NewTimes – New Trends in Materials Science and Engineering
1st International Virtual Conference
14-18 June 2021

Session: *New trends in nanotechnology, nanostructures and nanoscience*

Sustainable Liquid-Phase Exfoliation of Layered Materials with Nontoxic *Polarclean* Solvent

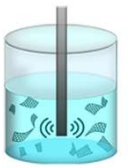
J. De Santis[1], V. Paolucci[1], G. Di Iorio[1], A. Politano[2,3] and C. Cantalini[1]

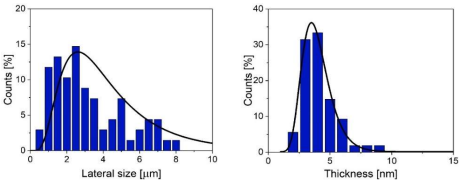
1. Dept. of Industrial and Information Engineering and Economics, Piazzale Pontieri, 1 – 67040 Monteluco di Roio – University of L'Aquila, Italy
2. Dept. of Physical and Chemical Sciences, University of L'Aquila, via Vetoio, 67100 L'Aquila (AQ), Italy
3. CNR-IMM Istituto per la Microelettronica e Microsistemi, VIII strada 5, I-95121 Catania, Italy

Introduction

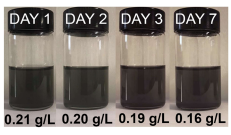
Liquid-phase exfoliation (LPE) is the most suitable platform for large-scale production of two-dimensional materials. One of the main open challenges is related to the quest of green and bio-derived solvents to replace state-of-the-art dispersion media, which suffer several toxicity issues. Here, we demonstrate the suitability of methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv®Polarclean) for sonication-assisted liquid-phase exfoliation of layered materials for the case-study examples of WS_2, MoS_2 and graphene. Given its compatibility in terms of physicochemical properties and its *green* features, Polarclean paves the way to large-scale production of layered materials suitable for applications in agri-food industry (i.e., for concentration of fruit juices, volatile aroma compounds and whey proteins) or sea-water desalination for production of drinking water, to date hindered by the toxicity of state-of-the-art solvents for LPE (i.e. NMP and DMF).

WS_2 powder was dispersed in 40 mL of solvent and sonicated for 3h in bath sonicator in a thermostat bath to prevent excessive temperature rise (T≤25 °C).
In order to physically remove the solvent, several centrifuges were carried out.





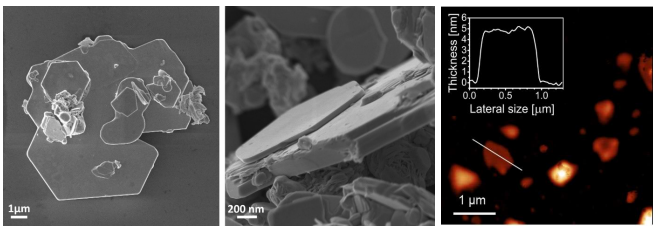
Statistical analysis of lateral size and thickness of WS_2 flakes based on SEM and AFM images demonstrate that lateral size and thickness of the flakes approximately follow log-normal distribution peaked at ~3 µm and ~4 nm respectively.



The efficiency of Polarclean for obtaining high-yield and stable dispersions of flakes of 2D materials was validated by means of the analysis of dispersed flakes for the case-study example of WS_2.

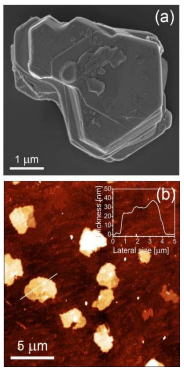
Results

The morphological characterization of exfoliated WS_2 flakes was carried out by means of SEM and AFM microscopy. The images reveal the occurrence of flakes with different lateral sizes generally larger than 1 µm and well-defined hexagonal edges.

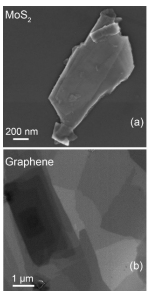


The representative AFM and the corresponding height profile collected along the white line, allow concluding that Polarclean assisted LPE provides flakes with an aspect ratio of ~10^3.

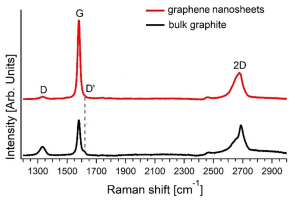
Direct comparison, carried out in the same operating conditions, with LPE using N-methyl-2-pyrrolidone (NMP) solvent revealed that the yield of few-layers flakes (with thickness <5 nm) in dispersions obtained by using Polarclean is increased by ~350% as compared to the case of liquid-phase exfoliation performed with NMP, maintaining comparable values of the average lateral size.



The procedure was extended also to MoS_2 and graphene. Regarding MoS_2, statistics reveal results comparable with that of WS_2. For graphene, remarkably the distribution of lateral size shows an average value of 10 µm, which is one of the largest ever reported for LPE.



Moreover, the I_D/I_G ratio as low as 0.07±0.01 in graphene Raman spectra evidences the very low amount of defect induced by exfoliation.



Conclusion

Our results indicate that Polarclean represents a green candidate solvent for large-scale and scalable production of functional inks based on 2D materials, which naturally enables expanding the use of 2D materials in several application fields, for which state-of-the-art solvents have represented so far serious obstacles, owing to their toxicity.

References

1. Paolucci, V.; Olimpio, G. D.; Lozzi, L.; Mio, A. M.; Ottaviano, L.; Nardone, M.; Nicotra, G.; Le-Cornec, P.; Cantalini, C.; Politano, A., *ACS Sustain. Chem. Eng.* 2020.
2. Coleman, J.N.; Lotya, M.; O'Neill, A.; Bergin, S.D.; King, P.J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R.J.; et al., *Science (80).* 2011, *331*, 568–571.
3. Salavagione, H.J.; Sherwood, J.; De Bruyn, M.; Budarin, V.L.; Ellis, G.J.; Clark, J.H.; Shuttleworth, P.S., *Green Chem.* 2017, *19*, 2550–2560.
4. Paolucci, V.; Emamjomeh, S.M.; Nardone, M.; Ottaviano, L.; Cantalini, C. , *Nanomaterials* 2019, 1–17.
5. Randová, A.; Bartovská, L.; Morávek, P.; Matějka, P.; Novotná, M.; Matějková, S.; Drioli, E.; Figoli, A.; Lanč, M.; Friess, K., *J. Mol. Liq.* 2016, *224*, 1163–1171.