Graphite nanoplatelet chemical cross-linking by elemental sulfur

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Abstract

Graphite nanoplatelets (GNPs) react with elemental sulfur to provide a mechanically stable, spongy material characterized by good electrical conductivity and high surface development; such unique property combination makes these novel nanostructured materials very useful for applications in different technological fields. The carbon-sulfur reaction can be accurately investigated by thermal analysis (differential scanning calorimetry and thermogravimetric analysis) and energy-dispersive X-ray spectroscopy combined with scanning electron microscopy. The thermal treatment required for the formation of electrically conductive monosulfur connections among the GNP unities has been investigated.

Keywords: Graphite nanoplatelets, Sulfur, Mechanical stabilization, Calorimetry

PACS: 81.05.Ue, 81.05.Rm, 81.16.Be

Background

Graphene, a single layer of carbon atoms arranged in a hexagonal network, is a 2D nanostructure with outstanding physical properties [1]. The successful isolation of graphene has had great interest for experimental investigations and has opened the way to a wide range of novel technological applications [1]. Recent studies have been directed toward using graphite nanoplatelets (GNPs) and graphene as a substrate to support nanostructures (e.g., quantum dots, metal catalysts, magnetic nanoparticles, etc.) because of their wide surface area, chemical stability, mechanical strength, and flexibility [2-4].

śp² carbon nanoforms (e.g., fullerenes, CNTs, graphite nanoplatelets, and graphene) can be chemically cross-linked and polymerized by reaction with elemental sulfur. The resulting synthetic solid phases can be considered as a sort of three-dimensional polymers of sulfur and structurally complex carbon-based monomers. This carbon-sulfur chemical reaction may result in a certain importance in the preparation of novel bulky nanostructured materials [5].

For example, a highly spongy graphite-based material (graphite aerogels) can be prepared by drying concentrated GNP colloids, achieved by exfoliation of expanded graphite in nonpolar liquids with ultrasounds [6]. This novel material is quite fragile and has a measured apparent density of 0.5 g/cm³. A mechanical stabilization treatment is required to exploit this system in technological applications. The carbon-sulfur chemical reaction can be advantageously used for the mechanical stabilization of the very fragile spongy graphite material. The introduction of sulfur in this spongy graphite structure is quite simple since the sulfur molecules (S₈) are soluble in nonpolar organic media (hydrocarbons, etc.), and it can be dissolved in the GNP colloid before the drying process. Then, the dry GNP-based material is heated at ca. 180°C to allow the sulfur molecules to open, producing sulfur bi-radicals (S₈⁻) which bridge the graphene layers of closed nanoplatelets [7]. In particular, the ring of sulfur molecule (S₈) breaks at a temperature of ca. 169°C, producing linear sulfur bi-radical fragments, and such endothermal process is named as λ-transition [8]. The permanence of the system at temperatures above the λ-transition allows the polysulfur molecular chains (C-(S)ₙ-C) to break successively and the generated sulfur radicals to react again with the edges of graphene sheets above to achieve a high density of monosulfur chemical cross-links (C-S-C) between them. The monosulfur bridges allow electron delocalization among the graphene sheets, and therefore, they represent a sort of electrical connections in the

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material. When the spongy graphite is devoted to technological applications in the electrical/electronic field (e.g., supercapacitor electrodes, battery cathodes, electrodes for electrolytic cells, etc.) [9], the presence of monosulfur bridges among the GNP unities is a very convenient characteristic. In addition, the material stiffness is related to the length of sulfur bridges, and monosulfur connections lead to a much more rigid and tough material.

**Methods**

**Materials**
Expandable graphite flakes (Asbury, Asbury, NJ, USA) underwent a thermal shock at 750°C for 3 min in a muffle furnace to produce expanded graphite (worm-like graphite). As-received elemental sulfur (99.9%, Sigma-Aldrich, Milan, Italy) was dissolved in octane (purum, Carlo Erba Reagents, Milan, Italy), and the expanded graphite filaments were added step by step to this sulfur solution during an ultrasound processing of the liquid system, done with a horn sonicator (20 KHz, 200 W, model UW2200, Bandelin Sonoplus, Berlin, Germany) at room temperature. The resulted expanded graphite filaments were completely converted to GNPs after ultrasound application. The final product was a sort of paste, which was dried in air at room temperature to produce a highly porous graphite/sulfur mixture, successively annealed in oven at 300°C in order to cross-link the material.

**DSC analysis**
Dynamic scanning calorimeter tests were carried out by a differential scanning calorimeter (DSC; Q2920, TA Instruments, New Castle, DE, USA). Measurements were performed under fluxing nitrogen at a rate of 10°C/min ranging from 20°C to 300°C.

**TGA analysis**
Thermogravimetric analysis (TGA) was carried out using a thermobalance (Q5000, TA Instruments). In particular, the samples were heated from 30°C to 800°C at a rate of 10°C/min in fluxing air.

