Abstract

Since time immemorial the need and consumption of energy has played an innate role in shaping every civilization. The ever rising demand of renewable and resourceful energy has influenced and steered the course of science and research. This doctoral thesis has been performed with the goal of delving into the quintessence of nanostructuring of semiconductor materials for the solar assisted splitting of water. The ultimate goal of these investigations is the production of hydrogen, a high energy source (oxygen as by-product) with the assistance of a semiconductor as the photocatalyst, water as the source and sunlight.

In order to fabricate favourable photocatalysts, a deeper insight in the physico-chemical built of each semiconductor has to be rendered. This work encompasses the understanding of the influence of molecular precursor tailoring, the dexterity of dimensionality in nanostructuring, the elucidations of electronic and chemical states and ultimately the integration of these materials for photoelectrochemical water splitting.

TiO_2, known for its high photocatalytic activity forms the base of this doctoral research. Due to the existing wide band gap of this material (the bottle neck), attempts have been undertaken to either minimize the band gap through band gap engineering or introduction of other metals/metal oxides to enhance efficient separation and transfer of photogenerated charge carriers.

The importance of dimensionality has been discussed thoroughly in this work, where through electrospinning, novel 1D nanofibres have been fabricated. This technique allows the production of not only monolithic but also composite core-shell fibres.

Mild plasma techniques have been implemented for the band gap engineering, where the facile creation of surface defects and oxygen vacancies in the crystal lattice of TiO_2 show enhanced photocatalytic activity.

Co-catalysts such as Au, Fe_2O_3 and VO_2/V_2O_5 have been integrated into the TiO_2 matrix either through an external technique or through coaxial electrospinning. These additives have shown interesting patterns in the case of photocatalytic activity,

which has paved a way for further intensive studies in this area of heterogeneous 1D nanostructuring.

Electrospinning with existing alkoxide libraries as starting materials can be challenging due to the stability and sensitivity of these compounds. Therefore as an illustration, the moisture sensitive $V(O^tBu)_4$ was stabilized using the ligand modification scheme. Hereby two new heteroleptic vanadium (IV) compounds could be synthesized and characterized. The additional acquired stability renders easy handling for the fabrication of VO_2/V_2O_5 nanofibres.

Addendum to these investigations, a comparison to the existing TiO_2 system (pristine and modified) has been performed with a wide band gap ternary oxide $SrNb_2O_6$ using a single source precursor $SrNb_2(O^iPr)_{12}(HO^iPr)$.

All results obtained have shown the importance of dimensionality, surface states and interfacial effects. The existing data provide a pathway for the conception and integration of new methodologies in order to augment photocatalytical properties of nanostructured metal oxides and semiconductors.