

Abstract

Semiconductor metal oxides have received increasing attention in the past several decades as heterogeneous catalysts, photocatalysts, energy storage and drug delivery materials. Among these, TiO_2 is a prominent semiconductor oxide which has been extensively studied for heterogeneous catalysis, photocatalysis, high temperature gas sensing and selective catalytic reduction of NO_x , due to its abundance, chemical inertness, high thermal stability and non-toxicity. In addition, it offers large surface area for the surface adsorption/reaction processes and also offers different surface facets (crystal planes). The surface activity of different crystal planes varies due to the change in Ti-O coordination and associated Ti-O bond lengths. Creation of surface defects by oxygen vacancy formations and foreign metal/nonmetal doping can also have a significant impact on the surface activity of TiO_2 . Creation of bulk and surface defects in the TiO_2 lattice results in the surrounding Ti-O bond distances to vary thereby activating the lattice oxygen and leading to surface oxidation reactions. Therefore, it's important to study the effect of bulk and surface defects by the creation of oxygen vacancies and metal/nonmetals doping on the structure-property relationships of TiO_2 . We report these effects via computational investigations performed by using the density functional theory (DFT) approach.

Creation of oxygen vacancies and its effect on the structure-property relationships in pristine TiO_2 was investigated using DFT. Anion (oxygen) vacancies at different unique sites were created in both bulk and surface exposed planes of TiO_2 . Two non-identical crystal planes (001) and (100) were chosen for computations. Differential bond length formation and corresponding bond length distributions for the vacancy induced TiO_2 have been described. Net oxygen activation (NOA) was analysed based on the bond length distributions for the quantification of lattice oxy-

gens available for the catalytic reactions. Different vacancy sites were observed to show different oxygen activations over (001) and (100) planes. It was found that (100) plane exhibited higher net oxygen activation and smaller rigidity towards the surface reconstructions. Hydroxyl group formation over the surface of TiO_2 was found to be energetically favorable and was predicted to take place via two routes, either by dissociation of H_2 over oxidative catalyst or by dissociation of H_2O over the reduced catalyst.

Metal/nonmetal doping at substitutional sites of bulk and surface exposed TiO_2 was investigated. Pd, C and N were chosen as the metal/nonmetal dopants to substitute at Ti and O sites in order to form the substitutional solid solutions of TiO_2 . Oxygen vacancies were created at different unique locations in the substitutional solid solutions and the feasibility of oxygen vacancy formations were examined from the formation energies. It was revealed that the substitution of Pd in TiO_2 exhibited the higher NOA of 26% followed by 25.3% for Pd/N-codoping when compared to C, N-monodoped and Pd/C-codoped TiO_2 .

Effects of C and N-substitution and oxygen vacancy formation on the lithium incorporation characteristics of TiO_2 were explored for the potential application of substitutional solid solutions of TiO_2 in high performance lithium ion batteries. Different interstitial sites were chosen for the doping of lithium and the feasibility of interstitial lithium incorporation was determined from the formation energies. The formation energies, cell potentials and charge capacities unveiled the superior electrochemical performance of pure, C and N-substituted TiO_2 towards high performance lithium ion batteries. Change in concentration of lithium doping indicated the hybrid behaviour of battery to pseudocapacitor and supercapacitors of lithiated pure, C and N-substituted TiO_2 .

Titania has been used in biomedical field as a white pigment in the preparation of tablets and drug delivery materials for the control delivery of drugs. Interaction of various functional groups of biomolecules with the metal oxide surface plays a vital role in the biochemical activity

of TiO₂. Adsorption of two amino acids: arginine and cysteine, and one nucleobase, guanine, on the nano-TiO₂ cluster was studied to understand the interaction of different functional groups of biomolecules with nano-TiO₂. Thermodynamic stability and energetic favorability of adsorption of arginine, cysteine and guanine were predicted from the changes in adsorption energies and Gibbs free energies. Adsorption of these amino acids were found to take place via the interaction of -COOH and -NH₂ groups for arginine and cysteine adsorbed TiO₂ whereas the interaction was due to the attack of purine ring in case of guanine adsorption. Band gap narrowing was observed for the amino acids adsorbed nano-TiO₂ which indicated the enhancement of photoresponse of nano-TiO₂ towards the visible light region in presence of tested biomolecules.

Density functional theory (DFT) calculations were performed in the entire set of works to explore the structure-property relationships of pure and metal/nonmetal doped TiO₂. The studies provided the detailed insights into the activity of different surface planes considered highlighting surface sites which are significant for the surface adsorption/reactions. Site specific activities are often difficult to understand from the experiments and this work provides the guidelines to experimentalists for the synthesis of particular crystal plane with the favorable sites exposed which possess superior catalytic and electrochemical activities. Reduced titania with cation substitution is expected to be a good composition to act as a redox catalyst for applications like CO oxidation and the water-gas shift reaction. Lastly, the biocompatibility of TiO₂ was demonstrated via the interaction of various functional groups of amino acids which can guide further experimental studies.

Keywords: TiO₂; metal/nonmetals doping; substitutional solid solutions; bond lengths distribution; net oxygen activation; density functional theory; surface reconstructions; oxygen vacancies