Hybrid semiconductor-metal nanoparticles as photocatalysts

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Hybrid nanoparticles (HNPs) combine disparate materials onto a single nanosystem thus providing a powerful approach for bottom-up design of novel architectures. Beyond the fundamental development in synthesis, the interest in HNPs arises from their combined and often synergetic properties exceeding the functionality of the individual components. These ideas are well demonstrated in hybrid semiconductor-metal nanoparticles [1], which are the focus of this talk. The synergistic optical and chemical properties of hybrid nanoparticles resulting in light-induced charge separation and charge transfer, allow photocatalytic activity which can promote surface chemistry redox reactions, and open a pathway for converting solar energy to chemical energy stored in a fuel. An additional area of interest is in use of the HNPs for light-induced generation of radicals.

We will report on the effects of the surface coating [2] and the co-catalyst metal size [3] on the photocatalytic function of metal tipped semiconductor nanorods as a model hybrid nanoparticle system. Both tested parameters were found to influence the photocatalytic efficiency and charge transfer dynamics. The work combines advances in synthesis of well-controlled hybrid nanoparticles, hydrogen evolution efficiency measurements, steady state and time resolved emission measurements, as well as ultrafast transient absorption measurements to gain a complete view on the effects of these parameters on photocatalysis with metal tipped semiconductor nanorods. A model was devised to capture the essential effects of the size of the metal tip on the photoctalytic efficiency. The understanding of the effects of the hybrid nanosystems properties on the photocatalytic processes contribute to the rational design of hybrid nanostructures in photocatalytic applications. An additional aspect we will discuss concerns the use of the HNPs in generation of reactive hydrogen species and its application for light-controlled enzymatic activity (Fig. 1) [4] and in additional areas where on-demand light-induced radicals formation is of relevance.

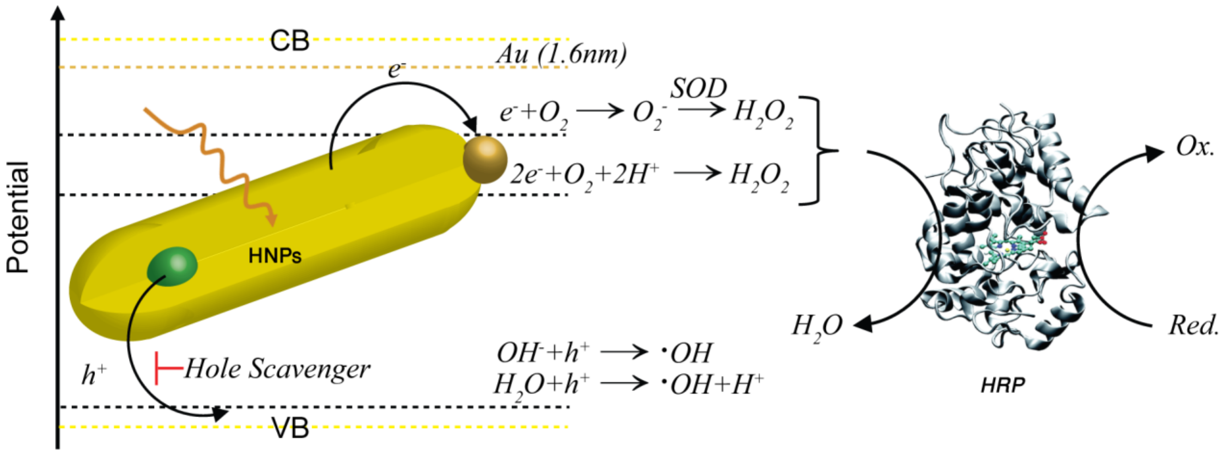

Fig. 1 . Summary scheme showing the different pathways for ROS formation after HNP light activation, and their use for HRP modulation. Excitation of the semiconductor rods results in charge separation followed by reduction of molecular oxygen by the excited electrons. This results in direct formation of H_2O_2 that can be used as a substrate for HRP or in formation of superoxide that can be converted to H_2O_2 with the aid of SOD (superoxide dismutase). In parallel, the holes can be used to produce hydroxyl radicals or could be scavenged by hole acceptors..

1) T. Mokari *et al*., *Science*, **2004**, *304,* 1787.
2) Y. Ben-Shahar *et al.*, *Small*, **2015**, *11*, 462.
3) Y. Ben-Shahar *et al.*, *Nature Communications*, **2016***, 7,* 10413.
4) N. Waiskopf *et al*., *Nano Letters* **2016**, *16*, 4266.