Nitrogen-Doped Graphene Synthesis and Characterization

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Crystalline sp^2 carbon materials (*e.g.* carbon nanotubes, graphene) are better electrical conductors than amorphous carbons. Graphenes are of great interest for hydrogen storage [1] since they are characterized by high specific surface area (SSA) when properly exfoliated [2].

Very often the ultrasonication of graphite does not produce high SSA graphene [3]. In order to obtain a high-SSA microporous 3D structure, a different synthetic strategy was used: first, as a reference, polyacrylamide (PAM) was carbonized and activated to obtain a defective structure with sp^3 atoms in the sp^2 C sheets (cPAM) able to promote hydrogen adsorption [4]; then, acrylamide was polymerized in-situ with graphene oxide (GO), with the aim to introduce spacers between GO sheets, followed by activation (GO-cPAM).

Porosimetry (BET, N_2, 77K, 1 bar, Figure 1) indicate a micro-mesoporous structure for the three materials and an increased value of SSA for GO-cPAM (800 m^2/g) with respect to GO (97 m^2/g) and cPAM (509 m^2/g). This reveals a certain synergic contribution of both starting materials in the composite.

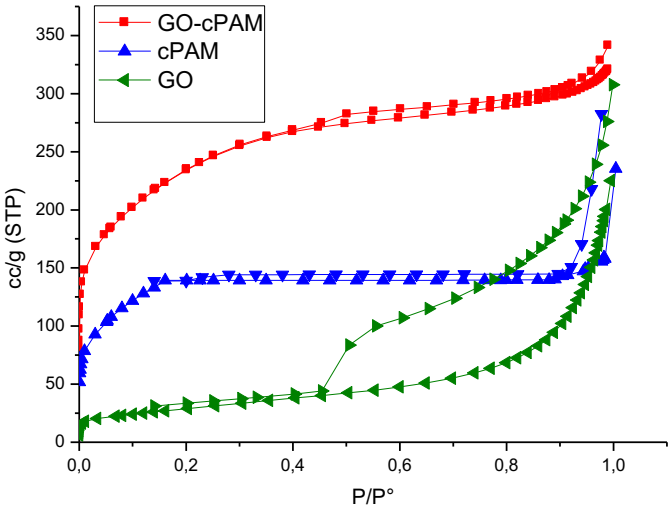

Figure 1: N_2 sorption isotherm at 77K of GO, cPAM and of GO-cPAM.

References

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The main features in the Raman spectra of carbons are the so-called G and D peaks, which lie at around 1560 and 1360 cm^{-1}, respectively, for visible excitation. The G peak is due to the bond stretching of all pairs of sp^2 atoms in both rings and chains. The D peak is due to the breathing modes of sp^2 atoms in rings [5]. The intense T peak (1094 cm^{-1}) in the GO spectrum, due to large amounts amorphous carbon, may be due to the high oxidation extent of the pristine graphite. The typical signals of graphene-like materials are displayed in the Raman spectra (Figure 2) but with significantly differences in intensity and shift of the peaks. Doping up-shifts and sharpens the G peak for both holes and electrons, this effect is more evident for GO-cPAM. Disorder can be monitored via the D peak: the higher intensity and broadening indicate a higher number of defects in GO-cPAM.

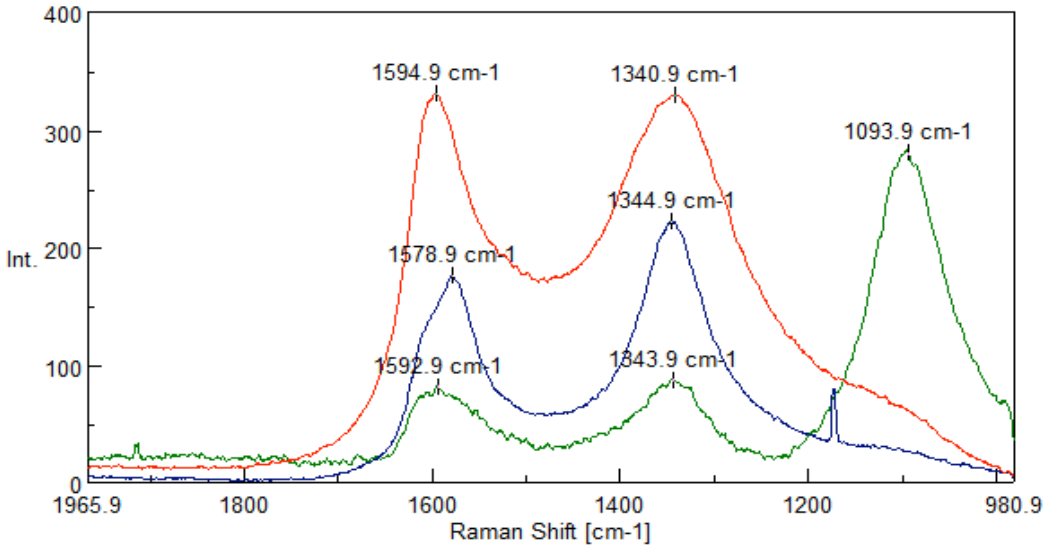

Figure 2: Raman spectra (λ = 532.11 nm) of GO (green), cPAM (blue) and GO-cPAM (red).

SEM images (Figure 3) show some differences in the morphology for the two materials: both exhibit highly curved, wrinkled smooth surfaces; GO-cPAM is more heterogenous with a more bumped surface (Figure 3b).

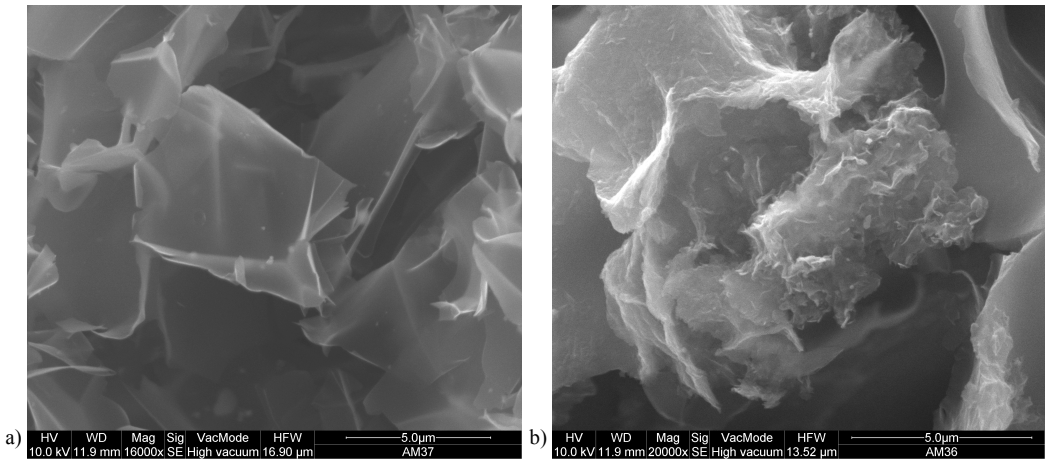

Figure 3: SEM images of cPAM (a), and of GO-cPAM (b).

In conclusion, N-doped porous graphene has been prepared and characterized: it has been demonstrated that the acrylamide polymerization can swell GO and it is able to enhance the micro-porosity of the resulting carbonaceous material. The production of GO (graphite oxidation and exfoliation) needs to be optimized in order to increase the SSA of the final materials, before it can be usefully applied for hydrogen storage.