Production of graphene-like thin film from carbon black by wet chemical method

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Abstract

Graphene attractive chemical-physical properties are largely exploited for numerous applications including the fabrication of electronic and optoelectronic devices, energy-storage materials and mechanical resonators. Graphene can also be used as conductive sheet upon which nanometer scale devices may be patterned to create single electron or few electron transistors [1].

It is widely accepted that the bottleneck in the graphene-based technology is its production on a large scale [1]. Various approaches have been used to produce graphene or graphene-like materials including one-step graphite exfoliation, chemical vapor deposition (CVD) of methane gas, graphite stamping, graphite oxide reduction and carbon nanotube unzipping. Among these, the production of graphite oxide (GO) from graphite powder and its further reduction (through chemical, thermal, or ultraviolet-assisted reduction methods) to graphene-like material is a convenient and cheap way of graphene-like sheet fabrication.'

A new approach for producing graphene-like thin films from carbon black (CB) has been recently reported [2]. In the proposed method graphene-like layers were produced in mild conditions and in aqueous environments with high yields (55% mass yield) through a two-step CB oxidation and reduction. The graphene-like layers presented a good suspendibility in water and when they dry undergo to self-assembling resulting in water-insoluble thin film.

The selected oxidative treatment provides the partial demolition of the CB microstructure and the functionalization at the edge of the basal planes of the graphitic layers (Figure 1, middle) and not on them. In this way, differently from GO, the oxidized CB preserves the original graphitic network useful for the conductivity and electronic properties. This approach for making graphene-like thin film is environmentally advantageous because all procedures are performed in aqueous media, and it is highly compatible to an industrial scale-up process.

The selected CB (furnace carbon black, N110 type) is arranged in chain-like aggregates of spherical primary particles (15-20 nm) with a narrow size distribution (Figure 1, left). CB was oxidized according to the procedure reported by Kamegawa [3]. The CB powder was treated with hot nitric acid (67 wt.%, 100 °C) under stirring for 90 hours. The purified hydro philic product (HNP) was reduced with hydrazine hydrate (100 °C under reflux) for 24 h obtaining a HNPR (Figure 1, right). Additional information about the sample preparation were reported in Alfè et al. [1]. The dried HNPR was insoluble in water and in the most common organic solvents, both polar and non-polar (water, ethanol, NMP, dichloromethane, heptane, DMF). This was attributed to an increase of hydrophobicity of the material caused by a decrease in the polar functionalities on the surface and consequent intimate self-assembling interaction between the restored graphitic planes.

Elemental analysis indicates that the hydrogen content tends to increase from 0.48 to 1.21 after the oxidation step, testifying the reduction of the dimension of the graphitic basal planes. This finding was also confirmed by UV-visible spectroscopy. The increase of the H/C ratio from 0.058 (raw CB) to 0.27 (HNP) also confirms this hypothesis. The oxidation results in the introduction of oxygenated functional groups (hydroxyl, carboxylic, carbonylic) as testified by the increase of the oxygen content from 0.6% (raw CB) to 44% (HNP). The increase of nitrogen from 0.04% (raw CB) to 1.12% (HNP) as a consequence of the introduction of nitro groups is also observed. The HNP reduction step introduces nitrogen functionalities likely in the form of hydrazones or similar structures, leading to an increase of nitrogen percentage from 1.12 (HNP) to 6.09 (HNPR). Is it noteworthy that the oxygenated functionalities are not completely removed upon the chemical reduction. However it represents an expected result, since it is well known that CB oxidized with nitric acid has not oxygen atoms on basal planes in the form of epoxides, but only on their edges [3]. The H/C ratio kept nearly constant (0.27-0.32) after the reduction step suggesting that the size of the graphitic units remains rather unchanged.

The ATR-FTIR investigation demonstrates the introduction of different types of oxygenated functionalities that are completely absent in the raw CB. In both HNP and HNPR the presence of C=O is detected. The intensity of the C=O signal is significantly lower in the HNPR as a consequence of the removal of carboxylic-carbonylic functionalities upon the reductive treatment. The reductive treatment also introduce NH_2 functionalities in the form of hydrazones. The presence of nitrogen atoms in both HNP and HNPR in the form of nitro groups is also detected.

Thermogravimetric analyses indicate that the oxygenated functionalities begins to decompose at 150 ℃ (up to 40% weight loss). The HNPR mass loss is lower (up to 20% weight loss) as a consequence of the lower number of oxygenated functionalities, partially removed upon chemical reduction.

The bulk oxidation of both HNP and HNPR (590 ℃) occurs at a lower temperature with respect to the pristine CB (690 ℃) consistently with the strong degradation of the graphitic backbone upon the wet oxidative treatment. It is noteworthy that the oxidation of HNP and HNPR occurs at the same temperature, suggesting a similar size of the graphitic core.

The HNPR is characterized by a good suspendibility in water (ζ-potential lower than -30 mV in a wide pH range). When a HNPR suspension dries on a plane surface the graphene-like layers undergo to self-assembling resulting in flat water-insoluble thin film that easily conform to any feature of that surface.

AFM measurements provide information about the surface features of the HNPR film. Figure 2 shows the topographic images acquired on the HNPR deposited on a mica plate and dried at room temperature. The image, acquired in the True Non Contact^{TM} mode of operation of a XE-100 Park system, is reported together with a line profile representative of the surface morphology. The surface of the HNPR film looks atomically flat over large areas.

Raw CB and HPN did not reveal any electrical current up to an applied voltage of 10 V. On the contrary, on the HPN film shows an ohmic behavior of the I−V characteristic. The evaluated resistivity on a 20 nm thick film is 6 Ω m.

For a convenient exploitation of the process and film thickness control it is fundamental to explore carefully each aspect of the film preparation. It has been found that the quality of the thin film is strongly dependent on the pH of the graphene-like layers suspension. Studies are underway to clarify this important point.

References

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Figures

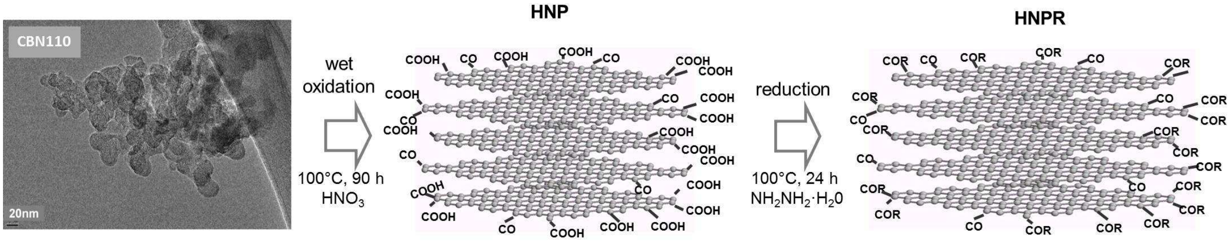

Figure 1

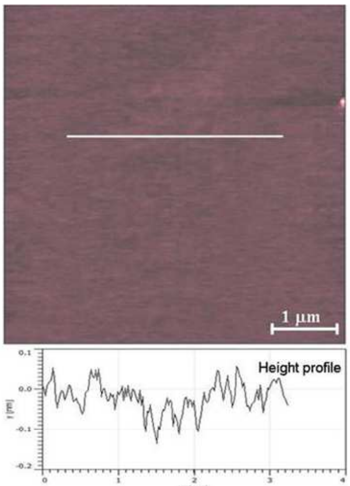

Figure 2. Non-contact AFM topographic image on the HNPR, 5 µm x 5 µm; together with the height profiles, along the white line in the image.