

Photoactive Hybrid Materials based on Colloidal Nanocrystals and CVD Monolayer Graphene

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Graphene (G) has attracted interest of scientific community for its unique electrical and thermal conductivity, light transparency from visible to infrared and high surface area [1]. As a matter of fact, at present, G is an extraordinarily attractive structural material for sensors, solar cells, supercapacitors, batteries and photocatalytic devices. A large variety of molecular hybridization strategies can be implemented for decorating G, in order to improve its pristine functionalities or to convey novel properties. Colloidal nanocrystals (NCs), prepared by means of solution-based colloidal chemistry routes, are particularly interesting for chemically decorating G, because their surface is coordinated by a layer of surfactant molecules, whose chemistry can be tuned by implementing suitable ligand exchange procedures, and allows to immobilize them on diverse surfaces. NCs with their unique fundamental properties, have been widely exploited in a plethora of applications, such as electronics, energy conversion, environment and life science. Thus, chemical functionalization of G with NCs allows preparation of hybrid materials with original properties, since the outstanding functionalities of G merge with the original size- and shape-dependent properties of the NCs [2].

Here, a solution-based strategy is proposed for functionalizing a large area, monolayer G film, grown by chemical vapor deposition (CVD), with size-tunable light absorbing colloidal PbS NCs and photoactive semiconducting TiO₂ NCs [2]. A surface capping exchange procedure has been performed on the organic-coated NCs for functionalizing them by 1-pyrene butyric acid (PBA), resulting in stable and optically transparent solutions, where the nano-objects preserve morphology and optical properties. Then, the PBA-coated NCs have been immobilized on CVD G film by incubation of G in a dispersion of the nano-objects. The proposed use of pyrene as capping ligand directly coordinating the NC surface for linking chemically the nano-objects to G, to the best of our knowledge, represents an original approach, that has not been reported in literature so far. The achieved hybrid materials have been investigated by spectroscopy, microscopy and electrical techniques. The results demonstrate that the NCs successfully anchor on G platform in highly interconnected multilayers, by means of multiple and cooperative π - π stacking interactions promoted by the pyrene ligand coordinating NC surface (Fig.1 A-B). After functionalization, the hybrid based on PbS NCs and G exhibits a sheet resistance ca. 3% lower than that of bare G (Fig. 1 C) which is explained by transfer of holes at the interface from PbS NCs to G according to the energy level diagram reported in panel D of Fig. 1 [2]. The manufactured hybrid materials can be interesting for integration in components for optoelectronics, photocatalytic systems, sensors and optical communication and information technology devices [3].

References

[1] A.K. Geim et al. *Nat. Mater.* 6 (2007) 183

[2] C. Ingrosso et al. *ACS Appl. Mater. Interfaces* 7 (2015) 4151

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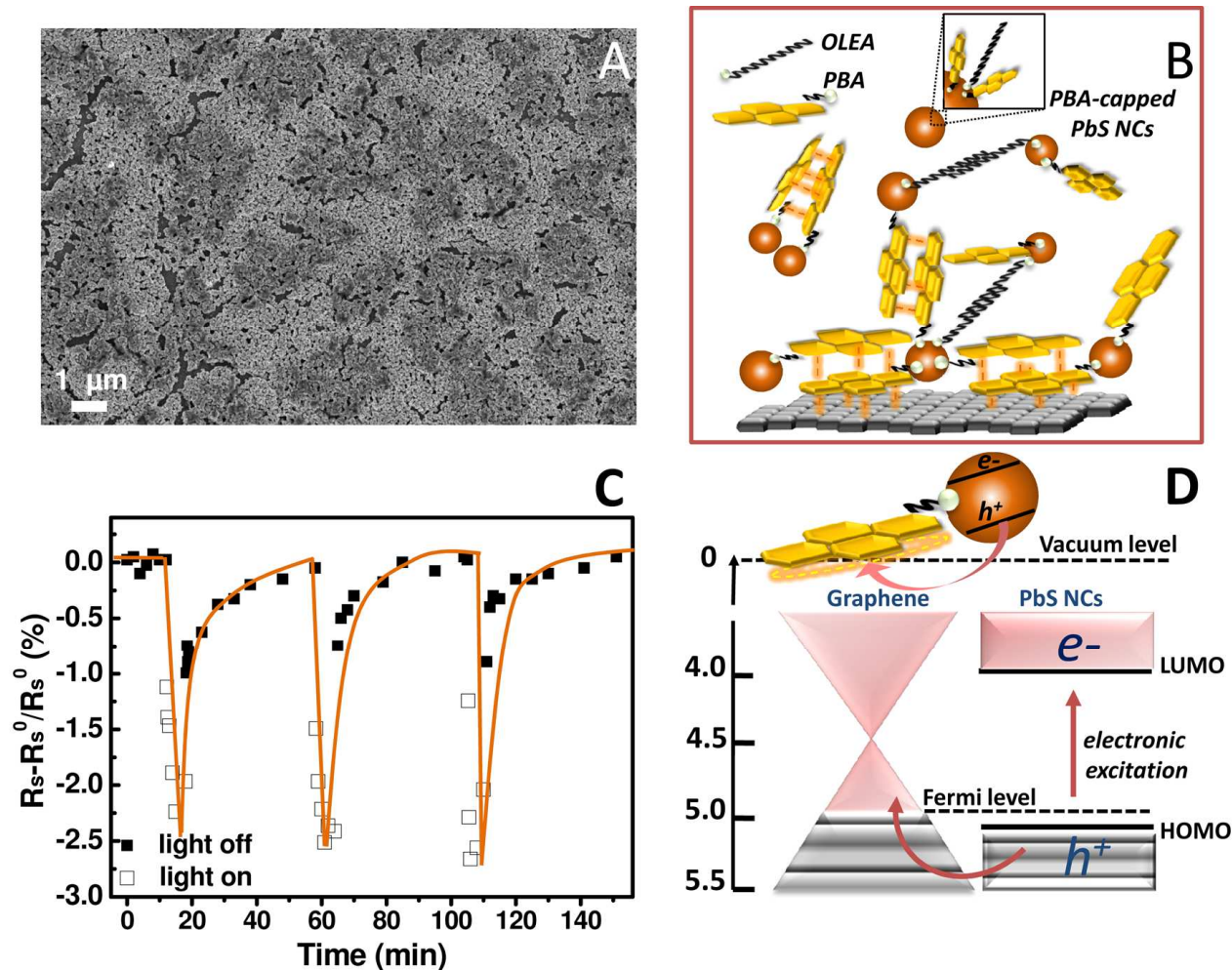


Figure 1. (A) SEM micrograph of CVD G film decorated by PBA-capped PbS NCs. (B) Sketch of the PBA-coated PbS NCs anchored to G. (C) Monitoring of the change of the sheet resistance of G decorated with PBA-capped PbS NCs under three cycles of light irradiation being $R_s^0 = 1000 \text{ Ohm}\times\text{sq}^{-1}$ the sheet resistance in the dark. (D) Sketch of the energy level diagram of G and PbS NCs and cartoon of hole stabilization by the pyrene linker capping NC surface.