of the original graphene oxide films.

The first electronic transport studies of chemically reduced graphene oxide sheets, which potentially provide access to large-scale production of graphene monolayers, were performed by Gomez-Navarro et al. Individual graphene oxide sheets subjected to chemical reduction were electrically characterized as a function of temperature and external electric fields. Before reduction the graphene oxide monolayers were insulating (conductivity about 10–3 S/cm). The fully reduced monolayers exhibited conductivities ranging between 0.05 and 2 S/cm and field-effect mobilities of 2–200 cm2/Vs at room temperature.

Thus the conductivity of the reduced graphene oxide monolayers was found to be approximately 3 orders of magnitude higher compared to the starting graphene oxide. However, for fully reduced graphene oxide, the room-temperature conductivity and carrier mobility were found to lag behind those of graphene by 3 and 2 orders of magnitude, respectively, predominantly due to defects present in the structure compared to pristine graphene.

Reduction process has a strong effect on solubility and stability. A comparison of the dispersion behavior of graphene oxide and reduced graphene oxide in different polar and nonpolar organic solvents has shown that while graphene oxide has better solubility and stability (long-term stability) in polar solvents, the reduced graphene oxide has better interaction with nonpolar solvents like chloroform, toluene, and chlorobenzene. Similar to graphene oxide, reduced graphene oxide gives very good dispersions in NMP, water, and ethylene glycol, which implies that oxygen-containing functional groups are still present at defect sites in reduced graphene oxide.

These studies are important for processing of these materials for different applications when stable aqueous or colloidal dispersions are required.

Covalent chemical functionalization of graphene oxide through the addition of other functional groups to graphene oxide via reactions at the chemically reactive oxygen functionalities, such as carboxylic acid groups, on the edges and epoxy and hydroxyl groups in the basal plane result in chemically modified graphene. Such chemical modifications improve dispersion of these materials in polar aprotic organic solvents. An important reaction of graphene oxide sheets is the isocyanate treatment of graphite oxide where organic isocyanates react with the hydroxyl and carboxyl groups of graphene oxide sheets to form carbamate and amide functionalities, respectively. Well-dispersed modified graphene oxide sheets in polar aprotic solvents can be obtained by isocyanate treatment (Figure 1).
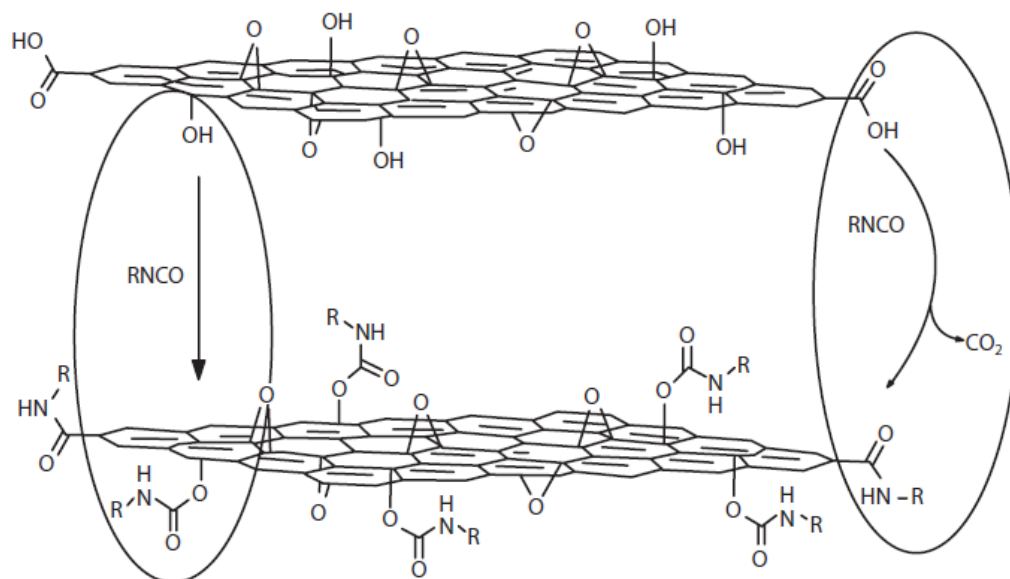
(a)
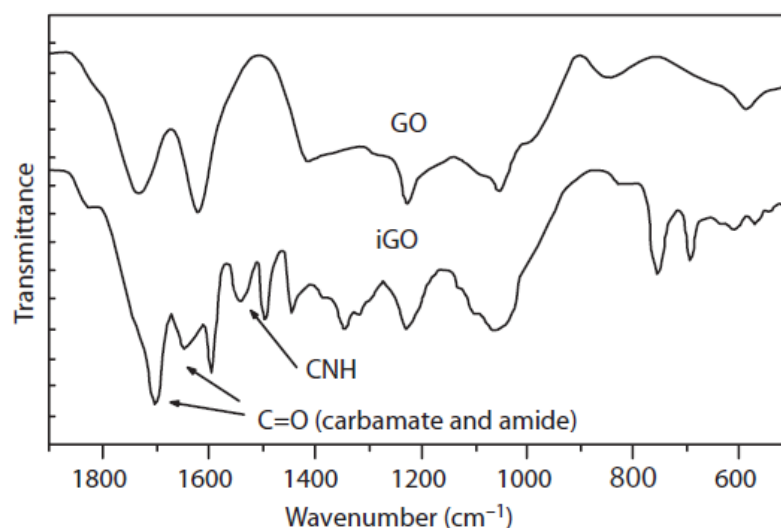
(b)

FIGURE 1. (a) Proposed reactions during the isocyanate treatment of graphite oxide (GO) where organic isocyanates react with the hydroxyl (left oval) and carboxyl groups (right oval) of graphene oxide sheets to form carbamate and amide functionalities, respectively. (b) FT-IR spectra of GO and phenyl isocyanate-treated GO.