Efficient hydrogen photoproduction in water with hybrid systems composed of quantum dots and molecular catalysts

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Semiconductor nanocrystals (quantum dots) emerged in the last years as an appealing alternative to molecular photosensitizers, owing to their superior stability, intense light absorption and bright luminescence. In particular, non-cadmium quantum dots seem to be a particularly interesting choice as they display good optoelectronic properties while containing no toxic elements with respect to CdSe and CdTe.[1] In the field of artificial photosynthesis, very efficient ”hybrid” photocatalytic systems for hydrogen production in water were obtained by associating Cd-based quantum dots as photosensitizers with molecular H_2-evolving catalysts in presence of a sacrificial reductant. [2,3]

In this communication, we describe new hybrid systems associating environmentally friendly (Cd-free) quantum dots with molecular catalysts based on earth-abundant metals, in order to perform photocatalytic H_2 production in purely aqueous environment.

Core-shell $CuInS_2$/ZnS nanocrystals capped with glutathione were synthesized in the aqueous phase, and their structural and optical properties were fully characterized. The nanocrystals exhibit a broad absorption throughout the visible range with orange luminescence in aqueous solution. For the photocatalysis process the colloidal solution was mixed with a cobalt macrocyclic catalyst [4] and a sacrificial reductant, and the H_2 production under irradiation was quantified by gas chromatography. This hybrid system exhibited extremely interesting performances, with a turnover number (TON, with respect to the Co catalyst) of 5900 at pH=5. The CIS/ZnS nanoparticles were also compared to widely studied CdSe nanocrystals, using the same catalyst, and the former give remarkably better performances in terms of TON.

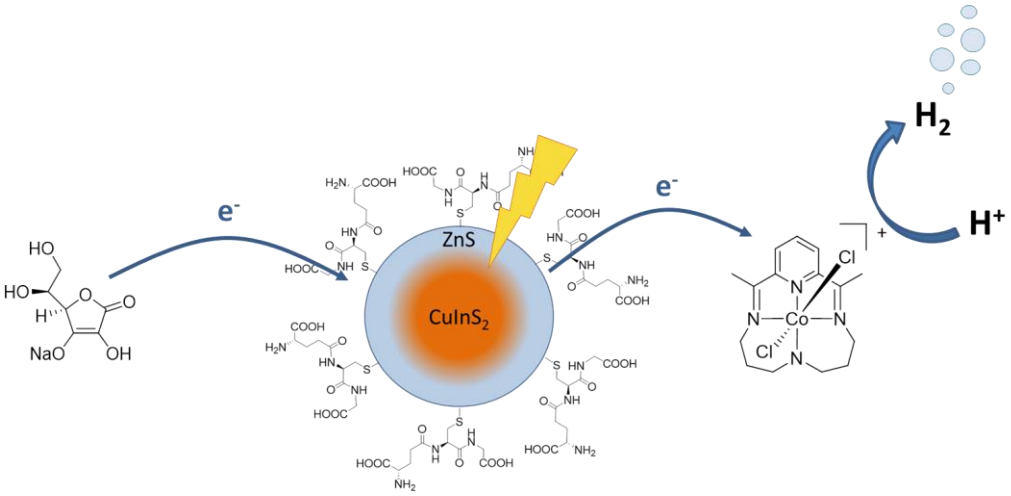

Fig. 1 Hybrid system used for the photocatalysis experiment.

1) D. Aldakov *et al.*, *J. Mater. Chem. C* **2013**, *1*, 3756-3776.
2) C. Gimbert-Suriñach *et al.*, *J. Am. Chem. Soc.* **2014,** *136*, 7655-7661.
3) Z.J. Han *et al.*, *Science* **2012,** *338*, 1321-1324.
4) S. Varma *et al.*, *Phys. Chem. Chem. Phys.* **2013**, *15*, 17544-17552.