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Variation of flatband potential of oxide nanocrystalline particles with core-shell structured semiconductor-MgO composites

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Abstract

SnO_2 thin films and particles show feeble solar cell performance and poor photocatalytic activity respectively. It has been reported that coating of a thin MgO layer on SnO_2 particles results in enhancement of both solar cell performance and catalytic activities. The promoting effect of MgO layer was owing to barrier effect where MgO acts as a barrier layer for charge recombination. We noticed negative shift of flatband (FB) potential of SnO_2 with the increase of pH values and coating of a thin MgO layer on SnO_2 particles. It is shown how the negative shift in FB potential may contribute to enhance the solar cell efficiencies and photocatalytic activity in addition to the barrier effect of MgO layer.

1. INTRODUCTION

The primary process of any photochemical reaction is the absorption of light by a suitable light absorbing material i.e. a semiconductor or dye. The direct band gap excitation of semiconductors leads to the generation of electron hole pairs and the use of semiconductor oxide particles as photocatalysts is well established and has shown great utility in the complete mineralization of organic pollutants [1-5]. In the same way, in dye sensitized solar cells (DSSC), dye molecules which are attached to thin oxide film transfer excited electrons from the dye molecules to the conduction band (CB) of the oxide. Transferred electrons in the CB of oxide thin film are either diffused to the conducting glass or recombine with the dye cation. In photocatalysis and in DSSC, the kinetics of recombination process is considered as one of the most important factors that controls the photocatalytic activity as well as the efficiency of solar cells [6-9]. Therefore, in optimization of the photoelectrochemical processes, recombination should be minimized. Hence, a wide charge

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separation is a prerequisite for better photocatalytic activity as well as higher solar cell performances. Wider charge separation has been achieved using composite semiconducting materials with different band positions such as TiO_2/SnO_2 [10], TiO_2/ZnO [11]. It has been reported about the use of an insulating layer on thin semiconducting films to increase the solar cell efficiencies and photocatalytic activities [12-16]. An interrelation between retardation of charge recombination in the presence of an insulting layer and the enhancement of the cell efficiencies and photocatalytic activities has been observed. We noticed negative shift of flatband (FB) potentials of oxide thin films with the introduction of thin MgO layer on oxide particles. Here we report how the flatband potential of oxide nanocrystalline particles vary with the core-shell oxide-MgO composite and its impact on performance of DSSC.

2. EXPERIMENTAL

For electrochemical measurements, thin films of nanocrystalline SnO_2 and SnO_2/MgO were prepared by mixing SnO_2 or SnO_2/MgO in an agate motar adding few drops of carbowax and polyethylene glycol. The final slurry was applied on a cleaned conducting glass by using doctor blade method and sintered in air at 450^{O} C for 30 min. The flat-band (FB) potentials of the oxides were determined from Mott-Schottky plots (i.e a plot of C^{-2} vs V, where C was the capacitance and V was the potential across the space charge layer) and on-set potential methods. The experimental details are given in [17-19]. To measure the capacitance, oxide coated plates were immersed in Na_2SO_4 solution and the capacitances were measured as a function of the potential across the space charge layer at frequencies of 500 Hz and 1 kHz. It should be noted that even though both methods give comparable FB potential values, the deviations in measured FB potential values among the same and different measurement techniques were observed.

3. RESULTS AND DISCUSSION

It has been shown that an oxide like TiO_2 follows Nernest equation and flatband potential depends on pH with the slope of -59 mV/pH and the dependence of flatband on pH was elucidated considering the following dissolution equilibrium at the TiO_2 surface [19],

$$\mathrm{Ti}-\mathrm{O}^{2-} + \mathrm{H}^{+} \longrightarrow \mathrm{Ti}-\mathrm{OH}^{-} \qquad (1)$$

$\mathrm{Ti}-\mathrm{O}^{2-}$ = TiO_2 lattice at the surface, $\mathrm{Ti}-\mathrm{OH}^{-}$ = protonated lattice

A thermodynamic reasoning leads to the following formula for the shift in the equilibrium potential ($\Delta\theta$) of the $TiO_{2,}$

$$\Delta\theta = \text{constant} \; + \left(\frac{RT}{F}\right) \ln \left(\frac{a_{(Ti - O^{2-})}}{a_{(Ti - OH^{-})}}\right) - \frac{2.3RT}{F}\,pH \qquad (2)$$

For TiO_2, pH dependence of the second term is negligible. A change in pH by a unit produces a change in the potential difference within the Helmholtz layer of *2.3RT/F* or 59 mV at room temperature. Fig. 1 shows the flatband variation of SnO_2 particles as a function of the solution pH value. Similar to TiO_2, the flatband potential of SnO_2 decreases or shifts negatively as the solution pH increases. However, according to Fig. 1, the flatband potential of SnO_2 particles varies linearity on pH with a slope of -29 mV/pH. i.e It has flatband potential of 0.02 eV at pH 0.0 and it decreases to -0.28 eV at pH 10.0. The deviation of the dependence of θ of SnO_2 with solution pH indicates that entire surface of SnO_2 lattice does not protonated instead it undergoes passivation with the increase in solution pH.

