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Stability and efficiency improvement of TiO₂-based dye-sensitized solar cells by surface modification of MgO

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Abstract

The efficiencies of dye-sensitized solar cells are limited by the recombination of the electrons in the conduction band of the n-type oxide semiconductor with the photogenerated dye cation and acceptors in the electrolyte. Attempts have been made to resolve this problem by inserting ultra-thin barriers of insulating material between the oxide surface and the dye layer. The strategy has been successful in boosting the efficiency of cells based on SnO_2 . However, according to previous studies, the adoption of this technique to TiO_2 has not been successful, because of the constraints of depositing pin hole free ultra-thin films of oxide insulators over TiO_2 . Here, a simple method is described for deposition of ultra-thin films of MgO on TiO_2 . Cells prepared by this technique deliver an efficiency of 10.03% compared 9.27% those based on bare TiO_2 films. Studies conducted reveal that DSCs based on TiO_2/MgO films are highly stable than bare TiO_2 films.

Keywords Dye-sensitized solar cells · Recombination · Titanium dioxide · Magnesium oxide

Introduction

The dye-sensitized solar cell (DSC) and related innovations that originated following the work of Grätzel and coworkers continue to be an active area of intense research investigation [1]. Although DSCs tend to give efficiencies of over 14% [2], much effort is still diverted towards finding ways for further enhancing their efficiencies. The two main issues associated with DSCs are their relatively narrow spectral response and charge carrier losses due to recombination. The former requires identification of dyes with broader spectral responses that are capable of injecting electrons to the conduction band of TiO₂ at near unity quantum efficiency [3, 4]. Alternatively, techniques need to be developed to adopt more

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than one pigment to achieve effective panchromatic sensitization. An equally challenging problem is the mitigation of recombination reactions in DSCs. These devices encounter three types of recombinations: (1) geminate recombination, i.e., the back reaction between the dye cation and the injected electron [5]; (2) combination of electrons transferred to the TiO₂ nanocrystalline network and acceptors in the electrolyte (e.g., I_3^{-}) [6, 7]; and (3) recombinations at the points where the conducting glass surface (on which TiO₂ is deposited) is exposed to the electrolyte [8]. The extent of geminate recombination depends on the structure and the mode of anchoring of the dye molecules to the semiconductor surface and the nature of the semiconductor. Recombinations of the types (1) and (2) are determined by nature of the surfaces (i.e., TiO_2) and conducting glass respectively), mode of interaction of the electron acceptors in the electrolyte, and the surface and the state of electrons in the solid substrate. Consequently, the rates of the processes (1) and (2) depend on the position the of quasi Fermi level (QFL) of electrons in the solid material. As recombinations of all types adversely affect the buildup of the QFL, the kinetics of recombinations is highly nonlinear and is not fully understood. The general consensus is that the process (2) predominates over other loss mechanisms and extensive investigations have been conducted to identify methods of suppressing the reaction of electrons in the nanostructured semiconductor with the acceptors in the

Table 1	The	maximum	conversion	efficiencies	obtained	for
SnO ₂ -b	ased	dye-sensitized	solar cells	with different	ultra-thin	layers
of insul	ator/	wide band gap	semiconduo	ctors covering t	he SnO ₂ su	rface

Ultra-thin layer	Only SnO ₂	SnO ₂ /ultra-thin	Reference	
	η (%)	η (%)		
MgO	1.74	7.21	[15]	
ZnO	1.30	7.30	[<mark>16</mark>]	
CaCO ₃	3.00	5.04	[17]	

electrolyte [5–9]. An important finding in this direction has been the observation that incorporation of tert-butylpyridine to the electrolyte boosts the open-circuit voltage of the cell thereby increasing the efficiency. Mechanism involved seems to be passivation of some of recombination centers on the TiO₂ surface by adsorbed *tert*-butylpyridine molecules. Nitrogen-containing organic bases adhere to Lewis and/or Brønsted acid sites on oxide surfaces [10–12]. However, even after tert-butylpyridine treatment, the observed opencircuit voltage falls behind the theoretical value by about 300 mV indicating that other recombination pathways also are in operation. A strategy attempted has been to cover the nanocrystalline semiconductor surface with an ultra-thin barrier of an insulator or high band gap semiconductor material [13, 14]. Here, the barrier acts as a blockade preventing the tunneling of electrons from the semiconductor to the electrolyte interface. Efficiencies of DSCs made from nanocrystalline SnO₂ films dramatically increases on deposition of ultra-thin outer shells of MgO, CaCO₃, or ZnO on the SnO₂ crystallite surface. The conversion efficiencies obtained for SnO₂-based dye-sensitized solar cells with different ultrathin layers of semiconductors covering the SnO₂ surface are summarized in Table 1 [15–17].

