Electron transfer rate *versus* recombination losses in photocatalytic H_2 generation on CdS nanocrystals

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Cadmium chalcogenide nanocrystals combined with co-catalyst nanoparticles hold promise for efficient solar to hydrogen conversion. Despite the progress, achieving high efficiency is hampered by high charge recombination rates and sample degradation. Here, we report varying the decoration of platinum nanoparticles on CdS nanorods and nanoplatelets, as well as the length of the nanorods, to demonstrate the important role of pathways for the photoelectrons to the co-catalyst (see Fig 1a). Contrary to expectations, the shortening of the path, by increasing the number of co-catalyst particles, increases the transfer rate, but decreases the photocatalytic performance.[1] We show that with tip-decorated nanorods, the quantum yield of H_2 production can reach and sustain nearly 90%, provided an efficient mechanism of mediated hole extraction is employed.[2] The approach demonstrates that highly efficient photocatalysts may be prepared with only minimal amount of co-catalyst and thereby suggests future pathways for solar to H_2 conversion with semiconductor nanocrystals.

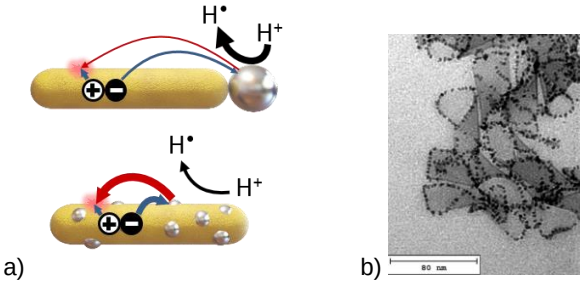

Fig. 1 a) Illustration of electron transfer and recombination rates in Pt-decorated CdS nanorods, b) Pt-decorated CdS nanoplatelets.

We furthermore show that the CdS nanocrystals (*e.g.* Fig. 1b) can be converted in aqueous solution to Cu_2S nanocrystals using light induced cation exchange and subsequently used for photocatalytic carbon dioxide reduction to CO and CH_4.[3] Control over co-catalyst deposition on the nanocrystals provides means to control selectivity of the reduction reaction to either carbon monoxide or methane.[4] In this context, we show that the procedure enables preparation of selective CO_2 reduction photocatalysts from readily available Cd-based nanostructured templates.

1) T. Simon *et al*., *ACS Energy Lett.*, **2016**, *1*, 1137-1142.
2) T. Simon *et al.*, *Nat. Mater.*, **2014**, 13, 1013-1018
3) A. Manzi *et al.*, *J. Am. Chem. Soc.*, **2015**, *137*, 14007-14010.
4) J. Mony *et al*., *in preparation*.