Carbon-based Materials for Solar-driven Catalysis

C. Casadevall[1,2,3], V. M. Badiani[3], A. Lage[3], A. Vijeta[3], M. Garcia-Melchor[4], E. Reisner[3]

[1]Department of Chemistry, University Rovira i Virgili (URV), C/ Marcel.lí Domingo, s/n, 43007, Tarragona (Spain)
[2]Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona (Spain), ccasadevall@iciq.es
[3]Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, U.K.
[4]School of Chemistry, Trinity College Dublin, College Green, Dublin 2, Ireland.
ccasadevall@iciq.es, carla.casadevall@urv.cat

Carbon dots (CDs) and carbon nitrides (CNxs) are promising carbon-based materials that have garnered increasing interest as they are easy and inexpensive to synthesize, biocompatible, environmentally benign, water soluble, and display excellent photoluminescence and fluorescence, together with tunable optical properties.[1-3]

On the one hand, CDs are pseudospherical polydisperse nanoparticles (1-10 nm) that consist of a carbonaceous core stabilized by oxidized surface groups. We have applied them to produce solar fuels and chemicals. First, we deconvoluted the different sizes that form the bulk material. TEM and DLS confirm size-dependent separation and the monodisperse fractions show a size-dependent UV-vis and fluorescence spectroscopy response. A size-dependent effect on the photocatalytic H2 evolution performance of the CDs in combination with a Ni cocatalyst has been demonstrated with a maximum activity at approximately 2-3 nm CD diameter. Then, for the first time, positively and negatively surface-functionalized CDs have been interfaced with the CO_2-to-formate reducing enzyme formate dehydrogenase to study the enzyme-material interface during photocatalytic CO_2 reduction.[4] Finally, we show CDs for metal-free light-driven trifluoromethylation of aromatic compounds, including biological molecules, as well as cross-coupling of aldehydes, and a light-driven dual Ni/CDs photocatalytic system for photoredox catalysis.

On the other hand, CN_{xs} are emerging organic semiconductors that have had an increasing interest in organic photocatalysis, due to their scalable synthesis, recyclability and robustness due to their heterogeneous nature. In this line, graphitic carbonitride (CN_x), a polymeric material composed of heptazine units, has emerged as one of the most promising heterogeneous photocatalysts.[5] CNx has a broad absorption in the UV/Vis region and an optical band gap of approximately 2.7 eV, making it suitable for various photocatalytic applications.[6-7] In this context, we have developed a Ni doped mpg-CN_x integrated heterogeneous photocatalysts that works as a Ni single-site photocatalyst for the cooperative photocatalytic C-O and C-N bond formation reactions.[8,9]

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