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# Tuning of the flat-band potentials of nanocrystalline $\rm TiO_2$ and $\rm SnO_2$ particles with an outer-shell MgO layer

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#### ARTICLE INFO

ABSTRACT

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#### 1. Introduction

Shifting of the flat-band (FB) potentials of semiconductors plays an important role deciding their photocatalytic as well as photoelectrochemical properties of thin oxide films and powders. The shifting of FB potential can be harnessed in solar energy conversion processes in numerous ways. In dye sensitized solar cells (DSSC), photovoltage ( $V_{oc}$ ) is determined by the difference between the quasi-Fermi level of electrons in the oxide film and the energy of the redox couple in the electrolyte [1]. Consequently, the shift of FB potential in the negative direction results in increase in barrier height and hence in the attainable  $V_{oc}$  of the solar cell. Similarly, the FB potential can be shifted negatively in order to electrolyze a redox couple that is otherwise too positive in the electrochemical series to be reactive at the illuminated semiconductor surface [2].

In DSSC, dye molecules which are attached to a thin oxide film transfer excited electrons from the dye molecules to the conduction band (CB) of the oxide [3]. The transferred electrons in the CB of oxide thin film either diffuse to the conducting glass or recombine with the dye cation formed [4–6]. In DSSC,  $V_{oc}$  and  $I_{sc}$  (short-circuit photocurrent) are critical parameters that determine the energy conversion efficiency of the cell and the kinetics of recombination process is considered as one of the most important factors that control the efficiency of solar cells [7–10]. Specially,  $V_{oc}$  is determined by the rate of recombination and the band-edge position and consequently  $V_{oc}$ 

insulating MgO layer. For core-shell structured  $TiO_2$ -MgO and  $SnO_2$ -MgO composites, incorporation of 1% (w/w) of MgO results in negative shift in FB potential of  $TiO_2$  and  $SnO_2$  nanoparticles by -0.15 eV and -0.38 eV, respectively. The negative shift of FB increased with the increase of MgO content. The highest shifts in FB potential reached -0.85 eV and -0.65-0.70 eV (vs Standard Calomel Electrode) when MgO content was equal to 10% (w/w) and 10-15% (w/w) for  $SnO_2$  and  $TiO_2$  respectively. In this investigation, interconnection between the negative shift in FB potential and the efficiencies of dye sensitized solar cells based on the prepared materials are discussed.

Flat-Band (FB) potentials of TiO<sub>2</sub> and SnO<sub>2</sub> nanoparticles shifted negatively once they were coated with a thin

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can be tuned changing either recombination rate and/or band-edge position.

It has been reported the slow charge recombination in the presence of an insulating layer such as MgO or Al<sub>2</sub>O<sub>3</sub> on semiconductor thin films and the retardation of charge recombination in the presence of an insulating layer has been utilized to improve the photochemical processes [11–13]. In the core-shell structure reported in [11–13], the outer MgO (or Al<sub>2</sub>O<sub>3</sub>) layer acts as a barrier for charge recombination and an interrelation between retardation of charge recombination and the enhancement of the solar cell efficiency in the presence of an insulting layer has been established [13–17]. Similarly, it has been reported that the device performance for the different metal oxide electrodes depends on differences in acid/base properties of the over layers [17].

Based on these observations, we have investigated how the MgO coating on  $TiO_2$  and  $SnO_2$  affect their FB potential levels. We noticed that a fine tuning of FB potentials of semiconductor nanoparticles could be achieved by coating of a thin MgO layer on semiconductor particles. Here we report our observations on how the negative shift in FB potentials of semiconductor particles varies with the composition of the core-shell oxide-MgO composites and its impact on performance of DSSC:

#### 2. Experimental details

Colloidal SnO<sub>2</sub> aqueous solution (1 ml, Alfa Chemicals, 15% SnO<sub>2</sub>) ground with 100  $\mu$ l of acetic acid were well dispersed with ethanol (10 ml) and finally sonicated for 10 min using ultrasonic horn. To



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**Fig. 1.** (a) Mott–Schottky plots of SnO<sub>2</sub> in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution obtained from impedance spectra measurements at pH 1.0 ( $\Delta$  – 500 Hz and  $\blacktriangle$  – 1 kHz) and pH 10.0 (0 – 500 Hz and  $\blacklozenge$  – 1 kHz). (b) Variation of FB potential of SnO<sub>2</sub> nanocrstallites as a function of solution pH. The FB values were calculated from the Mott–Schottky plots shown in (a).