Such barriers invariably interfere with the electron injection, and the effect is conspicuously observed in SnO_2 DSCs because here the recombination rate is intrinsically high. Many attempts have been made to improve the efficiency of TiO₂ DSCs by deposition of outer shells of semiconductor or

Table 2 The efficiencies obtained for TiO_2/MgO -based dye-sensitized solar cells with different techniques of MgO deposition

MgO deposition method	Only TiO ₂ efficiency η (%)	TiO ₂ /MgO efficiency η (%)	Reference
Reactive DC magnetron sput- tering	6.45	7.57	[18]
Liquid phase deposition	5.08	5.44	[19]
Dip coating	3.99	5.01	[20]
Sol-gel spin coating	2.41	3.78	[21]
Solution growth technique	3.91	4.10	[22]

insulating materials. This surface modification on TiO₂ film suppresses the backward electron transfer. Several efforts have been taken depositing MgO as an insulating material with a large band gap of 7.8 eV on TiO_2 and used them in DSCs. Wu et al. surface modified the TiO₂ electrode using MgO by reactive DC magnetron sputtering [18]. Xuhui et al. coated the metal oxide layers on the TiO₂ electrode by direct liquid phase deposition method [19]. Photiphitak et al. prepared TiO₂/MgO composite films by dip coating from magnesium acetate solution [20]. The sol-gel spin coating method was used by Amar et al. to deposit a thin MgO layer onto the TiO_2 film [21]. Karuppuchamy et al. constructed core-shell structured TiO2/MgO electrodes synthesized by solution growth technique [22]. The efficiencies obtained for TiO₂/MgO-based dye-sensitized solar cells with different techniques of MgO deposition are shown in Table 2.

Although there is good evidence for enhancement of the open-circuit voltage, the conclusive evidence is not available to determine whether efficiencies above the optimized cell can be achieved by this method. It seems that in most experiments the effect of the barrier in reducing the injection efficiency had outweighed the gain from suppression of recombination. TiO_2 is a semiconductor having a band gap of 3.2 eV, and MgO has a wide band gap energy of 7.8 eV which is insulator [23, 24]. Photoexcited electrons can tunnel through the MgO to the conduction band of the TiO2. The tunneling of excited dye electrons across MgO barrier is energetically feasible since the excited level of the dye is located above the conduction band of the TiO_2 . At the same time, this MgO barrier prevents the backward transfer of electrons and minimizes the electron recombination. Therefore, the insertion of wide band gap MgO on the TiO₂ electrode has enhanced the open-circuit voltage by suppressing recombination. Furthermore, the MgO coating has supported the dye adsorption, and hence, better solar energy absorption resulted in increased photocurrent. Figure 1 explains this phenomenon.

We have found that at surface coverage of MgO on TiO₂, there is clear evidence for enhancement of efficiency above that of equivalent cells composed only of TiO₂. The other virtue of incorporation of MgO into the TiO₂ film happens to be the improvement of cell stability against photocatalytic degradations induced via TiO₂ band gap radiation. Evidence is presented to show that MgO passivates recombination and photocatalytically active sites on the TiO₂ surface.

Experimental

Preparation of TiO₂ photoanode

The TiO_2 photoanodes were prepared according to the method descried previously [25]. Titanium tetraisopropoxide (8.0 mL) and acetic acid (1.0 mL) were mixed with ethanol



Fig. 1 Energy level diagram showing the suppression of recombination of injected electrons due to the coverage of semiconductor nanoparticle surfaces by a thin layer of high band gap magnesium oxide

(8.0 mL), and steam was passed through the solution for rapid hydrolysis of titanium isopropoxide. The expulsion of ethanol by steaming then formed a transparent solid mass consisting of TiO₂ nanoparticles. The resulting colloid was ground with (20.0 mL) of de-ionized water in a motor. Finally, the prepared colloidal solution was autoclaved, at 150 °C, for 3 h, and TiO₂ colloidal solution was completed. The TiO₂ colloidal solution (30 mL), acetic acid (8.25 mL), Triton X-100 (8 drops), and ethanol (30 mL) were mixed to prepare TiO₂ suspension. TiO₂ suspension was sprayed on heated (150 °C) FTO glass substrates using a purpose-built spray gun.

