

## Toward multifunctional gold nanoparticles/graphene hybrid assemblies associated to photoactive molecules

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Light-induced doping with excited-state electron donors or electron acceptors is a versatile strategy for the fabrication of photoactive carbon-based nanocomposites (CBN).

Important contributions stem from  $\pi$ - $\pi$  interactions with amphiphilic porphyrinoids. Depending on the architecture organization, photophysical studies showed strong electronic communications between the chromophoric moieties and carbon nanotubes.[1]

Gold nanoparticles (AuNP) are one of the most interesting nanostructures. Among their excellent properties, the presence of a surface plasmon band in the visible region of the electromagnetic spectrum makes these materials suitable for many attractive applications in fields such as medicine, sensors, and catalysis. For these applications, an optimization of the gold particle size, the distribution of particle sizes and their dispersion on the graphene surface is desirable.

With this in mind, we have prepared AuNP supported by different CBN: graphene oxide (GO), N-doped graphene (N-G) and soft functionalized graphene (fG). The AuNP were supported in two different ways: a) by a modification of the literature sonolytic method,[2] which consists in the sonication of the support and the Au salt in aqueous suspensions; b) by the simple mixing of pre-synthesized AuNP with the support. The morphology and size distribution of the nanoparticles within the supports were studied by AFM and TEM. N-G was found to have a strong influence on the particle density and size distribution (**Figure 1**). Very fine particles in the size range of 1-3 nm were observed even though some particles were much bigger in size even up to 20 nm.

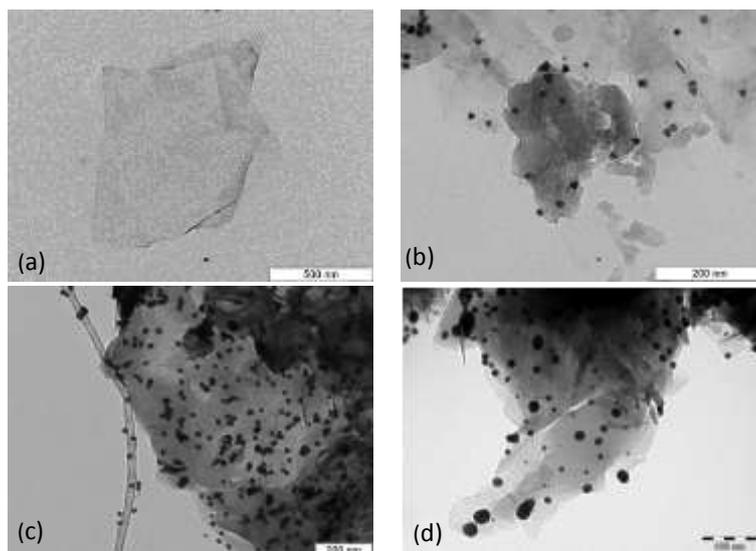
The covalent and non-covalent interactions of these hybrid materials with porphyrinoids (Por, **Figure 2**) was subsequently investigated using both steady-state and time-resolved fluorescence, including FLIM microscopy. The luminescence quenching observed (**Figure 3**) is tentatively assigned to a competition between two possible processes: photoinduced electron transfer and energy transfer. However, in the presence of CBN-AuNP composites there is an enhancement of the porphyrinoid fluorescence involving a surface plasmon coupling effect. These new nanostructures are thus expected to have selective photocatalytic and sensing abilities.