prepare thin films, the above colloidal SnO<sub>2</sub> solution was placed in an agate mortar and 50 µl of carbowax (Fluka, A.G.) and 50 µl polyethylene glycol (Fluka, A.G.) were added and mixed thoroughly. The final slurry was applied on cleaned conducting glass by doctor blade method [18] and sintered in air at 450 °C for 30 min. To make SnO<sub>2</sub>/MgO composite, desired weight percentage of magnesium acetate was added to SnO<sub>2</sub> colloidal solution and mixed thoroughly using the same procedure as above. Thin films of SnO<sub>2</sub>/MgO were prepared after mixing of SnO<sub>2</sub>/MgO mixture with 50 µl of carbowax and 50 µl polyethylene glycol and applied on conducting glass by doctor blade method and sintered in air at 450 °C for 30 min. TiO<sub>2</sub> thin films were prepared by similar method using TiO<sub>2</sub> powder (Degussa P-25 TiO<sub>2</sub>). 0.5 g of TiO<sub>2</sub> was mixed with 100  $\mu$ l of acetic acid and Triton (5 drops) followed by addition of 1.0 ml of ethanol. On cleaned ITO glass, the above mixture was coated by doctor blade method and the film was sintered at 450 °C for 30 min in air.

The FB potentials of the oxides were determined from Mott– Schottky plots. A three electrode single compartment was used for capacitance analysis. TiO<sub>2</sub> coated conducting glass was used as working electrode while Platinum and SCE were used as counter and reference electrodes respectively. To measure the capacitance, oxide coated plates were immersed in 0.5 M Na<sub>2</sub>SO<sub>4</sub> 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. The capacitance was plotted against V and from the intercept of the plot, the FB was calculated (i.e. a plot of  $C^{-2}$  vs. V, where C was the capacitance and *V* was the potential across the space charge layer). The pH of the solution was adjusted using either HCl or NaOH solutions. When studying effect on the FB potential with variation of MgO content on TiO<sub>2</sub> or SnO<sub>2</sub> surfaces, pH 5.0 was selected as the aqueous suspensions of bare  $TiO_2$  and  $SnO_2$  found to have pH~5.0. The FB potentials were also measured using on-set potential method. TiO<sub>2</sub> or SnO<sub>2</sub> coated conducting glass, Pt and SCE electrodes were used as working, reference and counter electrodes respectively. The potentiostat (Hokuto Denko potentiostat/galvanostat model 301) is used to control the potential and current measurements. The potential was swept at the desired rate with respect to SCE. The amplified photocurrent was plotted as a function of applied potential after rectifying the low photocurrent. The current was measured with and without irradiation and compared to obtain FB potential values. The experimental details are given in [19-21]. It should be noted that even though both methods give comparable FB potential values, the deviation in measured FB potential values among the same and different measurement techniques are observed.

#### 3. Results and discussion

Fig. 1a shows the Mott-Schottky plots of SnO<sub>2</sub> particles at pH values 1 and 10 (Mott-Schotkky plots of other pH values are not shown for clarity of the figure). The FB potential values as a function of the solution pH value for SnO<sub>2</sub> particles are shown in Fig. 1b. These values are calculated from the Mott-Schottky plots shown in Fig. 1a for SnO<sub>2</sub> particles. As shown in Fig. 1b, as the solution pH increases, the FB potentials of SnO<sub>2</sub> decreases or shifts negatively. i e. at pH 1.0, SnO<sub>2</sub> has FB potential of 0.02 eV (vs SCE) and the FB potential decreases to -0.26 eV (vs SCE) at pH 10.0. According to Fig. 1b, the FB potential of  $SnO_2$  particles depends on linearity on pH with a slope of -28 mV/pH. TiO<sub>2</sub> particles showed the similar FB potential variation with the change of the solution pH values. It has been shown that an oxide like TiO<sub>2</sub> particles in aqueous medium follows Nernst equation and FB potential depends on pH with a slope of -59 mV/pH and the pH dependence of FB was elucidated considering the following dissolution equilibrium at the  $TiO_2$  surface [21],

$$Ti-O^- + H^+ \rightarrow Ti-OH$$
 (1)

 $Ti-O^{-}=TiO_{2}$  lattice at the surface, Ti-OH= protonated lattice.

