

# Preamble

---

Catalysis using nanostructures has been a topic of substantial interest for fundamental studies and for practical applications in energy and environmental sectors. The growing demand for production of energy and in the cleaning of polluting hazardous vehicles/industrial wastes has led to several studies in catalysis. Despite the substantial growth of heterogeneous catalytic technologies in last decade, they are still far from reaching their full potential in terms of efficiency, selectivity as well as durability. It is often difficult to simultaneously tackle all the mentioned issues with single component catalysts. Most of these challenges are being overcome with heterostructure/supported hybrid catalysts by modifying their interfaces.

The properties of heterostructure hybrids arise not only from the individual contributions of the individual components but also from strong synergetic effect arising from the interface. Engineering the interfaces provides pathways to promote the catalytic performance and hence has been explored. In this regard, we have focused on the progress in investigating the active interfaces that affect the performance of metal oxide-metal, semiconductor-metal and coupled semiconductor nanocatalyst hybrids. We explored a wide spectrum of their applications in photocatalytic, electrocatalytic as well as gas-phase reactions and highlighted the importance of the interface for overall performance.

The entire study reported in the thesis is organized as follows:

Chapter 1 is a general introduction of hybrid nanocatalyst and their role in wide spectra of catalytic reactions in photo/electrocatalysis as well as gas-phase reactions. This chapter describes the motivation behind modulating the interface between two or more nanostructures to obtain multifunctional nanocatalysts. Nanocatalysts to achieve high throughput with active interfaces are elaborated while indicating the role of morphology, internal induced state, charge transfer, geometric, support, as well as electronic effect for enhanced performance. Motivation behind specific nanocatalyst hybrid, synthesis routes as well as characterization techniques are detailed in the respective chapters. Specific details for different hybrids are described in the following chapters.

Chapter 2 describes the synthesis of high dense ultrathin Au wires on ZnO nanorods for electrocatalytic oxidation of ethanol, where the prerequisite step is the formation of amine-modified support. Oleylamine modification not only serves to anchor Au nanowires on ZnO but also passivates surface defects of ZnO, which in turn enhances the photocurrent. In addition to the stability, the support induces electronic effect on Au nanowires, which facilitates redox process at low potential. Most importantly, the support promotes the activity of Au nanowires upon photoirradiation, and thus leading to synergy between electro and photooxidation current. This is of immense importance for photofuel cell technologies. Moreover, the method enabled the first time electrocatalysis on these nanowires that revealed ultrathin nanowires are potentially interesting systems for catalysis applications provided they are stabilized by a suitable support.

Chapter 3 deals with the growth of ultrathin Au nanowires on metal oxide ( $\text{TiO}_2$ ) coupled with graphene hybrid support in order to overcome the low conductivity of metal oxide. Oleylamine, used for growth of Au nanowires simultaneously functionalizes the support and leads to room temperature GO reduction. With respect to catalytic activity, we also synthesized the binary counterparts (rGO/Au,  $\text{TiO}_2$ /Au ultrathin nanowires) to delineate the contribution of each of the components to the overall electrocatalytic oxidation of ethanol. Comparative analysis of photo and electrocatalytic activity between the different binary and ternary hybrids provides interesting information. Both, electronic effect of  $\text{TiO}_2$  and electrical conductivity of rGO add their specific beneficial to the nanowires, leading to superior ternary system.

Chapter 4 rGO supported ultrathin Au nanowires exhibits high electrocatalytic performance for oxidation of borohydride with a lower onset potential compared to rGO/Au nanoparticles. Electrochemical impedance spectroscopy measurements display abnormal inductive behavior of the synthesized hybrids, indicative of Au surface reactivation. DFT calculations indicate that the origin of the high activity stems from the shift in the position of the Au d-band center.

Chapter 5 Different aspect ratio ZnO nanostructures are obtained by varying the solvothermal reaction time. We observed a direct correlation between observed photocatalytic activity, measured photocurrent and length of the ZnO nanorods. Furthermore, photoresponse of the high aspect ratio ZnO nanorods are improved by

attaching Au nanoparticles, intimate contact of two components leads to band bending. Thus, the synthesized ZnO/Au heterostructure favors for prominent separation of photogenerated charge carriers.

Chapter 6 TiO<sub>2</sub> and PbO/TiO<sub>2</sub> hybrids are synthesized via non-hydrolytic sol-gel combustion method. Hybrid exhibits higher photocatalytic activity for the degradation of dye than TiO<sub>2</sub>. The estimated photogenerated species reveals that the origin of enhanced activity stems from the direct oxidization of dye via photogenerated hole rather than radicals.

The semiconductors are matched based on their band edge positions, for the formation of energetic radicals to degrade the pollutants. Based on this study, we infer that semiconductors should not neglected (for example Si) based on calculated mismatch of their valence band edges position for photooxidation reaction via radicals.

Chapter 7 describes the Pd dopant associated band engineering, a strategy for tuning the optoelectronic properties of ZnO towards enhanced photocatalytic activity. Incorporated Pd heterocation induces internal energy states within the ZnO band gap. The created energy level leads to trends mismatch between photocatalytic activity and measured photocurrent. Formed energy level arrests the photogenerated electrons, which make them not contribute for the photocurrent generation. Hence, the isolated photogenerated hole efficiently oxidizes the pollutants through hydroxyl radicals, and thus leads to enhanced photocatalytic activity.

Chapter 8 employed Pd-substituted zinc stannate for CO oxidation as heterogeneous catalyst for the first time. Compared with SnO<sub>2</sub> support, zinc stannate based materials exhibits abnormal sudden light-off profiles at selective temperatures. On the basis of DRIFT studies under relevant conditions, we find that the initially formed product gets adsorbed over the catalyst surface. It leads to the accumulation of carbonates as a consequence, both lattice oxygen mobility and further CO interactions are disabled. As soon as Sn redox nature dominates over the accumulated carbonates, this leads to sudden release of lattice oxygen, and thus leads to a sudden full conversion. Therefore, choosing the suitable support material greatly influences the nature of the light-off CO oxidation profile.

Chapter 9 Although, reducible oxide supported gold nanostructures exhibits the highest CO oxidation activity; they still suffer from problems such as limited selectivity towards CO in the presence of H<sub>2</sub>. Both ex-situ and in-situ experiments demonstrate that, Au nanoparticles supported on Zn<sub>2</sub>SnO<sub>4</sub> matrix selectively oxidizes CO. DRIFT experiments revealed that the involvement of OH groups leads to the formation of hydroxycarbonyl under PROX conditions.

Chapter 10 This chapter discusses the conclusions for the previous chapters and highlights the possibilities for future scope for the developed nanocatalysts hybrids for energy and environmental applications.