



Bio Synthesis TiO_2 Nano Particles Coreshell

Mgo Based Solar Cell

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ABSTRACT

The synthesis of metallic nanoparticles is an active area of academic, application research as well and nanotechnology. Different chemical and physical procedures that are currently used for synthesis of metallic nanoparticles present many problems. These problems include generation of hazardous by-products, use of toxic solvents, and high energy consumption. Biological synthesis of nanoparticles by bacterial, fungi, yeast, and plant extract is the best alternative to develop cost effective, less labor, non-toxic using more green approach, environmentally benign nanoparticles synthesis to avoid adverse effects in many nanomaterials applications. Among the various metal oxide nanoparticles, titanium dioxide nanoparticles have wide applications for dye-sensitized solar cells, in air and water purification, due to their potential oxidation strength, high photo stability and non-toxicity. Till now, titanium dioxide (TiO_2) is the cornerstone semiconductors for dye-sensitized (DSSC) nanostructured electrodes for dye-sensitized solar cells. The synthesis of TiO_2 nanoparticles, $\text{TiO}_2@\text{MgO}$ core-shell film was obtained by using a simple chemical bath deposition method to coat a thin MgO film around TiO_2 nanoparticles. The core-shell configuration was characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), Lattice fringes were observed for the TiO_2 particles, and the MgO shell showed an amorphous structure, revealing a clear distinction between the core and shell materials. Applying the core-shell film as photoanode to the dye-sensitized solar cells (DSSCs), it shows a superior performance compared to the pure.

Keywords— $\text{TiO}_2@\text{MgO}$; core-shell; electrode; dye-sensitized solar cell (DSSC).

I. INTRODUCTION

The dye-sensitized solar cells (DSSCs) have a significant potential as a low-cost solar cell as compared to the traditional silicon batteries. The DSSCs are typically constructed from thick films of semiconductor nanoparticles that are sintered into mesoporous network with a large internal surface area for the adsorption of light harvesting dye molecules, such as TiO_2 , SnO_2 , and ZnO films[1-3]. The semiconductor is deposited onto a transparent conducting optical (TCO) glass, a redox electrolyte (I / I^-) – that acts as a conductor, and a TCO glass that is deposited by Pt as a counter electrode. Under illumination, electrons are injected from the photoexcited dye into the nanocrystalline film and holes, leaving the opposite side of the device by means of redox mediator[4]. Since the electrolyte penetrates throughout the nanoporous structure, a large surface area is available for a reaction between the photoinjected electrons in the semiconductor and the oxidized ions in the



redox mediator or oxidized dye at the semiconductor surface[5, 6]. The photoinjected electrons are prone to recombination with the oxidized ions or oxidized dye. Coating, although the various table text styles are provided. The formatter will need to create these components, incorporating the applicable criteria that follow.

another semiconductor (e.g., SrTiO₃ [7], Al₂O₃ [8], Nb₂O₅ [9], and In₂O₃ [10]) around the TiO₂ particle as a barrier layer is an effective way to retard the electron-hole pair from recombining. The Nb₂O₅ barrier layer restricts the electrons to the TiO₂ particles, therefore, reduces the recombination rate. Consequently, all parameters of the DSSC improved resulting in a 35% increase of the cell efficiency[9]. In common, the core-shell nanoporous elec-trode consists of a nanoporous inorganic semiconductor matrix that is covered with a shell of other metal oxide. The thicknesses of the shell films are often determined by X-ray photoelectron spectroscopy[11] by calculating the relative concentrations of the core and shell materials. However, the problem with the use of this method is the requirement for a large scan area over the nanostructure. Menzies et al[10] first introduced high-resolution transmission electron microscopy (HRTEM) technique to illustrate the In₂O₃ shell on TiO₂ core, and the thickness of the shell was observed directly from the HRTEM images. MgO is a typical wide band gap oxide (6.0-7.8 eV). Kumara et al[12] and Taguchi et al[13] reported that a thin layer of MgO coated TiO₂ retarded recombination of the holes and back transferred electrons in the solid-state DSSCs. Jung et al[14] blended magnesium methoxide with TiO₂ powder first rather than coating the TiO₂ electrode with a chemical bath deposition method. Recently, Grinis et al[15] reported a sol-gel electrophoretic deposition method that coated amorphous TiO₂ or MgO shell onto photoanodes for DSSC based on plastic substrate in low temperature. In this paper, a thin layer MgO film was coated on the TiO₂ nanoparticles by using a simple chemical bath deposition method. We demonstrate that the MgO layer on TiO₂ electrode can form a core-shell configuration by energy dispersive X-ray (EDX).