A thermodynamic reasoning leads to the following formula for the shift in the equilibrium potential ( $\Delta \theta$ ) of the TiO<sub>2</sub> [21], where *F* is the Faraday constant and *R* is the Avogadro constant.

$$\Delta\theta = \text{constant} + \left(\frac{RT}{F}\right) \ln\left(\frac{a_{(\text{Ti}-O^{-})}}{a_{(\text{Ti}-OH^{-})}}\right) - \frac{2.3RT}{F} \text{pH}$$
(1A)

Since pH dependence of the second term is negligible for TiO<sub>2</sub>, 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. However, in the case of SnO<sub>2</sub> as shown in Fig. 1b,  $\theta$  does not change by 59 mV as pH increased by a unit. The deviation of the dependence of  $\theta$  with solution pH for SnO<sub>2</sub> nanoparticles indicates the imperfect protonation of SnO<sub>2</sub> surface lattice. Such an imperfect protonation could be due to passivation of SnO<sub>2</sub> has been reported [22,23].

Mott-Schottky plots of SnO<sub>2</sub>/MgO and TiO<sub>2</sub>/MgO are shown in Fig. 2a. The calculated FB potentials of SnO<sub>2</sub>/MgO and TiO<sub>2</sub>/MgO with the variation of MgO amounts at pH 5.0 are shown in Fig. 2b. As shown in Fig. 1b ( $\Delta$ ), pure SnO<sub>2</sub> has a FB potential of -0.07 eV (vs SCE) at pH 5.0. Introduction of 1% (w/w) MgO resulted in shift in FB potential of SnO<sub>2</sub> to -0.43 eV (vs SCE) (Fig. 2a and b) and further increase in MgO amounts leads to shifting of the FB potential of SnO<sub>2</sub> further negative. The highest negative shift in FB potential of SnO<sub>2</sub> was observed when the MgO amount was equal to  $\sim 10\%$  (w/w) and the corresponding FB potential was -0.84 eV (vs SCE). Similar to SnO<sub>2</sub>/MgO, a coating of a thin MgO layer on TiO<sub>2</sub> results in negative shift in FB potential of TiO<sub>2</sub> and the variation of FB potentials of TiO<sub>2</sub> with the variation of MgO amount is shown in Fig. 2b (\$). According to Fig. 2b, the FB potential of bare TiO<sub>2</sub> is ~-0.25 eV (vs SCE), and after coating of a thin MgO layer on TiO<sub>2</sub> surface, the FB potential shifted to  $\sim$ -0.7 eV (vs SCE). The highest FB potential shift (-0.70 eV vs SCE) was noticed when the MgO amount was around ~ 15% (w/w). The negative shift of FB of TiO<sub>2</sub> with



**Fig 2.** Mott–Schottky plots of SnO<sub>2</sub>/MgO and TiO<sub>2</sub>/MgO composite films in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution at pH 5.0. (a) SnO<sub>2</sub>/MgO(1%), 500 Hz, (b) SnO<sub>2</sub>/MgO(1%), 1 kHz, (c) TiO<sub>2</sub>/MgO (1%), 500 Hz, (d) TiO<sub>2</sub>/MgO(1%), 1 kHz, (e) TiO<sub>2</sub>/MgO(10%), 500 Hz and (f) TiO<sub>2</sub>/MgO (10%), 1 kHz; (b) variation of FB potential of TiO<sub>2</sub>/MgO ( $\diamond$ ) and SnO<sub>2</sub>/MgO ( $\Delta$ )in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution at pH 5.0. as a function of the MgO content in the composite solution.

the variation of MgO amount is not as dramatic as in the case of  $SnO_2$  and the possible reason will be discussed later.

From the FB values, it can be assumed that coating of a MgO layers on semiconductor nanocrystallites leads to some sort of surface or structural modification of semiconductor particles resulting in the negative shift of FB potentials of TiO<sub>2</sub> and SnO<sub>2</sub> particles. The effect of MgO coating on negative shift in FB of semiconductor particles can be understood by considering the acidity and basicity of semiconductor particles and MgO. TiO<sub>2</sub> and SnO<sub>2</sub> nanocrystallites are acidic because of their point of zero charge (PZC) are 6.5 are 4.5 respectively while MgO is basic and its PZC is 12.0 which is supposed to be the highest basic oxide [17,24]. Therefore, in composites of TiO<sub>2</sub>–MgO and SnO<sub>2</sub>– MgO core-shell structures, there is a tendency of deprotonation of TiO<sub>2</sub> and SnO<sub>2</sub> surfaces by the basic MgO as given in reactions (2) and (3). The reactions (2) and (3) are similar to acid base deprotonation/ protonation reaction of TiO<sub>2</sub> in solution (reaction 1).