**Results and discussion**
The morphology of single GNP unities and their aerogels was investigated by scanning electron microscopy (SEM). The SEM micrograph of GNP is given in Figure 1a. The petal-shaped unities, shown in Figure 1a, have two main dimensions of ca. 80 μm and a thickness of only a few tens of nanometer. As visible in Figure 1b, these petal-like structures are randomly distributed in the aerogel bulk, and a very porous solid results.

Figure 2 shows the X-ray diffraction (XRD) diffractogram of a graphite nanoplatelet sample. According to the Scherrer equation, the average GNP thickness is 15 nm.

Graphite nanocrystals are much more chemically reactive than the ordinary graphite flakes; consequently, a number of graphite derivatives can be easily prepared using such nanoscopic graphite crystals as reactant (for example, graphite nanoplatelets can be quantitatively and quickly converted to graphite oxide by the Hummers method [10]). The free radical addition to the carbon-carbon double bond is a typical reaction involving benzene (C₆H₆) and other polycyclic aromatic compounds; as a consequence, graphene, fullerences, carbon nanotubes, and other nanostructures based on the $sp^2$ carbon could

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**Figure 1** SEM micrographs showing the morphology of the graphite nanoplatelets (a) and the GNP aerogel (b).

**Figure 2** XRD diffractogram of the graphite nanoplatelet sample.
also give the same type of reaction. Therefore, the chemical cross-linking of graphite nanoplatelets could be based just on this type of reaction, but a bi-radical molecule should be used in order to graft simultaneously two GNP unities. Elemental sulfur is made of S₈ rings, which is converted into a linear polymeric bi-radical molecules (·S-S₆-S·) at a temperature of 160°C; such reaction is known as \( \lambda \)-transition. The \( \lambda \)-transition of elemental sulfur is an endothermic process which is clearly visible in a DSC thermogram [11]. In particular, the DSC thermogram of elemental sulfur contains three endothermic signals: (1) the \( \alpha \rightarrow \beta \) transition of the sulfur crystals at 98°C, (2) the melting of the \( \beta \)-crystals at 116°C, and (3) the \( \lambda \)-transition at 160°C (see Figure 3 (thermogram a) and Table 1).

The isothermal annealing of the reactive sulfur/GNP system at temperatures higher than 160°C allows a more or less complete conversion of polysulfur bridges (C-S₈-C) to monosulfur bridges (C-S-C) which are sort of electrical connections between the graphene planes because conjugation is possible through the sulfur atom. When the GNP-based aerogels are devoted to electrical applications (e.g., electrodes for batteries and supercapacitors, electrolysis cells, etc.), such type of chemical cross-linking results are extremely convenient.

The \( \lambda \)-transition is characterized by a clearly visible endothermic signal (the enthalpy change is 1.10 J/g), and it can be detected also in the DSC analysis of S/GNP mixtures (see Figure 3 (thermograms a and b)). Consequently, important information on the chemical interaction between sulfur and GNP can be obtained by DSC analysis.

In particular, the change of the S-S bond concentration (i.e., the \([\text{S-S}] / [\text{S-S}]_0\) value) can be calculated by analyzing the change in the enthalpy variation of the \( \lambda \)-transition signal. In particular, the thermal treatment of the S/GNP systems significantly modifies the DSC thermogram: the melting peak of the \( \beta \)-sulfur at 116°C disappears, and the \( \lambda \)-transition peak results strongly decreased because the \([\text{S-S}]\) is proportional to \( \Delta H \) of the \( \lambda \)-transition. Such decrease of the \( \lambda \)-transition peak depends on time and temperature of the thermal annealing treatment. The fraction of reacted S-S bonds (\( \alpha \)) is given by the following expression:

\[
\alpha = 1 - \frac{[\text{S-S}]}{[\text{S-S}]_0} = 1 - \frac{\Delta H}{\Delta H_0}
\]

**Table 1** Thermodynamic properties of the S/GNP system obtained by DSC

| \( T_{\alpha \rightarrow \beta} \) | \( \Delta H_{\alpha \rightarrow \beta} \) | \( T_\beta \) | \( \Delta H_\beta \) | \( T_\lambda \) | \( \Delta H_\lambda \) |
|---|---|---|---|---|---|
| °C | J/g | °C | J/g | °C | J/g |
| 98 | 1.08 | 116 | 12.5 | 160 | 1.10 |

**Figure 3** DSC thermograms of the S/GNP system. First (thermogram a) and second (thermogram b) heating run.

**Figure 4** Behavior of the reacted S-S bond fraction with time. The experimental data points have been fitted by the exponential recovery law.

