Journal of
Materials Chemistry

Dynamic Article Links

Cite this: *J. Mater. Chem.*, 2011, **21**, 18730

www.rsc.org/materials

PAPER

Synthesis and properties of monolayer graphene oxyfluoride

Matteo Bruna,[a] Barbara Massessi,[ab] Cristina Cassiago,[c] Alfio Battiato,[b] Ettore Vittone,[b] Giorgio Speranza[d] and Stefano Borini*[a]

Received 3rd August 2011, Accepted 30th September 2011
DOI: 10.1039/c1jm13729h

Covalent bond-forming reactions can be used to tailor the properties of graphene, aiming at electronic band structure engineering and surface functionalization. We present a novel and easy method for the production of chemically modified monolayer graphene based on the electrochemical intercalation of graphite, that could be used for adding various functional groups to the graphene lattice. Oxy-fluorinated graphene layers have been produced and fully characterized in terms of their chemical composition and functionalization. Moreover, Raman spectroscopy allows ready discrimination between monolayers and few-layers, and field-effect devices have been fabricated in order to study the transport properties of monolayer graphene oxyfluoride. Interesting conduction mechanisms such as two dimensional Mott variable range hopping and colossal negative magneto-resistance are observed, making this novel material suitable for both fundamental research and graphene-based applications.

1 Introduction

The extraordinary properties of graphene continue to attract a lot of scientific interest aimed at the exploitation of all its potential in terms of basic research and applications. A recently risen research area deals with the chemical modification of graphene in order to tune the electrical and chemical properties of the material. For example, an energy gap can be introduced in the electronic band structure of graphene,[1] with important advantages in the realization of microelectronic applications. Moreover, the chemical functionalization allows the creation of graphene derivatives with a selected sensitivity towards various molecules, thus opening the way to the realization of new sensors.[2–4]

So far, three main derivatives of graphene have been experimentally investigated: graphene oxide,[3,5–8] hydrogenated graphene known as graphane,[1,9] and the most recent fluorinated graphene.[10–13] The first one, a graphene sheet decorated with oxygen rich functional groups, is obtained by the exposure of graphite to liquid oxidizing agents, and results in a highly defective insulating material with electrical and mechanical properties that can be partially restored by thermal or chemical reduction. Graphane is a single plane of hydrogenated graphene and an extremely promising material for organic electronics, although its synthesis is still difficult.[1]

[a]*Thermodynamics Division, INRIM, Strada delle cacce 91, I-10135, Torino, Italy. E-mail: s.borini@inrim.it*
[b]*Department of Experimental Physics, Centre of Excellence "NIS" University of Torino, via P. Giuria 1, I-10125, Torino, Italy*
[c]*Electromagnetics Division, INRIM, Strada delle cacce 91, I-10135, Torino, Italy*
[d]*FBK-IRST Sommarive str. 18, Povo, 38123, Trento, Italy*

Recently, the strength of the C–F chemical bond was exploited to produce fluorinated graphene flakes with various fluorine concentrations[11,12] up to a stoichiometric graphene derivative called fluorographene.[10] All of these derivatives have demonstrated the possibility of tuning the electrical, thermal and optical properties of graphene, but their production can be extremely challenging. Indeed, fluorination or hydrogenation of graphene are processes that involve the use of dangerous gases at high temperatures[10–12] or very well controlled plasma treatments.[1,14]

In this paper we propose a very simple method, based on the electrochemical intercalation of graphite, for the production of chemically modified graphene monolayers. In principle, such a procedure might be carried out with many different electrolytic solutions, for obtaining various graphene functionalizations. Here we report on the production and the study of the physical properties of graphene monolayers modified with fluorine and oxygen atoms.

2 Synthesis of the material

Chemically modified graphite samples were prepared by means of an electrochemical intercalation technique starting from natural graphite flakes. Such a process, normally employed in the production of graphite intercalation compounds,[15] was carried out in a PTFE cell filled with a hydrofluoric acid aqueous solution (50 wt%) at room temperature. A graphite flake contacted with a platinum wire and immersed in the acid solution was the working electrode while another platinum wire served as the counter electrode. A constant current, of the order of tens of mA, was then driven through the electrodes to start the intercalation process.