$$Ti-OH/MgO \rightarrow [Ti-O]^{-} \approx Mg^{+}OH$$
 (2)

$$Sn-OH/MgO \rightarrow [Sn-O]^{\sim}Mg^{+}OH$$
 (3)

As a result of deprotonation of TiO<sub>2</sub> and SnO<sub>2</sub> surfaces by the basic MgO, a layer of interfacial dipole can be formed between TiO<sub>2</sub> (or SnO<sub>2</sub>) and MgO and the interfacial dipole layer changes the electrostatic potential energy across the interface. Therefore, considering the dissociation reactions (2) and (3) together with equilibrium potential ( $\Delta\theta$ , Eq. (1A)), a negative shift in FB potentials of TiO<sub>2</sub> and SnO<sub>2</sub> can be justified [20,21].

The negative shift in FB of TiO<sub>2</sub> is not as dramatic as in the case of  $SnO_2$  even though variation of FB potentials of  $SnO_2$  and TiO<sub>2</sub> particles are similar with the variation of MgO content. The possible reason could be differences in crystalline nature of  $SnO_2$  and TiO<sub>2</sub> particles. The particle size of the  $SnO_2$  particles employed in this investigation is ~10–15 nm and the formation of uniform, well crystalline  $SnO_2$  particle size [13,25]. Since the Degussa P25 TiO<sub>2</sub> particles employed in this study are composed of different sizes of rutile/anatase clusters and agglomerates [26–28], a full MgO coverage on TiO<sub>2</sub> could not be clearly established. Consequently, partial protonation/deprotonation of TiO<sub>2</sub> surface by MgO particles could be expected. Therefore, considering the differences in crystalline nature of  $SnO_2$  and TiO<sub>2</sub> particles, variation of FB values with variation of MgO amount could be understood.

On the other hand, one might expect a negative shift in FB potential as a result of quantum confinement effect. As the starting materials already had well defined crystalline structure, quantum confinement effect for TiO<sub>2</sub> and SnO<sub>2</sub> could not be expected in this study. Hence, it is reasonable to assume that the observed negative shift in FB is not due to quantum confinement. Characterizations of MgO coated SnO<sub>2</sub> thin films and catalysts have been reported earlier [13]. The core-shell structure has been observed for TiO<sub>2</sub>/MgO by transmission electron microscopy study of MgO coated TiO<sub>2</sub> particles [29]. Using a similar preparation method described in this investigation and ref [13], homogeneous distribution of oxides like MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> on SnO<sub>2</sub> and TiO<sub>2</sub> nanocrystallites have been reported by Palomares et al. [17] and Zaban et al. [30]. (In our previous investigation [13], thickness of the MgO shell was estimated to be 0.1 nm while in their investigation Palomares et al. [17] estimated the shell thickness of ~900 A°.) As explained above, homogeneous distribution of MgO particles around TiO<sub>2</sub> and SnO<sub>2</sub> nanoparticles resulting in an efficient deprotonation of TiO<sub>2</sub> and SnO<sub>2</sub> surfaces and consequently the observed negative shift of FB potentials of TiO<sub>2</sub> and SnO<sub>2</sub> could be attributed to the electronic effect of MgO shell.

As mentioned earlier, shifting of the FB potentials of semiconductors plays an important role deciding their photocatalytic as well as photoelectrochemical properties of thin oxide films and powders. i.e. eV (SCE)



**Fig 3.** Schematic illustration of energy levels of TiO<sub>2</sub> and the redox couple for (a) without MgO over layer (bare TiO<sub>2</sub>) and (b) with MgO over layer (TiO<sub>2</sub>/MgO). The attainable  $V_{oc}$  is given by  $V_1$  and  $V_2$  respectively for (a) and (b).  $\Delta G_{trans1}$  (bare TiO<sub>2</sub>) and  $\Delta G_{trans2}$  (TiO<sub>2</sub>/MgO) are free energy change for the transfer of electrons from the excited state (ES) to the CB of the oxide.  $\Delta G_{recom1}$  (bare TiO<sub>2</sub>) and  $\Delta G_{recom2}$  (TiO<sub>2</sub>/MgO) are free energy change for the reactions from the CB of oxide to the VB of the oxide.

