Efficient hydrogen photoproduction in water with hybrid systems composed of $CuInS_2$ 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 and intense light absorption. In particular, non-cadmium quantum dots seem to be a particularly interesting choice to replace highly toxic CdSe and CdTe.[1] In the field of artificial photosynthesis, very efficient "hybrid" photocatalytic systems for H_2 production in water were obtained by associating cadmium-based quantum dots (photo-sensitizers) with molecular H_2-evolving catalysts and an electron donor.[2,3]
In this communication, we describe new hybrid systems associating more environmentally friendly (Cd-free) $CuInS_2$ quantum dots with molecular catalysts based on earth-abundant metals, in order to perform photocatalytic H_2 production in pure water.

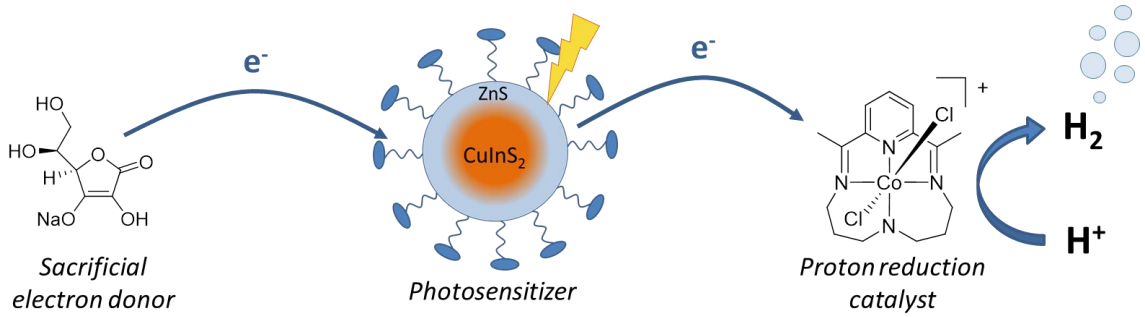

Figure 1. Hybrid system used for the photocatalysis experiment.

Water soluble core-shell $CuInS_2$/ZnS nanocrystals were synthesized in water, and their properties were characterized in solution and in the solid state. They exhibit broad absorption throughout the visible range, and orange luminescence in aqueous solution. The nanoparticles were associated to a cobalt catalyst[4] and a sacrificial reductant in acidic water (Figure 1), and H_2 photoproduction was quantified by gas chromatography. This hybrid system exhibited extremely interesting performances, with turnover number (TON) vs. catalyst of 5900 at pH=5. Compared to widely used CdSe nanoparticles and $[Ru(bpy)_3]Cl_2$, CIS/ZnS nanoparticles give remarkably better performances in terms of TON using the same catalyst. After use, the particles can be recycled in presence of fresh catalyst and electron donor without loss of activity.

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