

## Functional hybrids of multilayer CVD graphene and colloidal anatase nanocrystals

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UV-light photoactive hybrids based on CVD graphene (from 1 to 5 layers) decorated with TiO<sub>2</sub> nanocrystals (NC) surface functionalized with 1-pyrene butyric acid (PBA), were prepared by a simple solution-based procedure. PBA functionalization was obtained by a capping exchange procedure onto pre-synthesized organic-capped NCs [1].

An in-depth physico-chemical characterization demonstrated the successful immobilization of the colloidal NCs on the graphene multilayers, which preserves or even enhances the graphene intrinsic structural properties: the electrical conductivity is higher than that measured for bare graphene, due to a p-doping effect, related to a hole transfer from the nano-objects to graphene, mediated by the short aromatic ligand acting as a charge channel.

The hybrids properties are strongly dependent on the number of layers of CVD graphene. The use of two redox probes [inner-sphere, surface sensitive (K<sub>4</sub>Fe(CN)<sub>6</sub>) and outer-sphere, surface insensitive (Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>)], in a CV and EIS study, allowed to understand these features, showing a strong difference between the mono-, the bi- and the other multi-layers, in terms of different diffusional mechanism and redox active sites [2]. Moreover, the stacked layers of the pyrene-coated TiO<sub>2</sub> NCs are found to increase the electroactivity, the capacitive behavior, as well as the photo-electrical response of graphene, concomitantly maintaining its high charge mobility. The photoelectrical conversion of the hybrid is enhanced of 50% with respect to the bare graphene, with a long recombination lifetime of the photogenerated electron-hole pairs.

For all the above reasons, the photoactive composite has a great potential as an optically transparent component for manufacturing photoanodes to be integrated in solar cells or photodetectors and in FETs or (photo)electrochemical sensors, also exploiting the possibility of photorenovating the sensor surface [3].

[1] C. Ingrosso et al., *ACS Appl. Mater. & Interfaces* **7** (2015) 4151-4159.

[2] D.A. Brownson, D.K. Kampouris, C.E. Banks, *Chem. Soc. Rev.* **41** (2012) 6944-6976.

[3] V. Pifferi et al., *Anal. Bioanal. Chem.* **408(26)** (2016), 7339-7349.

**Acknowledgements** The authors acknowledge the MIUR National Project PRIN 2012 (prot. 20128ZZS2H).