our previous results on nanocrystalline SnO<sub>2</sub>-based dye sensitized photoelectrochemical solar cells have very low open-circuit voltages of 325–375 mV and efficiencies of ~1%. However, on coating SnO<sub>2</sub> crystallites with a thin film of MgO, the  $V_{oc}$ ,  $I_{sc}$  and efficiency were increased to 650–700 mV, 16 mA/cm<sup>2</sup> and 6.5%, respectively [13]. Similarly, Lee et al. [31] and Wang et al. [32] have shown that the coating of a thin CaCO<sub>3</sub> layer on TiO<sub>2</sub> particles resulted in increase in  $V_{oc}$ ,  $I_{sc}$  and efficiency i.e. uncoated TiO<sub>2</sub> thin films produced an overall efficiency of 6.9% ( $J_{sc}$ =11.38 mA cm<sup>-2</sup>,  $V_{oc}$ =0.816 V, FF=0.741) and after 1 wt.% CaCO<sub>3</sub> coating on the TiO<sub>2</sub> surface, the overall efficiency has been improved to 7.9% ( $J_{sc}$ =12.41 mA cm<sup>-2</sup>,  $V_{oc}$ =0.845 V, FF=0.758) [32]. Similar results have been reported by several other research groups [16,17,30].

As described above, coating of a thin insulating MgO layer on TiO<sub>2</sub> and SnO<sub>2</sub> particles increases the overall solar cell performance mainly by increasing the  $V_{oc}$ . Similarly, a significant increase in  $V_{oc}$  has been reported for the DSSC with the addition of 4-tert-butylpyridine (4-tbp) to the redox electrolyte [18,33,34]. The increase in  $V_{\rm oc}$  has been attributed to the shift of the TiO<sub>2</sub> band edge towards negative potentials [35,36]. The observed negative shift of FB potential of TiO<sub>2</sub> after addition of 4-tbp could be due to differences in basicity of TiO<sub>2</sub> and 4-tbp. Pyridine is a known basic compound and the basicity of pyridine derivatives has been reported with the effect of various substituents [37]. Similar to the effect of tbp on DSSC, coating of a thin MgO layer on TiO<sub>2</sub> and SnO<sub>2</sub> could lead to enhance the performance of DSSC by increasing  $V_{\rm oc}$ ,  $I_{\rm sc}$  and fill factor as well as photocatalytic activity. In dye sensitized solar cells,  $V_{\rm oc}$  is determined by the difference between the quasi-Fermi level of electrons in the oxide film and the energy of the redox couple in the electrolyte  $(\Delta V)$  [1]. As shown in Fig. 3, the attainable  $V_{\rm oc}$  without MgO layer on TiO<sub>2</sub> ( $\Delta V_1$ ) is less than the attainable  $V_{\rm oc}$  with an insulating MgO layer on  $TiO_2$  ( $\Delta V_2$ ) due to negative shift of FB potential after coating of a thin MgO layer on the semiconductor particles. Hence, the negative shift in FB results in increase in attainable  $V_{\rm oc}$  and hence barrier height for charge transfer reactions. Similarly, the FB potential can be shifted in order to electrolyze a redox couple that is otherwise too positive in the electrochemical series to be reactive at the illuminated semiconductor surface [2].

