

Visible light active inorganic/organic semiconductor hybrid materials based on TiO₂ and polyheptazines

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The development of photochemical systems capable of harnessing solar energy to produce electricity or chemical fuels has attracted significant interest motivated by the need to secure the future supply of clean and sustainable energy.^{1,2} Among other strategies, research has focused on novel types of semiconductor-based photoelectrochemical devices since semiconductors, due to their unique electronic and optical properties, enable efficient photon-induced generation and separation of charges which can subsequently undergo redox reactions with substrates or induce a photocurrent. One of the most promising semiconductors for photoelectrochemical applications is titanium dioxide, particularly due to its low cost, non-toxicity, and stability against photocorrosion.³ However, because of its wide bandgap (for anatase 3.2 eV; ~ 390 nm) the utilization of TiO₂ typically remains confined to UV light, a tiny fraction (2-3 %) of solar radiation reaching the earth's surface. Shifting the threshold of its photoresponse into the visible would therefore enhance its potential for chemical solar energy conversion and open possibilities for further applications like photoelectrochemical sensors or optoelectronic switches.

Recently we have developed a novel class of photoactive inorganic/organic hybrid materials – TiO₂ with the surface modified by semiconducting compounds containing nitrogen and carbon in the form of a polymeric network comprising heptazine units covalently bound to the TiO₂ surface (Fig. 1).⁴⁻⁷ Notably, the semiconducting properties of poly-heptazine based compounds have been recently recognized.^{8,9}

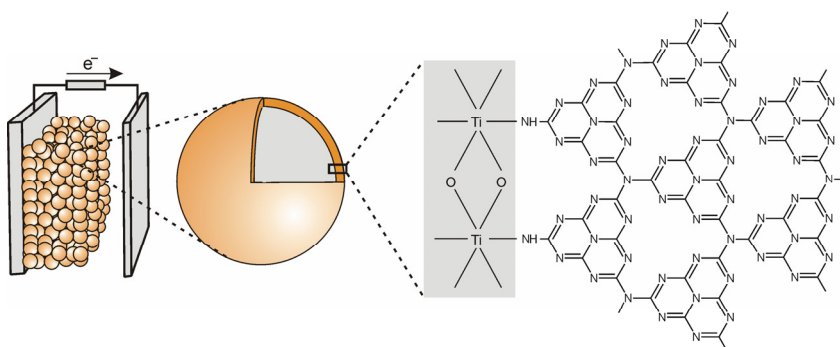


Figure 1. A simplified scheme depicting the macroscopic, nanoscopic and chemical structure of a typical inorganic/organic hybrid photoactive device: oxide nanoparticles are deposited onto an ITO-glass electrode and modified at the surface by polymeric heptazine compounds. Note that the surface layer is in reality three-dimensionally (3-D) structured due to graphite-like stacking of polypeptazine sheets.

The hybrid materials can be prepared, for example, by simply heating TiO₂ in a gaseous atmosphere of urea pyrolysis products.⁴⁻⁶ These materials show high activity in visible light photocatalytic oxidation of formic acid.^{6,7} Moreover, they can be utilized for fabrication of visible light active photoelectrodes or wavelength-controlled optoelectronic switches.^{5,10} Notably, the materials were highly stable and exhibited

significant photocurrent response in the visible down to 750 nm.⁵ Moreover, it was found that by simply varying the modification temperature the fundamental optical (bandgap energy) and photoelectrochemical properties (quasi-Fermi level) of surface-modified TiO₂ can be systematically controlled in an unprecedented way.

Our current research focuses on investigations directed to optimizing these hybrid materials in order to achieve higher conversion efficiencies in photoelectrochemical devices. Hitherto the strategies have focused on varying the morphology of the electron-collecting TiO₂, reaching a nearly ten-fold increase when going from simple flat films to nanotubular arrays.^{4,5,11}

In going beyond this approach, it is our intent to systematically alter the properties of the surface layer comprising of polyheptazine compounds, to use different electron collecting metal oxide components, and to manipulate the morphology of metal oxide/polyheptazine hybrid composites and the electronic interaction between both of the components. The talk will discuss some strategies to achieve these objectives, as well as efforts to utilize the hybrid materials in various applications.

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