Towards Novel Hybrid Materials for Photoelectrochemical Water Splitting

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The development of photochemical systems capable of harnessing solar energy to produce electricity or to drive chemical transformations has attracted significant interest motivated by the need to secure the future supply of clean and sustainable energy.[1-3] Among other strategies, research has focused on novel types of semiconductor-based photoelectrochemical devices allowing for solar energy to be captured, converted and stored in high-energy chemical bonds of hydrogen molecules produced by water splitting.[4-6] Importantly, it is the water *oxidation* reaction which is the real "bottleneck" of any water-splitting device.[7] This is because – in contrast to the two-electron hydrogen evolution reaction that is mechanistically relatively simple – the oxygen-evolving reaction is a highly complex process requiring proton-coupled transfer of four electrons from two water molecules.[8-11] This often translates into slow kinetics and considerable overpotentials required for efficient oxygen evolution.[12]

Accordingly, one of the fundamental challenges in photoelectrochemical water splitting is the development of highly efficient and stable photoanodes with suitable optical (bandgap), photoelectrochemical (position of band edges on the energy scale), and kinetics-governing surface properties.[6,13] The search for suitable photoanodes currently involves a great variety of diverse approaches including, for example, structural and surface engineering of pristine low-bandgap semiconductors (like, *e.g.*, Fe_2O_3, WO_3, or $BiVO_4$),[14-16] synthesis of doped and mixed-metal oxides using high-throughput combinatorial protocols,[17-20] or sensitization of nanocrystalline TiO_2 electrodes by ruthenium dye molecules coupled to a colloidal $IrO_2 \cdot nH_2O$ oxygen evolving catalyst.[21]

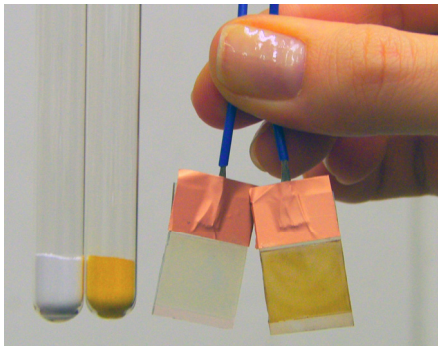

Figure 1: Pristine anatase TiO_2 (white) and TiO_2-polyheptazine hybrid materials (yellow).

Recently, we have been developing a novel class of visible-light photoactive inorganic/organic hybrid materials – TiO_2 with the surface modified by polyheptazine compounds bound to the TiO_2 surface.[22-26] Notably, polyheptazine materials represent a very stable delocalized system of conjugated π-bonds and their utilization as photocatalysts has been suggested recently.[27] However, in contrast to pristine polyheptazines showing only weak absorption in the near visible, the TiO_2/polyheptazine hybrids exhibit strong red shift in visible light absorption, which is based on formation of interfacial charge-transfer complex between polyheptazine

(donor) and TiO_2 (acceptor).[28] The talk will discuss in detail the structural, optical and electronic properties of these hybrid materials. The focus will be on our current research efforts directed to utilize these materials for visible light-driven water photooxidation.

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