Graphene Oxide: the role of chemical composition on the properties of thin films

R. Sánchez-Hidalgo,
D. López-Díaz and M.M.
Velázquez

rusahi@usal.es

Departamento de Química Física, Universidad de Salamanca, Plaza de los
Caídos s/n, 37008 Salamanca, Spain

Graphene oxide (GO) has recently become an attractive building block for fabricating graphene-based functional materials, this is because it possesses unique set of properties arising from oxygen functional groups that are introduced during chemical oxidation of the starting materials. Large-area GO thin-film offers a route towards GO-based thin-film electronics and optoelectronics. However, several issues can be explored to modulate the properties of these films. One important issue is to investigate the role of the chemical composition of the graphene oxide samples on the properties of thin films. This information is critical to modulate the structure of graphene oxide films according to the properties needed for different technological applications. With this objective in mind, we analyze the effect of the chemical structure on the graphene oxide films deposited onto Si/SiO$_2$. Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) methodologies were chosen. These methods were selected because they allow a great control of the packing density and since each technique provides different contact between the solid support and the molecules adsorbed at the interface we expect that allow us to understand the role of the chemical structure on the properties of GO thin films. To synthesize graphene oxide of different functionalization, two starting materials, graphite and GANF® nanofibers [1], were used. The oxidation procedure was a slight modification of Hummers method reported previously by our group [2,3]. The samples thus obtained were subsequently purified by alkaline washing and its chemical composition was analyzed by XPS. GO samples were also characterized by zeta potential and Dynamic Light Scattering measurements. Results show that the percentage of COOH groups attached to graphene oxide obtained from

nanofibers is twice the value corresponding to GO synthesized by graphite oxidation, while the percentage of hydroxyl or epoxy groups, localized at the basal plane for the former sample is higher. Moreover, the percentage of Csp^2 is similar for the non-purified samples. The purification procedure by alkaline washing increases the Csp^2/sp^3 ratio and renders samples of Csp^2 percentage similar to that reached by chemical reduction of graphene oxide. Small differences between the chemical compositions of purified samples synthesized from the two starting materials were observed. The electric charge and the size of sheets of graphene oxide synthesized by oxidation of graphite are higher than those corresponding to sheets obtained from GANF®. Comparison between the zeta potential values of purified and non-purified sheets allows concluding that the electric charge is always higher for purified samples than for non-purified ones. This fact is compatible with the elimination of highly oxidized organic fragments, Oxidation Debris (OD), originated by the chemical oxidation.

After samples characterization, the next step was to study the effect of the GO structure on the morphology and coverage of thin films obtained by the Langmuir-Blodgett and Langmuir-Schaefer methodologies. The morphology of films was analyzed by SEM and the coverage and the size of flakes deposited by the different methods were determined by ImageJ 1.46 software. Results show that the LB methodology renders higher coverage than the LS one. Moreover, the solid coverage reached by LB is almost independent of the C-O percentage while it increases with the percentage of C-O groups for films prepared by the LS methodology. Differences can be attributed to the distinct solid orientation in the two deposition techniques. Purified samples render lower coverage

than the non-purified ones. The OD elimination is responsible of this behavior. The flake size determined by DLS agrees very well with the value obtained from the analysis of SEM images.

References

[1] http://www.granphnanotech.com/
[2] B. Martín-García, M. M. Velázquez et al, ChemPhysChem, 13 (2012) 3682.
[3] D. López-Díaz, M.M. Velázquez, et al, ChemPhysChem, 14 (2013) 4002.