Surface modification of TiO₂ photoanode

The surface modification of TiO₂ photoanode was carried out by dipping in magnesium acetate solution $[Mg(C_2H_3O_2)_2]$. Experiments were directed as a function of $Mg(C_2H_3O_2)_2$ concentration on TiO₂ electrodes where the surface modification depends on the $Mg(C_2H_3O_2)_2$ concentration. The TiO₂ photoanodes were immersed in $Mg(C_2H_3O_2)_2$ precursor solutions of 1×10^{-4} , 5×10^{-4} , 1×10^{-3} , 5×10^{-3} , and 1×10^{-2} M concentration. Then TiO₂/Mg²⁺ electrodes were dried in air and sintered, at 500 °C, for 30 min, to result in MgO thin shell around TiO₂ nanoparticles (TiO₂/MgO). After that, TiO₂ and TiO₂/MgO photoanodes were heated to 80 °C and kept soaked overnight in a 3×10^{-4} M solution of rutheniumbased N719 dye which was prepared by dissolving the dye in a solution of acetonitrile and t-butyl alcohol 1:1 v/v ratio. XR



Fig. 2 X-ray diffractogram pattern for sintered TiO₂ and TiO₂/ MgO photoanodes



Fig. 3 SEM micrographs for sintered **a** bare TiO₂ and **b** TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanodes

diffractograms (XRD) and scanning electron micrographs (SEM) were taken for sintered TiO_2 and TiO_2/MgO photoanodes. Absorption spectra were recorded for TiO_2 and TiO_2/MgO (dipped in 1×10^{-3} M magnesium acetate solution and sintered) photoanodes without N719 dye and with N719 dye.

Construction of DSC

Lightly platinized FTO counter electrodes were clipped firmly with the dye-anchored TiO₂/MgO working electrodes, and the space between the two electrodes was filled with the liquid electrolyte containing I^-/I_3^- redox couple (0.1 M LiI, 0.05 M I₂, 0.6 M dimethylpropylimidazolium iodide and

tertiarybutylpyridine in acetonitrile). A mask with a window of 0.25 cm² was also clipped on the working electrode to complete the DSC configuration. In the same way, dye-anchored TiO₂ working electrode was clipped with a Pt-based FTO counter electrode for the comparison. Their solar cell performances were measured, at 100 mW cm⁻², under the illumination of AM 1.5 simulated sunlight.

Characterization techniques and instruments

The crystal structure of TiO₂ and TiO₂/MgO was studied by XRD data using Rigaku Ultima IV X-ray diffractometer equipped with a Cu anode and dual detectors (λ =15.4 nm).



Fig. 4 EDX of TiO₂/MgO photoanode (dipped in 1×10^{-3} M magnesium acetate solution)

Fig. 5 a Absorption coefficient spectra of TiO₂ and TiO₂/ MgO (dipped in 1×10^{-3} M magnesium acetate solution and sintered) without N719 dye and **b** absorbance spectra of TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution and sintered) with N719 dye



(a)



(b)





The UV–vis absorption spectra of photoanodes (with and without dye coating) were taken by a Shimadzu 2450 UV–vis spectrophotometer in the wavelength range from 300 to 800 nm. The morphology of the photoanodes was determined using SEM images of the surface by Zeiss EVO LS15 scanning electron microscope with different magnifications. Electrochemical impedance spectroscopy (EIS) measurements were carried out on DSC devices using the Metrohm Autolab potentiostat/galvanostat PGSTAT 128N with a FRA 32 M frequency response analyzer (FRA) in the frequency range between 10^{-2} and 10^{6} Hz. The impedance was obtained by applying the negative value of open-circuit voltage (– V_{OC}) as bias voltage under the illumination of 100 mW cm⁻². The *J-V* characteristics of the solar cells were obtained by exposing 0.25 cm² surface area of the completed cell to AM 1.5 at 100 mW cm⁻² simulated sunlight using SPD SS-25 LED solar simulator and VK-PA-300 K PV power analyzer. *J-V* measurements were repeated to at least four solar cell devices with identical conditions to guarantee the reproducibility. IPCE experimental setup included monochromatic light illumination from a Bentham PVE 300 unit with a TMC 300 monochromator and 150W Xenon arc lamp covering the 300 to 800 nm wavelength range.

