MULTI-FUNCTIONAL FREE-STANDING GRAPHENE OXIDE PAPER THROUGH SELF-ASSEMBLY AT THE LIQUID/AIR INTERFACE

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Graphene has attracted much recent attention for its unique and/or superior electronic, mechanical, optical, and thermal properties. Many approaches have been developed to prepare this 2D carbon sheets, mainly including micromechanical cleavage of highly oriented pyrolytic graphite, exfoliation of graphite intercalated compounds, sublimation of silicon from silicon carbide, chemical vapor deposition and chemical reduction of graphite oxide (GO). Very recently, it is highly concerned that assemble well dispersed graphene nanosheets into 3D hierarchical macrostructures is a best way to demonstrate its superb performance on macroscopic materials. For instance, template assistant assembly, vacuum filtration, Langmuir-Blodgett assembly, and direct chemical vapor deposition have also been employed to obtain graphene-based or graphene-oxide-based membranes on selected substrates. It is still a great challenge to get free-standing graphene based 3D nano-architecture with tunable surface property.

Here we explore a novel facile route that self-assembly of GO at a liquid/air interface approach to prepare macroscopic GO membrane by evaporating the GO hydrosol. In a typical preparation, GO was synthesized from natural graphite powder by a modified Hummers method. A GO suspension in water was treated in an ultrasonic bath, followed by high-speed centrifugation to remove impurities, which only resulted in a slightly precipitation. The stable GO hydrosol was heated at 353 K for a short period in a thermostatted water bath, during which time a smooth and condensed thin film was formed very rapidly at the liquid/air interface. Such a stable film was easily separated from the parent graphene oxide suspension by decanting the residual suspension into another beaker. After drying, a flexible, semi-transparent, and free-standing membrane was obtained and through this ultrathin membrane we can clearly identify the characters on a background paper. The size of the flexible membrane is solely determined by the area of the liquid/air interface, and a large-area membrane could be easily obtained so long as a large container was employed for the assembly. The as-obtained GO film is of uniform thickness and relatively smooth surface. The thickness can be precisely controlled in a range of 0.520 mm by adjusting the evaporating time of the hydrosol. Individual GO sheets can be clearly identified as "building blocks" for the film. The cross-sectional image exhibits a compact layer-by-layer stacking of GO sheets.

The as-obtained GO film strips of different membrane thickness (510mm) were employed for mechanical measurements. The self-assembly film is characterized by slightly lower modulus (average value of *ca.* 12.7 GPa) but similar tensile strength (average value of *ca.* 67.7 MPa) compared with the membranes prepared by filtration method. The mechanical performance of these membranes is apparently higher than that of the flexible graphite foils composed of stacked expanded graphite. After high temperature treatment or aqueous reduction, the GO films were reduced into free standing graphene film with good electronic conductivity. It can be served as paper electrode for supercapacitor. The preliminary cyclic voltammograms of the as-obtained GO films were close to rectangle shape with small redox peaks, indicating promising charge propagation within the electrodes. The specific capacitance maintains very well with the increase of scanning rate.

During the GO self-assembly at the liquid/air interface, the GO surface can be modified by B and P. With the addition of B and P precursor, free-standing GO film can be well organized. The implementation of an electron-attracting dopant, such as boron or boron oxide, will reduce the generation of highly reactive oxygen species. The electronic structure of GO film was also modulated. When it served as paper electrode, pseudo-reaction peaks can be observed on the cyclic voltammogram curves and the capacity of paper electrode were increased. As further investigation is undergoing, it is expected that graphene and graphene oxide film will be advanced energy materials to meet the highly demanded requirement for energy conversion and storage.

In summary, a thickness controlled, area adjustable, and free-standing GO/graphene film can be produced through a facile self-assembly process at the liquid/air interface. Such macroscopic membranes are constructed by individual graphene oxide sheets through layer-by-layer stacking, and illustrate excellent mechanical, electrochemical, electronic, and optical performances. This is expected to bring a family of multifunctional applications in the area of composites, catalysis, energy conversion and storage.

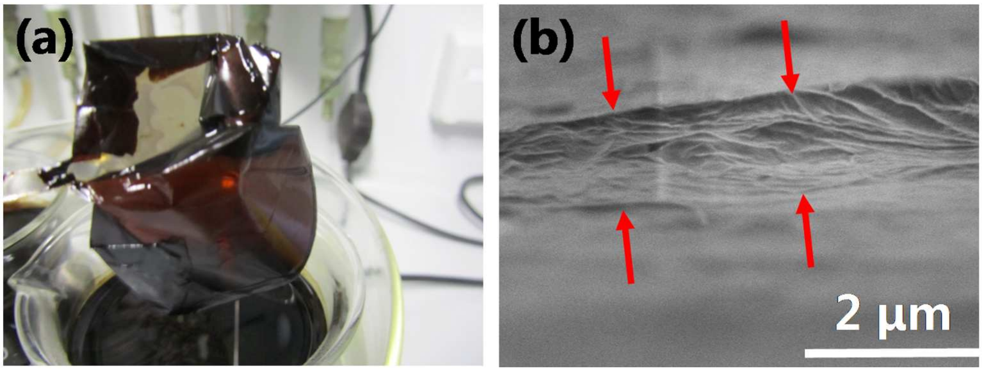

Figure 1: (a) Fishing up of a substrate-free GO membrane self-assembled at the liquid-air interface; (b) Typical FE-SEM image of the cross-section of a membrane harvested from the liquid-air interface.

References

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