Effect of Mg Doping on SnO\textsubscript{2} Energy Band and Power Conversion Efficiency of Dye-Sensitized Solar Cells

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Abstract. In this work, Mg-doped SnO\textsubscript{2} materials with different molar ratios were synthesized by hydrothermal method. Based on the UV-Vis study, band gap ($E_g$) of the Mg-doped SnO\textsubscript{2} is adjusted from 3.76 eV to 3.65 eV via 3 at% concentrations. Results of photovoltaic measurement for dye-sensitized solar cells (DSCs) based on Mg-doped SnO\textsubscript{2} film as photoanode indicate that the doping of Mg ions can improve the open-circuit voltage ($V_{oc}$) of the DSCs, while the electric current density ($J_{sc}$) of the DSCs is almost unchanged. The cells were measured at 3 days intervals within 24 days after fabrication. Power conversion efficiency (PCE) of 3 at% Mg-doped SnO\textsubscript{2} DSCs increases step by step and achieves 4.38% as the cell is tested after 18 days. Electrochemical impedance spectroscopy (EIS) analysis shows that Mg doping enhances light collection, increased the number of photogenerated electrons and inhibits charge recombination.

Keywords. Mg doping, energy band, dye-sensitized solar cells, power conversion efficiency.

1. Introduction
DSCs have been widely explored because of their superior photoelectric conversion capacity, easy production and lower price of raw materials. Since professor Grätzel introduced the concept of nanopores in the study of wide-band gap TiO\textsubscript{2} semiconductor in 1991 [1], the PCE of DSCs has grown rapidly from 7.1% to 14% in 2014 [2]. The semiconductor photoanode is the core part of DSCs. The ideal DSCs photoanode should have a larger specific surface area for the dye load and effectively transfer photoelectrons from the sensitizer to the external circuit. For effective photoelectron injection, its band gap must match the energy band of the sensitizer. This means that the conduction band of the sensitizer needs to be 0.2 to 0.3 eV higher than the semiconductor. Take into account these standards, TiO\textsubscript{2} [3-4], ZnO [5-6], SnO\textsubscript{2} [7-9] and other nanostructured semiconductor materials are usually used as photoanode. However, DSCs with pure SnO\textsubscript{2} as the photoanode have lower PCE due to faster electron recombination speed and low dye absorption [10-12]. Meanwhile, the open-circuit voltage and short-circuit current are lower than those with TiO\textsubscript{2} as the photoanode. In order to improve the PCE, researchers have made many attempts, such as surface chemical modification, metal oxide film coating, ion doping and so on. The cauliflower-like SnO\textsubscript{2} hollow microspheres as anode for DSCs was reported by Ganapathy, et al. [13], and got a PCE of 3.6%. To inhibit the recombination of charges, Wanninayake, et al. [14] used ZnO thin film to passivate SnO\textsubscript{2} nanoparticles surface of DSCs, and obtaining the PCE was 4%. Aponsu, et al. [15] obtained a 3.9% PCE using SnO\textsubscript{2} modified with gold nanoparticles on the surface as a photoanode for DSCs.
Many efforts have been explored to modify the band gap of photoanodes, for example by doping it with different metals, but this may change its electrical and optical properties. In recent years, several research groups have reported some studies related to the doping of metals (e.g., Al, Mg, Zn, Sb, etc.) into SnO$_2$ nanoparticles [16-21]. Li, et al. [22] reported Zn$^{2+}$ ion doped in SnO$_2$ nanoparticles and obtained a PCE of 4.18%, which increased to 7.70% after TiCl$_4$ treatment. Al doped SnO$_2$ hollow microspheres as photoanode materials for DSCs were reported by Xu, et al. [23], the PCE of 3.04% was obtained when the doping amount of Al reaches 1.5%. Liu, et al. [24] showed that Cu-doped SnO$_2$ DSCs reduced the energy band shift between the photoanode and the dye, and the PCE of the optimized Cu-doped SnO$_2$ reaches 4.01% after 15 days of slow growth. All these studies indicate that ion doping can effectively regulate the band gap of SnO$_2$ and improve the photoelectric performance of DSCs. In this work, Mg-doped SnO$_2$ nanoparticles with different molar ratios (0, 1, 3, 5, 7 at%) were synthesized and characterized by multiple technical methods. The cells were measured at 3 days intervals within 24 days after fabrication. PCE of 3 at% Mg-doped SnO$_2$ DSCs increases step by step and achieves 4.38% as the cell is tested after 18 days. Electrochemical impedance spectroscopy (EIS) analysis shows that Mg doping enhances light collection, increased the number of photogenerated electrons and inhibits charge recombination.