Results and discussion

X-ray diffractogram analysis

Figure 2 depicts the X-ray diffractogram of sintered TiO_2 electrode and TiO_2/MgO composite electrode. In

Photoanode	Current density J_{sc} (mA cm ⁻²)	Voltage V_{oc} (V)	Fill factor FF (%)	Efficiency η (%)
TiO ₂	19.59	0.686	0.69	9.27
$TiO_2/MgO (1 \times 10^{-4} M)$	20.61	0.689	0.68	9.66
$TiO_2/MgO (5 \times 10^{-4} M)$	20.71	0.688	0.69	9.83
$TiO_2/MgO (1 \times 10^{-3} M)$	20.74	0.691	0.70	10.03
$TiO_2/MgO (5 \times 10^{-3} M)$	19.35	0.698	0.70	9.45
$TiO_2/MgO (1 \times 10^{-2} M)$	18.05	0.704	0.70	8.90

 Table 3
 Performances of DSCs

 with different photoanodes





both XRD patterns, the characteristic MgO peaks could not be observed. The reason may be that the thickness of MgO film is not enough to be identified by the XRD [19]. The Debye–Scherrer equation $D = k\lambda/\beta \cos\theta$ was used to calculate the crystallite size of TiO₂ and TiO₂/ MgO. In this equation, k is a constant (0.9), λ is the X-ray wavelength (0.154 nm), β is full width at halfmaximum (FWHM) of the value in radians, and θ is the reflection angle. The average crystallite sizes obtained for TiO₂ and TiO₂/MgO are 15.22 nm and 11.54 nm, respectively. This corroborates well with the particle size determined from SEM images where the particle sizes are 44 nm and 35 nm, respectively (vide infra). Since the particle size is reduced due to the presence of the MgO thin layer, the increase in surface area results in the increased dye adsorption. This fact also contributes to increased conversion efficiency of the solar cell when the TiO_2 particles are covered with a thin layer of MgO.

Scanning electron micrographs analysis

The surface morphology of sintered bare TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution and sintered) photoanodes are detected by SEM and are shown in Fig. 3. It can be seen that average particle size of TiO₂/

MgO is 25% small compared to the bare TiO_2 . This could be because of the surfaces of TiO_2 particles are shielded by the thin layer of MgO (arose due to hydrolysis of magnesium acetate). Sintering eliminates moisture and helps MgO to firmly attach to the TiO₂ particles [20]. Energy dispersive X-ray (EDX) spectra at the surface of TiO₂/MgO electrode is shown in Fig. 4. The elemental analysis of Ti, Mg, and O in Fig. 4 indicates the presence of MgO on TiO₂ surface.

Optical absorption

Absorption coefficient spectra of TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution and sintered) without N719 dye and (b) absorbance spectra of TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution and sintered) with N719 dye are shown in the Fig. 5. As depicted by Fig. 5, the absorption coefficient spectra of TiO₂ and TiO₂/MgO without dye have nearly the same spectra, and the dye-coated TiO₂/MgO film has higher absorbance than that of the dye-coated TiO₂ film. The amount of dye absorption on photoelectrode is related to the extent of the optical absorption of dye. Therefore, TiO₂/MgO photoanode should have enhanced dye absorbance. Shielding TiO₂ surface with N 719 dye is difficult without having MgO coating because of intermolecular electrostatic repulsion. The enhanced basicity of MgO surface modified TiO₂

Fig. 8 a Nyquist plots of DSCs with TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanodes, b equivalent circuit model used to describe the EIS spectra, and c Bode plots of DSCs with TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanodes





improves the dye absorption using the carboxylic acid group of N719 dye [18].

Photocurrent-voltage (J-V) characteristics

Figure 6 shows the photocurrent–voltage characteristics of DSCs fabricated with bare TiO₂ and TiO₂/MgO (prepared by dipping in 1×10^{-3} M concentration of magnesium acetate solutions and sintering) photoanodes. The corresponding photovoltaic parameters for all the DSCs fabricated are summarized in Table 3. The TiO₂/

MgO (dipped in 1×10^{-3} M magnesium acetate solution and sintered) photoanode gives improved shortcircuit photocurrent (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*FF*) compared to the TiO₂ photoanode. The conversion efficiency (η) is also giving rise in 10.03%. Upon increasing Mg(C₂H₃O₂)₂ concentration, V_{oc} and *FF* have increased. But J_{sc} and conversion efficiency initially increased and lately decreased. That points out the extremely thick MgO layer beyond the tunneling distance is causing the depletion of the photoelectron injection process [18].

