

## Aqueous phase exfoliation of graphite by cellulose nanocrystals

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Producing processable graphene flakes in large quantities remains an ongoing challenge for large-scale applications. To that end, top-down approaches such as the exfoliation of powdered graphite in the liquid phase is a very promising route due to its simplicity, utilization of low-cost and readily available graphite, upscaling potential, integration with other processes such as blending or casting and no need of transferring processes from the growth substrate. In essence, liquid phase exfoliation (LPE) involves exfoliation of graphite by simple sonication to produce graphene sheets dispersed in a solvent [1]. As graphene sheets tend to restack due to strong Van der Waals forces, the sheets need to be stabilized by different means such as covalent functionalization or the use of various stabilizers such as surfactants [2], polymers [3] and aromatic molecules [4]. The most common route for LPE involving graphite functionalization is graphite oxidation followed by exfoliation in water to yield graphene oxide, which is subsequently reduced to obtain reduced graphene oxide whose properties differ from pristine graphene. On the other hand, direct exfoliation of unfunctionalized graphite by sonication and good dispersion of produced graphene sheets require the use of stabilizers that interact noncovalently with graphene and prevent their stacking.

In this regard, the development of novel exfoliating agents and stabilizers that are widely available, low-cost, environmentally-friendly and biodegradable would definitely bring LPE one step closer towards industrial viability. To this end, we have demonstrated that nanoscale cellulosic fillers, called cellulose nanocrystals (CNC) are very efficient for graphite exfoliation and stabilization of resulting graphene flakes in aqueous dispersions at high concentrations. CNCs can be regarded as very promising graphene stabilizers due to their interesting features such as low density, high surface area, good mechanical properties, biodegradability and availability from renewable resources, which has triggered rising interest during the past decade in these nanocellulose materials especially for nanoreinforcement and barrier property improvement in polymer matrices. Moreover, CNC can be obtained from cellulose, the most abundant biomass material in nature, which can be extracted from natural fibers, among other sources.

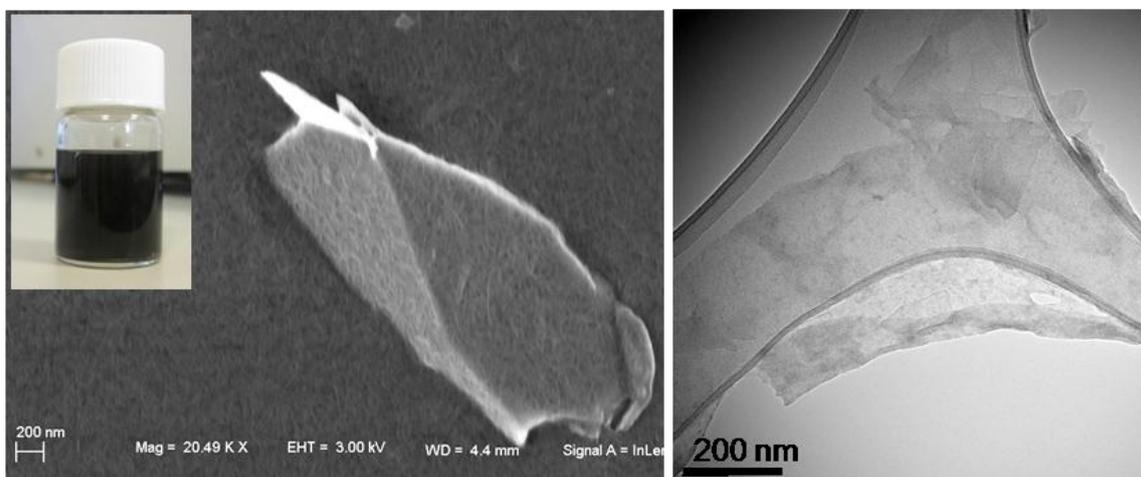
Here we have produced CNC from microcrystalline cellulose (MCC) by acidic hydrolysis. We will show that graphite can be effectively exfoliated and stabilized in aqueous CNC dispersions at very high concentrations by applying tip sonication for very short times (less than 4 h). Unexfoliated graphite is removed by centrifugation and the resulting dispersions are stable for months without noticeable precipitate. CNC-stabilized graphene dispersions have been characterized by FESEM, TEM, UV-Vis absorption and Raman Spectroscopy. Figure 1 show representative FESEM and TEM images of the exfoliated samples. In samples produced at large ratios of CNC to initial graphite concentration, cellulose nanocrystals are clearly visible as small whiskers covering the surface of the graphene flakes in the SEM image. Overall, TEM reveals the presence of large sheets of up to several micrometers in length whose size decreased with sonication time. We will show that the effectiveness of CNC as graphene stabilizers depends largely on the size and functionalization degree of the nanocrystals. Other parameters, such as the concentration of stabilizer and starting graphite as well as their concentration ratio, have been optimized in order to increase both final graphene concentration and graphene/stabilizer ratio. In the optimal conditions, stable 1.7 mg/mL graphene dispersions with remarkably high ratios of graphene to CNC concentration (up to 5.4) have been obtained, an aspect that is crucial as an excess of stabilizer can affect adversely the mechanical, thermal and electrical properties of graphene-based composites.

## References

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## Figures



**Figure 1.** FESEM (left) and TEM (right) images of exfoliated graphene flakes by cellulose nanocrystals. Inset: photograph of CNC-stabilized graphene aqueous dispersion