In DSSCs, oxygen vacancies on TiO₂ surfaces can be easily produced by annealing of TiO₂ films. However, the efficiency and photocurrent decreases with the abundance of oxygen vacancies, since these oxygen vacancies on TiO₂ surfaces provide electron traps and thus prevent electron transport in the system. To improve the photocurrent and efficiency of DSSCs, we must reduce oxygen vacancies, increase the amount of adsorbed dye and suppress interfacial recombination. In the process of sputtering, Ar plasma can enhance reactive activity while O₂ plasma can decrease oxygen vacancies and facilitate dye absorption. Moreover, the conduction band edge for MgO is negative for both the TiO₂ conduction band edge and dye excited state oxidation potential, indicating that MgO can function as a physical barrier layer for both electron injection and charge electron recombination reactions [9, 22–24]. Furthermore, the higher isoelectric point (iep) of MgO (iep at pH 12) compared to anatase TiO₂ (iep at pH 6.2) favors stronger dye adsorption and thus better light absorption [16]. On the basis of these considerations, we fabricate MgO-coated TiO₂ electrodes by reactive DC magnetron sputtering and investigate the influences of sputtering MgO for different times on micrograph, absorption and transmission properties, dye adsorption, surface states, interfacial electrochemical characteristic and the performance of DSSCs



II. EXPERIMENTAL DETAILS

A. Working electrode preparation)

All the reagents used were of analytical purity. Titanium Chloride, The Ru dye, N719 (Ruthenium 535 bis-TBA), and 1,2-dimethyl-3-n-propylimidazolium was purchased from Solaronix (Switzerland). Fluorine-doped SnO₂ conductive glass (FTO, transmission >80% in the visible, sheet resistance 20 Ω/square) obtained from China Yaohua Glass Group Corporation was used as the substrate for the deposition of TiO₂ films. The metal magnesium (purity 99.9%) target was purchased. The TiO₂ films (about 10 μm) were prepared as in the reported from method [25]. The MgO was deposited on TiO₂ by reactive DC magnetron sputtering to fabricate MgO-coated TiO₂ (TiO₂/MgO) electrodes. The sputtering target was magnesium metal (purity 99.9%) with the diameter of 60 mm. Different thicknesses of MgO were deposited on TiO₂ at a direct current power of 40 W under 1.3 Pa working pressure. The deposition rate of MgO was about 1 nm min⁻¹. The thicknesses of MgO were estimated by different sputtering times. To ensure fair comparison, the TiO₂ electrode was prepared and cut into two identical pieces. One was used to deposit MgO and the other served as a reference. A platinized conducting glass was used as a counter electrode. An electrolyte composed of 0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-n-propylimidazolium and 0.5 M 4-tert-butylpyridine in propylene carbonate was employed for DSSCs. Both TiO₂ and TiO₂/MgO electrodes were dipped in an N719 solution (0.5 mM in dry ethanol solution) for 12 h to adsorb dye.

B. Working electrode characterization

The films' thicknesses were measured with profilometer. Energy-dispersive x-ray spectroscopy (EDX, GENESIS 7000) was used to determine the chemical species of the electrode. The surface morphologies of electrodes were observed by scanning electron microscopy (SEM). The transmission spectra and UV-vis absorption spectra were recorded on a UV-vis-NIR spectrophotometer. The current-voltage (I-V) characteristics of cells were measured with a model 2400 Digital Source Meter. An Oriel 500 W Xe lamp served as the light source in conjunction with a GG420 filter to remove ultraviolet radiation. The Pinz Optics IR-3 filter was placed in the light beam to simulate AM1.5-type solar emission. The active area of the cells was 0.5 cm². The TiO₂ and TiO₂/MgO films (geometric surface area 1 cm²) were employed as working electrodes. A Pt wire and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. In order to detect the interfacial electron transfer related reaction in the anodic TiO₂/electrolyte, CV was performed at a potential ranging from -1.2 to 0.6 V versus SCE in 0.2 M LiClO₄ /PC solution (pH = 2) at a scan rate of 100 mV s⁻¹. The frequency range is 0.01–100 kHz and the magnitude of the modulation signal is 10 mV.

