Study on Non-covalently Stabilzed Graphene in chemical PVA-MA based Hydrogel

Yosra Toumia, Silvia Orlanducci and Gaio Paradossi

Department of Chemical Science and Technology, University of Rome "Tor Vergata",00133, Rome, Italy
toumiayosra@hotmail.com

Currently, graphene has been the most attractive nanomaterial in the scientific community and has lead to an explosion of creativity and productivity in different fields due to its 2D planar structure and its unique fascinating chemical and physical properties [1].

In the recent years, graphene has become a prevalent topic in the materials community, crossing numerous studies on soft materials aiming at biomedical applications such as sustained drug delivery. Thus, graphene and its derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) inspired the investigators to try to incorporate them in hydrogels, taking advantage of the flexible and ultrathin planar structure of graphene sheets in constructing a 3D network of hydrogels [2]. Most researches reported the use of graphene derivatives in hydrogels (as GO and rGO) because of the relatively high concentrated dispersions achieved by modifying the graphene surface structure through the oxidation process (up to 7 mg/ml) [3] . However, the use of pristine graphene is still limited. Herein, to the extent that we do not damage the structure and preserve the electric properties that does the pristine graphene have, we have directly exfoliated graphite to graphene in water-surfactant solution. Via ultrasonication and by a non destructive π-π stacking interaction with the poly(ethylene glycol) 2,4,6-tris(1-phenylethyl)phenyl ether methacrylate used as surfactant, we expect to preserve the graphene structure. Optimization of the conditions to obtain stable dispersions with a significant graphene content elicited the Raman characterization of the samples in order to gain information regarding the exfoliation quality and the presence of graphene monolayer as well as flakes formed by few layers sheets with limited defects. The surfactant functionalized graphene was then crosslinked via a free radical photo-polymerization to methacryloyl- modified polyvinyl alcohol (PVA-MA), a widely used polymer because of its good mechanical properties and biocompatibility [4], to form an hybrid hydrogel, i.e. graphene/PVA-MA/H_2O. The incorporation of graphene sheets in the hydrogel was confirmed by Raman spectroscopy. The hybrid hydrogel was characterized using rheology, differential scanning calorimetry, and confocal microscopy. We observed a significant increase in the elastic modulus, G', with respect to the native hydrogel, despite the low amount (0.1mg/ml) of graphene. In another experiment, oligomers of poly(N-isopropylacrylamide), pNiPAAm, a well known thermosensitive polymer, were also incorporated. In this way the graphene based hydrogel exhibits an additional property such as thermoresponsivity characterized by a volume phase transition at temperatures close to 37 °C.

Hydrogels based on multifunctionality and with interesting mechanical properties are a promoting material for wide applications in the design of drug carriers systems, tissue engineering and biosensoring.

References

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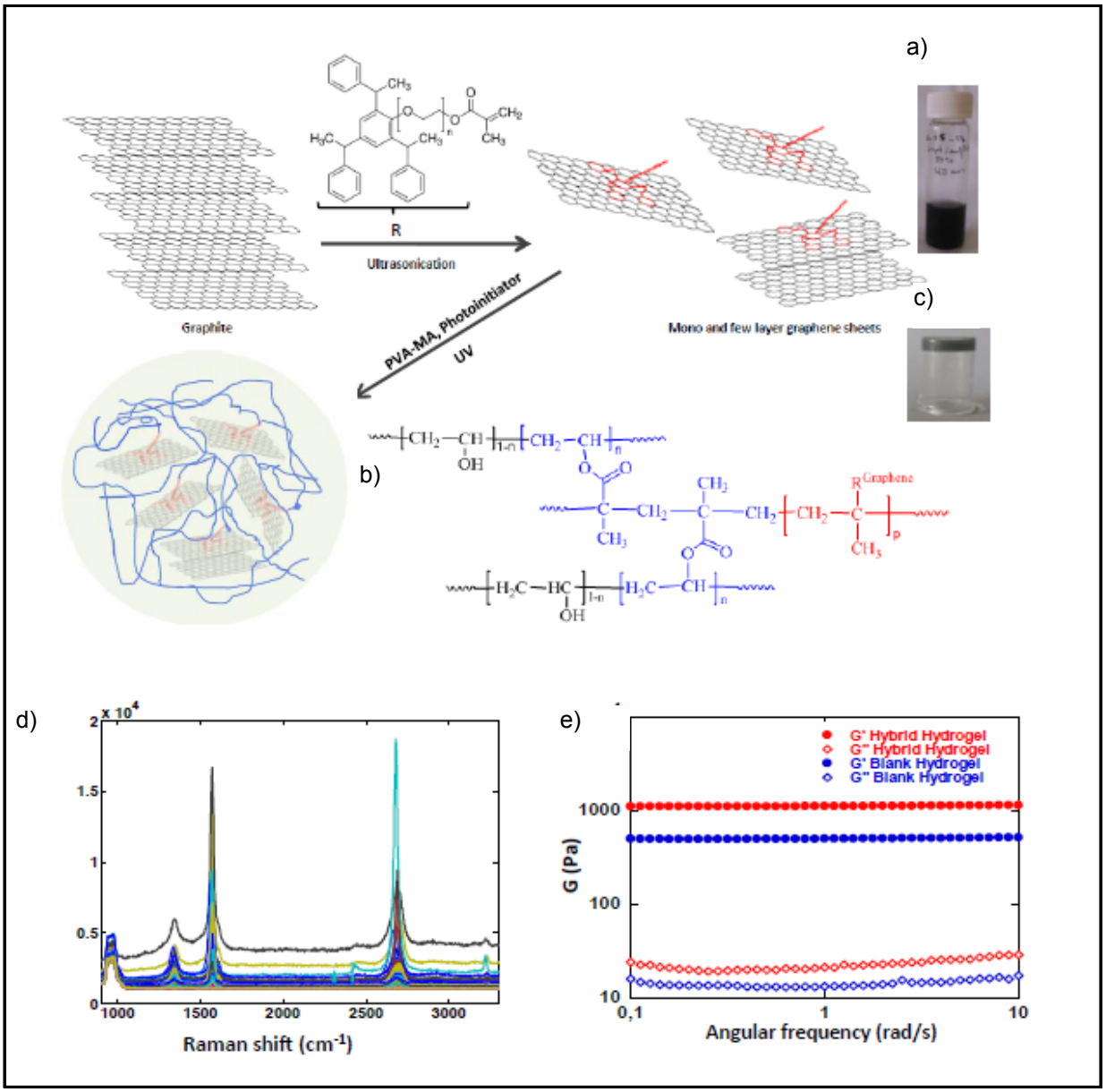
Figures



Water stabilized graphene (0.1 mg/ml) by surfactant poly(ethylene glycol) 2,4,6-tris(1-phenylethyl)phenyl ether methacrylate (a); Graphene PVA-MA hydrogel structure (b); Photograph of 0.2 % (w/w) grapheme / dry PVA-MA hydrogel (c); Raman spectra of the graphene dispersion, laser excitation 532 nm (d); Viscoelasticity measurements on 0.2 % (w/w) graphene/ dry PVA-MA hydrogel (Hybrid Hydrogel) and surfactant functionalized PVA-MA hydrogel (Blank Hydrogel) (e).

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