The results presented above clearly show that the  $V_{oc}$  and hence overall efficiency of DSSC could increase after coating of a thin insulating MgO layer on TiO<sub>2</sub> or SnO<sub>2</sub> particles. In addition to increase in  $V_{\rm oc}$ , thermodynamic as well as kinetic factors could also play a role in increasing the cell efficiency after coating of a MgO layer as explained below. As shown in Fig. 3, in thermodynamic point of view, the free energy change  $(\Delta G)$  for electron transfer from the excited dye molecules to the CB of uncoated oxide ( $\Delta G_{\text{transfer1}}$ ) is more negative than that of MgO coated oxide ( $\Delta G_{\text{transfer2}}$ ). Similarly, the free energy change for charge recombination for uncoated oxide ( $\Delta G_{\text{recombination1}}$ ) is less negative than that of MgO coated oxide ( $\Delta G_{\text{recombination2}}$ ). Therefore, in thermodynamic point of view, the negative shift in FB potential results in decrease in  $\Delta G$  for the charge transfer from excited molecules to the CB while increase in  $\Delta G$  was expected for the charge recombination process. Consequently, the negative shift in FB would impede the charge transfer from excited dye molecules to the CB while charge recombination process will be facilitated and such a situation would definitely decrease the efficiency of DSSC. Contrary, it has been demonstrated the increase in solar cell efficiencies once a thin insulating oxide layer is coated on TiO<sub>2</sub> and SnO<sub>2</sub> [13-17]. The possible explanation could be that the kinetically controlled forward electron transfer rate involves energetic electrons and the electron transfer rate is controlled by the coupling of the excited state of the dye to the conduction band energy levels in the semiconductor [38,39]. Due to electron acceptor level (i.e. CB) is composed of continuously distributed electronic energy levels, the forward electron transfer reaction is expected to be extremely rapid (i.e. fs scale) [40]. Also it has been reported that very thin insulating layer (~900 A°) does not hinder transfer of energetic electron from the excited dye molecules to the CB of TiO<sub>2</sub>, but instead it retards charge recombination rates [17]. On the other hand, the back-electron transfer reaction is thermally activated and is believed to lie in the Marcus inverted region [41]. Therefore, a decrease in back-electron transfer reaction rate is expected after coating of a MgO layer on TiO<sub>2</sub> and SnO<sub>2</sub> thin films. Further it can be assumed that the MgO coating on TiO<sub>2</sub> and SnO<sub>2</sub> may change the charge transfer and recombination kinetics which may in turn enhance the solar cell performance and photocatalytic activity.

#### 4. Conclusion

Fine tuning of FB potentials of  $TiO_2$  and  $SnO_2$  semiconductors was achieved by introducing a thin insulating MgO outer layer around  $TiO_2$  and  $SnO_2$  nanocrystallites. A negative shift of FB was noticed for coreshell structures of both  $TiO_2$ –MgO and  $SnO_2$ –MgO composites. It was shown that the negative shift of FB potentials of  $TiO_2$  and  $SnO_2$  was not due to quantum confinement of oxide particles but due to deprotonation of  $TiO_2$  and  $SnO_2$  surfaces by MgO. The optimum MgO amounts to achieve the highest negative shift in FB potentials of  $TiO_2$  and  $SnO_2$  were found to be 15% (w/w) and 10% (w/w) respectively. Negative shift in FB potential may contribute to enhance the solar cell efficiencies and photocatalytic activity.

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#### References

- [1] G. Schlichthorl, S.Y. Huang, J. Sprague, A.J. Frank, J. Phys. Chem. B 10 (1997) 8141.
- [2] C.M. Wang, T.E. Mallouk, J. Phys. Chem. 94 (1990) 4276.
- [3] G. Sauve, N.E. Cass, G. Coia, S.J. Doig, I. Lauermann, K.E. Pomykal, N.S. Lewis, J. Phys. Chem. B 104 (1997) 6821.
- [4] P.J. Cameron, L.M. Peter, J. Phys. Chem. B 109 (2005) 7392.
- [5] P.J. Cameron, L.M. Peter, S. Hore, S. J. Phys. Chem. B 109 (2005) 930.
- [6] G. Ramakrishna, A.K. Singh, D.K. Palit, H.N. Ghosh, J. Phys. Chem. B 108 (2004) 1701.
- [7] S.A. Hagfeldt, M. Gratzel, Chem. Rev. 95 (1995) 49.
- [8] F. Vogel, P. Poho, H. Weller, Chem. Phys. Lett. 174 (1990) 241.
- [9] J. Bandara, K. Tennakone, J. Colloid Interface Sci. 236 (2001) 375.
- [10] V. Subramanian, E.E. Wolf, P.V. Kamat, Langmuir 19 (2003) 469.