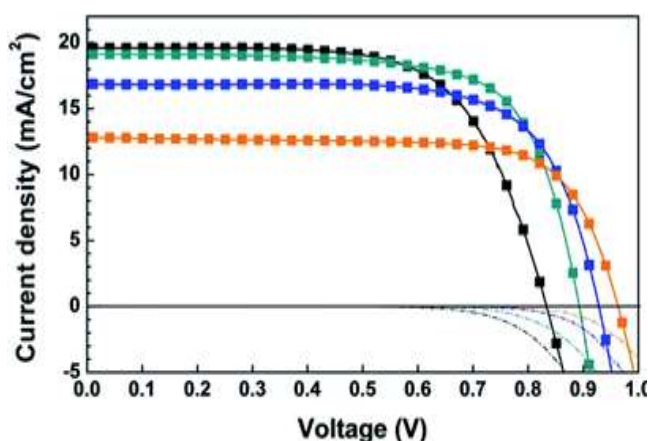
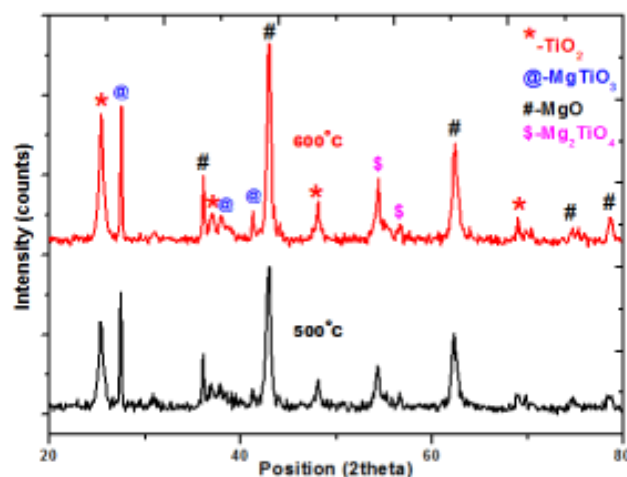
III. RESULTS AND DISCUSSION

To verify the formation of MgO on TiO₂, the TiO₂ sputtering MgO for 30 min (TiO₂/MgO 30 min) were carried out, and the results are shown in figure 1. The Mg2p, C1s, Ti2p and O1s can be observed easily. A peak assignable to Mg2p was detected at 50.86 eV, which was very close to the data for Mg2p in MgO (50.25 eV).

The peak at 457.36 eV was in close agreement with TiO₂ (458.75 eV) while the peak at 528.34 eV can be attributed to O1s. The binding energies were calibrated by taking the C1s peak (284.64 eV) as reference. To further confirm the formation of MgO on TiO₂, an EDX measurement was carried out as shown in figure 1(b). Due to the small thickness of MgO, it was difficult to distinguish the peak position of MgO from others. The peak positions of FTO and Pt are marked in figure 1(b). It can be seen from figure 1(b) that TiO₂/MgO 30 min is composed of Ti, Mg and O elements, besides Sn, Si of FTO and Pt element (resulting from vacuum deposition of Pt to increase conductivity). As shown in figure 1(b), chemical atomic wt% composition analyses for titanium, magnesium and oxygen estimated from the EDX spectrum well supported the formation of MgO on TiO₂. Figure 2 shows SEM micrographs for bare TiO₂.

TiO₂ and TiO₂/MgO 30 min. It can be seen that the average particle size in TiO₂/MgO 30 min is a little smaller than that of bare TiO₂.

