Abstract

Splitting of water using renewable energy has great applications in the degradation of organic pollutant via photo catalysis and hydrogen generation via photo-electrochemical cells. For this purpose, metal-oxide materials viz. Zinc oxide (ZnO) and Bismuth vanadate ($BiVO_4$) have been chosen as the targeted semiconductors for their potential abilities for water splitting applications. Both these materials, in pure and composite form, have been studied for their photo catalytic and photo-electrochemical property towards contaminants decomposition and hydrogen generation. Heterostructures of ZnO have tremendous applications in the field of splitting of water. Present research work is mainly aimed towards synthesis and investigation of the interface interaction mechanism of charge transfer and separation on photocatalytic and photoelectrochemical activity of ZnO and $BiVO_4$ based nanocomposites/photoanodes.

To study photocatalytic property of composite semiconductor, systematic investigations on the relationship between interface formation and enhanced photocatalytic activity of ZnO-$BiVO_4$ nanocomposite based on experimental techniques supported by theoretical calculations have been studied. The interaction between ZnO (101) nanosheets and $BiVO_4$ surface at the heterojunction was also investigated to study the charge transfer and separation mechanism responsible for enhanced photocatalytic response. XPS results and DFT computations mutually validate the reasonable existence of ZnO-$BiVO_4$ interface. The nanocomposite photocatalytic activity, tested for various weight ratios, has shown highest for ZnO-$BiVO_4$ (1:1) under visible-light irradiation. The remarkable increase in photocatalytic activity and reduced band gap (2.94 eV) of ZnO-$BiVO_4$, without the use of any supportive charge transport medium or co-catalyst, is due to the formation of intermediate band at interface, formed during mechanical milling and annealing process of synthesis. Moreover, the percentage removal of methylene blue was found to be greater than

Rhodamine B for the same time duration. The probable reason for this difference is discussed in this study. Steady state and time resolve photoluminescence were employed to understand the carrier lifetime and emissivity. Visible light driven high photoactivity exhibited by ZnO-$BiVO_4$ (1:1) was ascribed to the formation of intermediate band and comparatively low recombination rate that facilitates the separation of electron-hole pair. Theoretical analysis indicated that valence band maximum was occupied by Bi s orbital and conduction band minimum was occupied by Zn s orbital which indicates the maximum electron transition from $BiVO_4$ valence band to ZnO conduction band in ZnO-$BiVO_4$ composite. These results demonstrated that heterojunction semiconductors are an effectual strategy that can be successfully applied to develop photo catalysts that responds to visible light for organic pollutant degradation.

To study photo-electrochemical properties for water splitting applications, dual layer $BiVO_4$/ZnO photo anode was instigated. Two different photo catalytic layers of ZnO and $BiVO_4$, reduces charge carrier recombination and charge transfer resistance at photoanode/electrolyte junction. The concentration-specific, tunable and without 'spike and overshoot' features, photocurrent density response is originated by varying $BiVO_4$ concentration in the $BiVO_4$/ZnO photo anode. The crystal structure of $BiVO_4$ (monoclinic scheelite structure) and ZnO (hexagonal wurtzite structure) was confirmed by X-ray diffraction studies. The band gap of $BiVO_4$/ZnO was calculated to be ca. 2.42 eV through Kubler-Munk function $F(R\infty)$ using DRS (Diffuse Reflectance Spectroscopy). Electrochemical behavior of samples was analyzed with photocurrent measurements, electrochemical impedance and Mott-Schottky plots. The present study provides the proof of concept for developing photo anodes having concentration specific, tunable and without 'spike and overshoot' features, photocurrent density response with efficient utilization of solar spectrum and reduced electron-hole recombination by synergistically combining visible light driven photocatalyst $BiVO_4$ and wide band gap semiconductor ZnO. By varying the concentration of $BiVO_4$ it was possible to tune the photo response current density curve (by controlling two

competitive mechanisms, water oxidation and surface recombination) in the dual layer $BiVO_4$/ZnO based photoanode.