**Figure 5** Theoretical behavior of the time dependence of \( \alpha \) at different temperatures.
The temporal evolution of $\alpha$ at two different temperatures (300°C and 350°C) is shown in Figure 4. As visible, the experimental data are well described by an exponential recovery function (i.e., $\alpha = a - b \times e^{-kt}$). Such experimental behavior of the reaction conversion suggests the following three-step reaction mechanism:

\[
\begin{align*}
S - S & \rightarrow 2S \\
S + C & \rightarrow S - C - C \\
S + S - C - C & \rightarrow S - C - C - S
\end{align*}
\]

The first reaction step involves the cleavage of the S-S bond with the formation of two sulfur radicals. This elemental reaction is reversible and has a slow specific rate. In the second elemental reaction, one of the two sulfur radicals is added to the carbon-carbon double bond with the formation of S-C bond and one carbon radical. Such reaction should have a fast rate because an unstable reactant (the sulfur radical) is involved. In the last elemental reaction, the carbon radical combines with the second sulfur radical with the formation of a new S-C bond. Also, this step should be very fast because the combination of two radicals is involved. The full reaction rate depends only on the slowest step which is characterized by a first-order kinetic; consequently, the rate expression is $-d[S-S]/dt = k[S-S]$, which after integration provides an exponential recovery law ($\alpha = 1 - e^{-kt}$). Finally, according to the DSC analysis, the S/GNP chemical interaction is of the first kinetic order, and the involved mechanism is a direct reaction between the sulfur radicals generated at $\lambda$-transition and the $sp^2$ carbon atoms located at the edges of the graphite nanocrystals.

In order to establish the temperature dependence of the reaction conversion, the rate constant of the reaction has been evaluated at different temperatures, giving for example the following values:

\[
\begin{align*}
k(573^\circ K) &= 7.22 \times 10^{-3} \text{ min}^{-1} \\
k(623^\circ K) &= 1.59 \times 10^{-2} \text{ min}^{-1}
\end{align*}
\]

and these values have been used to evaluate the constants in the Arrhenius law:

\[
k = A \exp\left(-\frac{E_a}{RT}\right) = 136.76 \exp\left(-\frac{5644.0}{T}\right)
\]

In particular, the activation energy of the reaction (46.9 kJ/mol) is in the same order of magnitude as a chemical bond (the S-S bond energy is ca. 213 kJ/mol). The behavior of the reaction conversion ($\alpha$) under conditions different from that experimentally evaluated can be obtained by a simulation (the temperature values can be both interpolated or extrapolated). In Figure 5, the following expression has been used: $\alpha = a_{\text{max}} \times [1-\exp(-kt)]$ with $a_{\text{max}} = -0.454 + 3.86 \times 10^{-3} \times T(\text{°C})$ (a linear behavior has been assumed for the $a_{\text{max}}$). As visible in Figure 5, a conversion degree close to 100%, which corresponds to a complete formation of monosulfur bridges (C-S-C), is possible only at a temperature higher than 350°C for a time period longer than 300 min.
The S/GNP chemical interaction was also investigated by thermogravimetric analysis. In particular, during the heating run (at 10°C/min) of a S/GNP sample (50% by weight of sulfur), some of the elemental sulfur reacts with carbon and bonds at GNP edges. In fact, such sulfur fraction cannot evaporate also at temperatures higher than the pure sulfur boiling point (444°C), and a residual sulfur content (ca. 30% by weight) results in the material, as visible in the TGA thermogram shown in Figure 6.

It has been found that mechanically resistant GNP aerogels resulted after a cross-linking treatment with elemental sulfur at 350°C for 3 h (see Figure 7). A large number of electrically conductive monosulfur bridges should be generated in these conditions, and a good electrical conductor results (with resistivity of 3 Ω cm).

Conclusions
In conclusion, the graphite nanoplatelets are very useful nanostructured materials that can be easily prepared by the oxidation-expansion-exfoliation process. GNP-based aerogels can be simply obtained by drying the concentrated GNP colloidal suspensions, and the introduction of elemental sulfur in the GNP aerogel followed by an adequate thermal annealing treatment allows a very good mechanical stabilization of the material by formation of monosulfur and polysulfur bridges between adjacent GNP units.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
VR carried out the experiments and prepared the samples. GC conceived of the experimental design and carried out the kinetic analysis. SDN developed the theoretical model and co-wrote the paper. LN participated in the design of the experiment and coordination. All authors read and approved the final manuscript.

Authors’ information
GC is a senior researcher of the Italian National Research Council, Institute for Composite and Biomedical Materials. His present research interests are in the field of advanced functional materials based on polymer-embedded inorganic nanostructures. In particular, his activity concerns the development of new chemical routes for the controlled synthesis of metal and semiconductor clusters in polymeric matrices, the fabrication of devices based on properties of nanoscopic objects (e.g., luminescence of quantum dots, tunable surface plasmon absorption of nano-sized noble metal alloys, etc.), and the investigation of mechanisms involved in atomic and molecular cluster formation in polymeric media (nucleation, growth, aggregation, etc.) by optical and luminescence spectroscopy. He has authored 150 research articles published in international journals, ten patents, and many conference papers. He is the editor of two Wiley books devoted to metal-polymer nanocomposites and is a member of the editorial board of different scientific journals.

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Acknowledgments
We acknowledge Sherlyn C. Machica for her careful reading of the manuscript.

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Received: 31 December 2012 Accepted: 5 February 2013
Published: 20 February 2013

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doi:10.1186/1556-276X-8-94
Cite this article as: Carotenuto et al.: Graphene nanoplatelet chemical cross-linking by elemental sulfur. Nanoscale Research Letters 2013 8:94.