### References

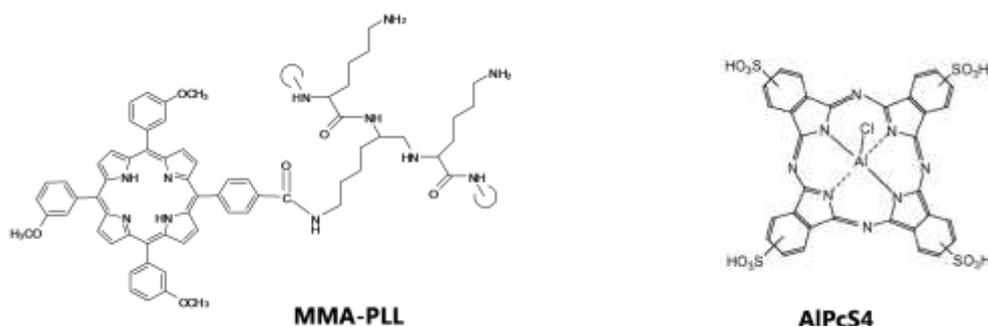
[1] S.M. Andrade, P. Raja, V.K. Saini, A.S. Viana, P. Serp, S.M.B. Costa, *ChemPhysChem* **13** (2012) 3622-3631.

[2] K. Vinodgopal, B. Neppolian, I.V. Lightcap, F. Grieser, M. Ashokkumar, P.V. Kamat, *J. Phys. Chem. Lett.* **1** (2010) 1987-1993.

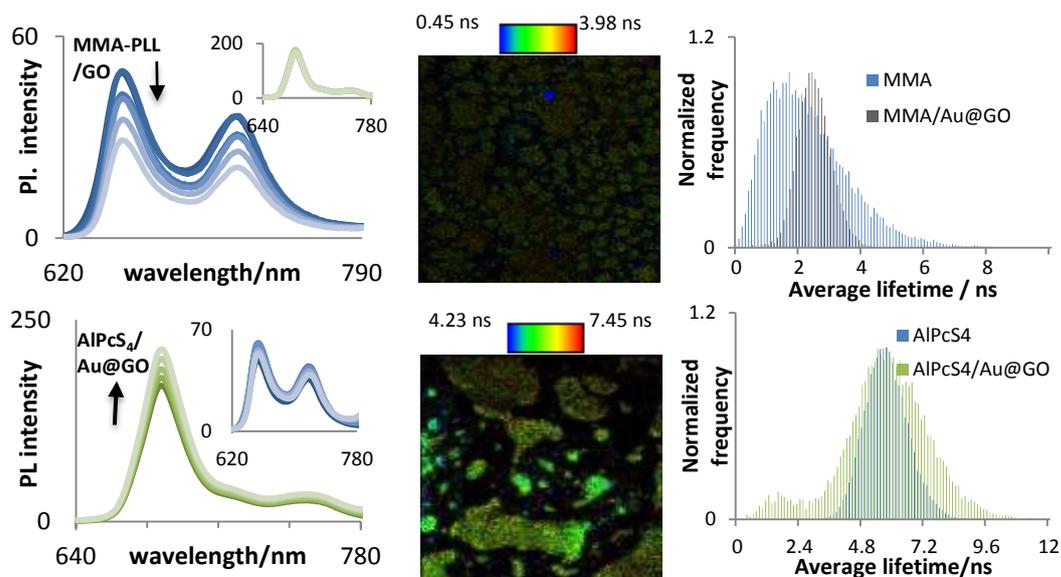
**Acknowledgements:** Project PTDC/Qui-Qui/117498/2010 funded by FCT is acknowledged.



**Figure 1.** TEM images showing (a) GO, and AuNP anchored on (b) GO; (c) N-G and (d) fG (right) sheets, prepared using a modified sonolysis method.



**Figure 2.** Porphyrinoids used in this study: *meta*-methoxy-phenyl porphyrin monosubstituted with a polylysine chain (MMA-PLL, left) and tetrasulfonated aluminium phthalocyanine (AIPcS<sub>4</sub>, right).



**Figure 3.** Left: Fluorescence spectra of Por/GO and Por/Au@GO (MMA-PLL, blue; AIPcS<sub>4</sub>, green); Center: FLIM images of MMA-PLL (top) and AIPcS<sub>4</sub> (bottom) in the presence of GO; and Right: Fluorescence lifetime distributions of MMA-PLL (top) and AIPcS<sub>4</sub> (bottom) alone and in the presence of Au@GO.