Figure 3 shows I–V curves for TiO₂ and TiO₂/MgO in the dark and under illumination with a light intensity of 60 mW cm⁻². The corresponding solar cell parameters were summarized in table 1. Compared with TiO₂, the TiO₂ sputtering MgO for 3 min (TiO₂/MgO 3 min) electrode gives higher short-circuit photocurrent (J_{sc}), open-circuit photovoltage (V_{oc}) and fill factor (FF). The efficiency is significantly enhanced from 6.45 to 7.57%. It shows the merits DSSCs. Upon increasing sputtering time to 15 min, the V_{oc} and FF further increase but J_{sc} decreases, resulting in the decreased conversion efficiency. On increasing sputtering time to 30 min, due to the drastic drop of all parameters, the TiO₂/MgO 30 min cell gives poor conversion efficiency. It indicated that the excessively thick MgO layer beyond the tunneling distance plays a negative of TiO₂/MgO electrodes by reactive DC magnetron sputtering in improving the performance of role in the photoelectron conversion process.


Fig 1.current and voltage of TiO₂/Mgo

Fig 2: XRD of TiO₂/Mgo

The phase structure of the films was examined by XRD. Figure 1 shows the XRD pattern of the pure TiO₂ film. The peaks denoted by asterisks attribute to the TCO glass, and the peaks at 25.8°, 47.3°, 53.3°, and 54.4° are corresponding to the planes (101), (200), (105), and (211), which is body-centered cubic and anatase TiO₂

(JCPDS Card No. 07-6173). The peaks are very sharp, implying that the TiO₂ films were well crystallized. The XRD pattern (not shown here) of the MgO coated TiO₂ film is found to be similar as that of pure TiO₂ film. No separate MgO phase is detected in the sample due to the extremely thin MgO layer.

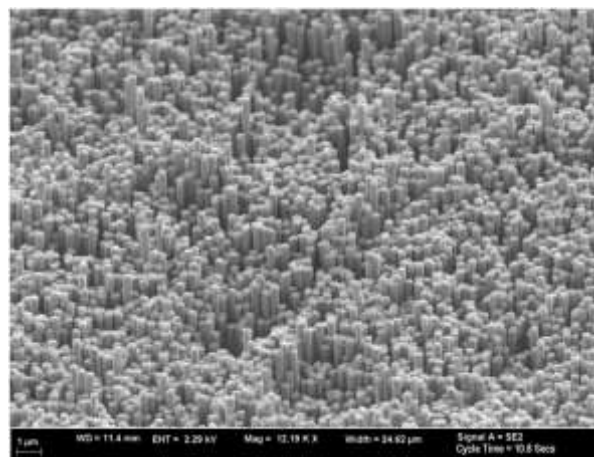
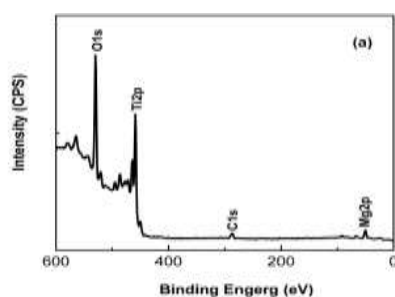


Fig4.Sem Image of coreshell

Electrode J_{sc} (mA cm⁻²) V_{oc} (V) FF η

(%) TiO₂ 8.740.6620.6696.45

TiO₂/MgO 3 min 9.510.6820.7007.57.