- [11] J. Bandara, C.C. Hadapangoda, W.G. Javasekera, Appl. Catal. B Environ, 50 (2004) 83.
- [12] J. Bandara, S.S. Kuruppu, U.W. Pradeep, Colloids Surf. A 276 (2006) 197.
- [13] K. Tennakone, J. Bandara, P.K.M. Bandaranayake, G.R.R. A Kumara, A. Konno, Jpn. J. Appl. Phys. 40 (2001) L732.
- [14] H.S. Jung, J. K. Lee, M. Nastasi, S.W. Lee, J.Y. Kim, J.S. Park, K.S. Hong, H. Shin, Langmuir 23 (2005) 13332.
- [15] J.H. Yum, S. Nakade, D.Y. Kim, S. Yanagida, S. J. Phys. Chem. B 110 (2006) 3215.
- [16] A. Kay, M. Gratzel, Chem. Mater. 14 (2002) 2930.
- [17] E. Palomares, J.N. Clifford, S.A. Haque, T. Lutz, J.R. Durrant, J. Am. Chem. Soc. 125 (2003) 475.
- [18] M.K. Nazeeruddin, K. Kay, I. Rodicio, R. Humphry, E. Muller, P. Liska, N. Vlachopoulos, M. Gratzel, J. Am. Chem. Soc. 115 (2003) 6380.
- [19] A.J. Bard, L.R. Faulkner, Electrochemical Methods, 1st ed. John Wiley and Sons, New York 1980
- [20] M. McCann, J. Pezy, J. Electrochem. Soc. 128 (1981) 1735.
  [21] K.S.V. Santhanam, M. Sharon, Photoelectrochemical Solar Cells, Elsevier, Amsterdam, 1988
- [22] E.R. Abd, S. Sayed, H. Hassan, H. Hamdy, N.F. Mohamed, Corros. Sci. 46 (2004) 1071.
- [23] E.R. Abd, S. Sayed, A.M. Zaky, N.F. Mohamed, J. Alloys Compd. 424 (2006) 88.
- [24] G.A. Parks, Chem. Rev. 65 (1965) 177.
- [25] S. Ito, Y. Makari, T. Kitamura, Y. Wada, S. Yanagida, J. Mater. Chem. 14 (2004) 385.
- [26] A.K. Datye, G. Riegel, J.R. Bolton, M. Huang, M.R. Prairie, J. Solid State Chem. 115 (1995) 236.

- [27] D.C. Hurum, A.G. Agrios, K.A. Gryy, T. Rajh, M.C. Thurnauer, J. Phys. Chem. B 107 (2003) 4545.
- [28] L. Zan, S. Wang, W. Fa, Y. Hu, L. Tian, K. Deng, Polymer 47 (2006) 2006.
- [29] H.S. Jung, J.K. Lee, M. Natasi, J.R. Kim, S.W. Lee, J.Y. Kim, J.S. Park, K.S. Hong, H. Shin, Appl. Phys. Lett. 88 (2006) 013107.
- [30] Y. Diamant, G.G. Chen, O. Melamed, A. Zaban, J. Phys. Chem. B 107 (2003) 1977. [31] S. Lee, J.Y. Kim, S.H. Youn, M. Park, K.S. Hong, H.S. Jung, J.K. Lee, H. Shin, Langmuir
- 23 (2007) 11907.
- [32] Z.S. Wang, M. Yanagida, K. Sayama, H. Sugihara, Chem. Mater. 18 (2006) 2912.
- [33] G. Boschloo, H. Lindstron, E. Magnusson, A. Holmberg, A. Hagfeldt, J. Photochem. Photobiol., A. Chem. 148 (2002) 11.
- [34] H. Kusama, Y. Konishi, H. Sugihara, H. Arakawa, Sol. Energy Mater. Sol. Cells 80 (2003) 167.
- [35] G. Boschloo, L. Haggman, A. Hagfeldt, J. Phys. Chem. B 110 (2006) 13144.
- [36] G. Schlichthorl, S.Y. Huang, J. Sprague, A.J. Frank, J. Phys. Chem. B 101 (1997) 8139.
  [37] A. Borowiak-Resterna, J. Szymanowski, A. Voelkel, A. J. Radioanal. Nucl. Chem. 208 (1996) 75.
- [38] P.V. Kamat, I. Bedja, S. Hotchandani, L.K. Patterson, J. Phys. Chem. 100 (1996) 4900. [39] R.J.D. Miller, G.L. McLenden, A.J. Nozik, W. Schmickler, F. Willig (Eds.), Surface Electron Transfer Processes, VCH, New York, 1995.
- [40] B. Burfeindt, T. Hannappel, W. Storck, F. Willig, J. Phys. Chem. 100 (1996) 16463.
- [41] J.E. Moser, M. Gratzel, Chem. Phys. 176 (1993) 493.