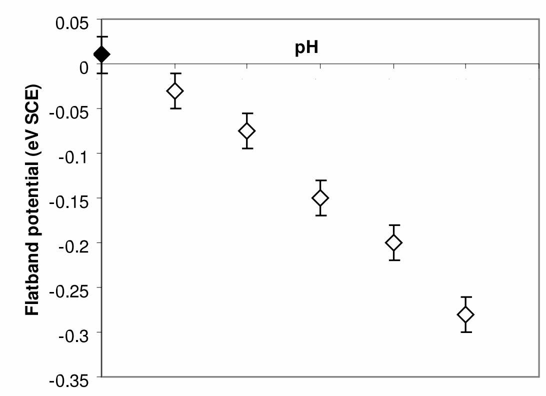

Fig. 1 Variation of flatband potential for SnO_2 as a function of solution pH.

Fig. 2 shows the flatband values for the SnO_2/MgO composite with the variation of MgO amounts at pH 5.0. As shown in Fig. 2, pure SnO_2 has a flatband potential of - 0.07 eV at pH 5.0 (vs SCE). Introduction of 1% MgO results in shift in flatband potential of SnO_2 to -0.43 eV and further increase in MgO leads to the negative shift in flatband potential. The flatband potential of SnO_2 is at optimum when the MgO amount was found to be 10% and corresponding flatband potential of SnO_2 particles at the optimum MgO was found to be -0.84 eV. From the flatband values, it can be assumed that coating of MgO layer on SnO_2 particles leads to some sort of surface or structural modification in SnO_2 particles resulting a negative shift of flatband potential. The effect of MgO coating on negative shift in FB of SnO_2 can be understood considering the acidity and basicity of

SnO_2 and MgO. SnO_2 is acidic because of its point of zero charge (PZC) is 4.5 while MgO is basic and its PZC is 12.0 which is supposed to be the highest basic oxide. In SnO_2-MgO core-shell structure, there is a tendency of deprotonation of SnO_2 surface by basic MgO similar to acid base deprotonation/protonation in solutions. Recently Jung et.al have investigated the TiO_2-MgO core shell structure and demonstrated that TiO_2-MgO core-shell structure possessed a large number of hydroxyl groups [20]. Deprotonation of SnO_2 surface by basic MgO could lead to negative shift in FB of SnO_2 as described above for the TiO_2 particles.

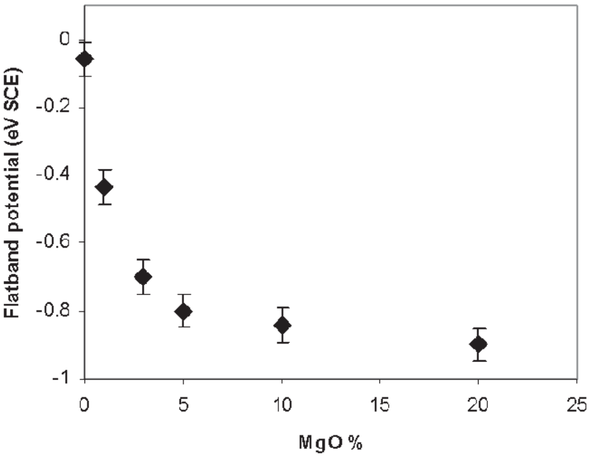

Fig. 2 Variation of flatband potential for SnO_2 with the change of % of MgO at pH 5.0.

The negative shift of FB of SnO_2 with the change of pH and coating of a thin MgO layer could lead to enhance the performance of DSSC as well as photocatalytic activity. As described in the introduction and mentioned in literature, the performance of DSSC strongly depends not only on efficiency of charge transfer from the excited dye molecules to the CB of oxide but also on charge recombination kinetics between transferred electrons in the CB and the oxidized dye cation. In thermodynamic point of view, the negative shift in FB potential results in decrease in free energy change for the charge transfer from excited molecules to the CB while increase in free energy change was expected for the charge recombination process. Consequently, the negative shift in FB will facilitate the charge transfer from excited dye molecules to the CB while charge recombination process will be more difficult and such a situation favourably increases the efficiency of DSSC.

4. CONCLUSION

The FB potential of SnO_2 varies linearly with the increase in solution pH with a slope of -29 mV/pH. The passivation of SnO_2 surface may result in deviation from the Nernstein behavior. Negative shift of FB of SnO_2 was also observed with the introduction of a thin insulating MgO layer on SnO_2 particles and the FB of SnO_2 is at optimum when the MgO amount was found to be 10%.

Deprotonation of SnO_2 surface by MgO was found to be the reason for the observed negative shift of FB of core-shell structured SnO_2/MgO composite. Negative shift in FB potential may contribute to enhance the solar cell efficiencies and photocatalytic activity in addition to the barrier effect of MgO layer.

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