Table 4 The data extracted from equivalent circuits of the DSCs with TiO_2 and TiO_2/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanodes

Photoanode	$\boldsymbol{R}_{\boldsymbol{S}}\left(\Omega\right)$	$R_r(\Omega)$	$C_{\rm dl}$ (mF)	$Z_w (\Omega s^{1/2})$	$\boldsymbol{R}_{\mathrm{ct}}\left(\Omega\right)$	$C_{\rm ce}~({\rm mF})$
TiO ₂	15.31	0.72	33.92	4.78	9.01	11.99
$TiO_2/MgO (1 \times 10^{-3} M)$	15.28	1.56	36.54	2.68	10.80	11.41



Fig. 9 Comparison of the time variation of the efficiencies of DSCs based on bare TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanode

Incident photon to current conversion efficiency (IPCE) analysis

Figure 7 shows the IPCE spectra of DSCs fabricated using TiO_2 and TiO_2/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanodes. It can be seen that DSC with TiO_2/MgO photoanode gives slightly higher IPCE than DSC with TiO_2 -based photoanode.

Electrochemical impedance spectroscopy (EIS) analysis

Electrochemical impedance spectroscopy process is a technique which can be used to identify electrochemical kinetics of the DSC processes. It can be used to analyze the electron transport process which determines the efficiency of the DSCs. Figure 8a depicts the Nyquist plots of DSCs fabricated using TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanodes measured between 1×10^{-2} and 1×10^{6} Hz under 1 sun illumination (AM 1.5, 100 mW cm⁻²). The equivalent circuit for the dye-sensitized solar cell has the following components. The overall series resistance R_s is applying at the highest frequency domain. This follows the parallel connection of the recombination resistance (R_r) , and the double layer capacitance indicated by a constant phase element C_{dl} appears in the frequency range of 0.05-126.82 Hz. The ionic diffusion of the electrolyte can be described by the Warburg impedance, Z_w , which appears next. Finally, the electron transfer of the counter electrode is described by the parallel connected electron transfer resistance R_{ct} and the corresponding double layer capacitance at the counter electrode/electrolyte interface which appears as a constant phase element C_{ce} . Therefore, the best fitting equivalent circuit should have circuit elements which are connected serially. The best-fitted equivalent circuit is shown in Fig. 8b. The Bode plots are also given in Fig. 8c. As shown in the Bode plots, in the high and low frequency region, the phase remains almost constant justifying the selection of constant phase elements. The χ^2 is 0.0030 for the equivalent circuit fitting for the TiO₂-based solar cell which is almost same for the TiO₂/MgO-based solar cell (0.0032). The fact that the χ^2 is much lower than 0.01 indicates the accuracy of the circuit elements chosen and connected to get the equivalent circuit. As the data indicates in Table 4, the recombination resistance R_r with TiO₂ alone is 0.72 Ω , whereas that in TiO₂/MgO system is 1.56 Ω . The increase in the recombination resistance by factor of 2.16 times due to the presence of MgO thin layer clearly shows the suppression of recombination by a factor of 2.16.

Stability of the TiO₂/MgO photoanode

Figure 9 depicts the time variation of the efficiencies in DSCs based on bare TiO₂ and TiO₂/MgO (dipped in 1×10^{-3} M magnesium acetate solution) photoanodes under AM 1.5 at 100 mW cm⁻² illumination during 1-h period. A measurable decrease of the efficiency was not observed in the DSC made with TiO₂/MgO photoanode throughout this period of illumination. The DSC fabricated with bare TiO₂ photoanode has shown a gradual decrease of the efficiency. The improved stability of the TiO2/MgO system is due to reduction of photodegradation of dye.

Conclusion

Strategies to improve the efficiencies of dye-sensitized solar cells above the optimum attract much attention. The main constraint limiting the efficiencies of dye-sensitized solar cells is recombination of electrons in the conduction band of the n-type oxide with the photogenerated dye cation and acceptors in the electrolyte. The rate of this recombination is well known to depend on the nature of the n-type oxide and of the familiar n-type oxides, and TiO_2 is proven to be the best and the average efficiency, measured under standard conditions for cell of active area 0.25 cm^2 is around 9.5%. Insertion of insulating barriers between oxide surface and dye layer is known to enhance the efficiency cells based on SnO₂, and the previous experimentation has not succeeded in increasing the efficiency TiO2-based cell beyond the optimum. The simple method of coating layer of MgO on TiO_2 described in this work enhances the efficiency from 9.27 to 10.03%. Additionally, an enhancement of the stability is also observed as photocatalytic dye degradation has been suppressed by the MgO surface barrier.

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Data availability The datasets generated/analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests The authors declare no competing interests.

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