TiO₂/MgO 15 min 7.160.7010.7165.99

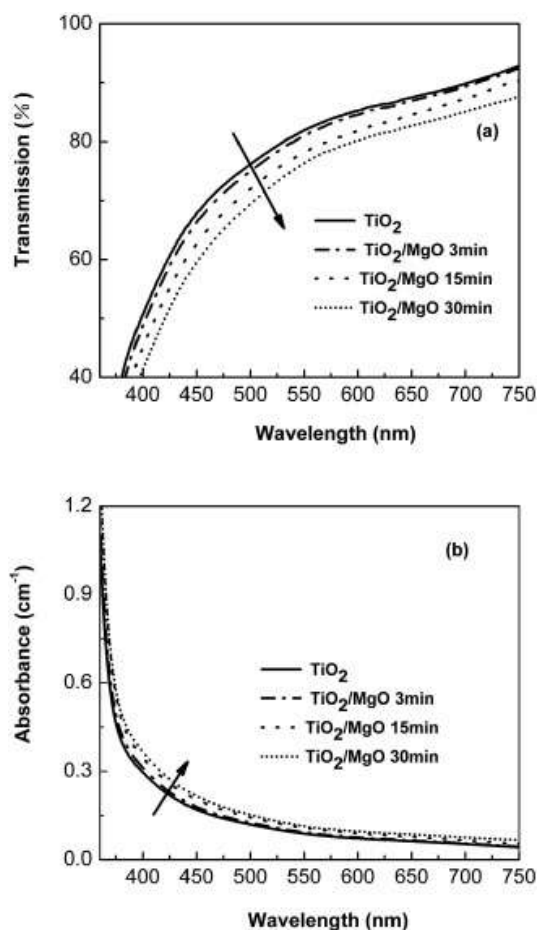
TiO₂/MgO 30 min 4.470.6430.6483.10

addition, the dark currents for the DSSCs were measured and are shown in figure 3. It can be seen that the dark currents change slightly while the magnitude of the dark current is reduced to some extent in TiO₂/MgO 3 min and TiO₂/MgO 15 min cells. The variations of dark current explain the fact that the V_{oc} is not changed noticeably. The dark current at potentials more negative than that of TiO₂ is reduced in TiO₂/MgO 3 min and TiO₂/MgO 15 min, which also indicates that the reaction between triiodides and conduction band electrons is suppressed. Based on these results, it can be seen that the cell performance is so sensitive that an appropriate sputtering time is needed in the DSSCs. More detailed analyses were carried out to understand the properties of TiO₂/MgO.

Since DSSCs were illuminated from the FTO substrate side in working conditions, we carried out absorption and transmission spectra of TiO₂ and TiO₂/MgO. As shown in figure 4, the absorption and transmission spectra indicate that dye-free TiO₂/MgO 3 min has almost the same spectra as TiO₂. However, the TiO₂/MgO 3 min cell gives better J_{sc} , V_{oc} and FF, which indicates that the increase of J_{sc} is not due to the higher light harvest.

It is difficult for the N719 dye to fully cover the TiO₂ surface without the basic MgO coating due to intermolecular electrostatic repulsion. The higher basicity of the MgO-coated surface favors the dye adsorption through the carboxylic acid group of the N719 dye [3, 4, 16]. Also exposing TiO₂ films to O₂ plasma during the sputtering can decrease oxygen vacancies and enhance dye absorption [20, 21]. The increased dye adsorption is

supported by the absorption spectra in figure 5. As shown in figure 5, since the degree of dye adsorption on the electrode is proportional to the intensity of the optical adsorption of the dye, TiO_2/MgO electrodes apparently enhance the dye adsorption with increasing sputtering time, which suggests the merit of TiO_2/MgO electrodes.



by the sputtering method. Also the increased dye adsorption facilitates the enhancement of J_{sc} in TiO_2/MgO . However, too thick an MgO layer might reduce electron injection efficiency, resulting in the decrease of J_{sc} . In addition, it should be noted that the maximum absorption peak for N719, which is assigned to the metal-to-ligand charge-transfer (MLCT) band, blueshifted gradually with increasing sputtering time. It was reported that N719 showed almost the same MLCT band positions in solution and on the TiO_2 surface [26]. The blueshift is attributed to the increased surface basicity due to MgO modification. It is well known that the dye is covalently bound to the surface Ti^{4+} of the electrode [27, 28], where Ti^{4+} behaves as an electron-withdrawing moiety. Upon MgO coating, the coordination of Ti^{4+} to the carboxylates on the N719 dye is strengthened, thus resulting in the decrease in the electron density at the Ru (II) center. The decrease in electron density will stabilize the t_{2g} orbital and induce blueshifts of the MLCT bands [29]

IV.CONCLUSION

In summary, a surface modification method based on TiO₂ electrodes coated with MgO was successfully developed in DSSCs by reactive DC magnetron sputtering. The study results show that the O₂ plasma treatment and MgO coating in the sputtering increases dye adsorption, decreases trap states and suppresses charge recombination at the TiO₂ /dye/electrolyte interface. Sputtering MgO for 3 min on TiO₂ increases all cell parameters, resulting in improving efficiency.

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