2. Experimental Details

2.1. Materials
SnCl$_4$·5H$_2$O, MgCl$_2$, OP-10 emulsifier, ammonium hydroxide, Ethyl cellulose and Terpineol were purchased from traditional Chinese medicine Co., Ltd. TBP was purchased from Aldrich. Iodide (I$_2$), LiI, 3-methoxypropionitrile (MePN), and 1, 2-methyl-3-propylimidazolium iodide (DMPII) were purchased from Fluka. Absolute ethyl alcohol was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

2.2. Synthesis of Mg-Doped SnO$_2$ Nanoparticles
Mg doped SnO$_2$ nanoparticles were synthesized with a slightly modified as the reported method [25]. Firstly, SnCl$_4$·5H$_2$O (10.52 g) and a certain amount of MgCl$_2$ (the molar ratio of Mg and Sn was 0%, 1%, 3%, 5% and 7%, respectively) were stirred and dissolved in ethanol/deionized water (1:3). Then, the above mixed solution was put into an 80 mL autoclave respectively, and the temperature was maintained at 200 $^\circ$C for 12 hours. After the solution was cooled, the reactants were poured into a centrifuge tube. The centrifuge was set to rotate at 8000 rpm for 10 min each time. The reactants were washed with deionized water and anhydrous ethanol in turn until neutral. The five kinds of dried SnO$_2$ precipitates were respectively ground for half an hour, and finally annealed at 650 $^\circ$C for 2 hours. The powder were sealed and stored for further analytical characterization and application.

2.3. Fabrication of DSCs
SnO$_2$ slurry was prepared by rotary evaporation. First of all, SnO$_2$ powder (1 g), ethyl cellulose (0.5 g), terpenol (4 g) and OP-10 emulsifier (0.4 g) were added in 40 mL of anhydrous ethanol with ultrasonic shock for 48 hours. After the shock is completed, the solution is heated by rotating at 90$^\circ$C for 8h to obtain a SnO$_2$ slurry with the appropriate viscosity. The prepared SnO$_2$ slurry was applied to the FTO substrate by screen printing and then heated in a muffle furnace at 500$^\circ$C for 30 minutes. Repeat the above step four times to obtain the desired film thickness. After that, the photoanodes were placed into N719 ethanol dye (0.5 mmol/L) for 24h to ensure complete loading of the dye. The prepared solar cell is a sandwich structure with photoanode in the upper layer, Pt counter electrode in the lower layer and iodine electrolyte (0.08 mol/L I$_2$, 0.1 mol/L LiI, 0.5 mol/L TBP, and 0.6 mol/L DMPII in MePN) in the middle layer. The solar cells were assembled with heat sealing method. The area of the cell is 0.25 cm$^2$. 


2.4. Characterization and Photovoltaic Measurements

SnO₂ powder was characterized by X-ray diffractometer (XRD, D8ADVANCE, Bruker). The morphology of pure and Mg-doped SnO₂ films was characterized by field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM450). Quantitative analysis of Mg-doped SnO₂ film was measured by energy dispersive X-ray spectroscopy (EDS, INCA 250 X-MAX50, Oxford) attached to the FESEM. Ultraviolet-visible spectrophotometer (UV-3600, Shimadzu) was used to confirm the optical band energy of the sample.

Photocurrent density-voltage (J-V) curve of DSCs was measured by using a Keithley 2400 digital source meters and was controlled using text point software under a 450W xenon lamp (Oriel USA) with a filter (AM 1.5, 100 mW/cm²). The EIS measurements were done in the dark with an electrochemical workstation (German Zahner Company) with a perturbation amplitude of 10 mV and a frequency range of 100 kHz to 100 mHz. The information on the impedance parameters of the DSCs is calculated from the transmission line model. The cells were placed in a dry and cool environment after manufacture. These DSCs were measured for J-V and EIS every 3 days for 24 days.

3. Results and Discussion

3.1. Microstructure of SnO₂

Figure 1(a) shows the XRD patterns of pure and Mg-doped SnO₂ powder. The diffraction peaks are indexed to the rutile SnO₂ (JCPDS: 41-1445). No peaks of other impurities were found in Figure 1(a), indicating that the doping of Mg ions did not alter the crystalline phase of SnO₂. A slight change in the center and width of the diffraction peaks in the XRD pattern implies that the doping concentration has some effect on the lattice spacing. The half peak width (FWHM) of XRD peak (110) and grain size varies with doping concentration are shown in figure 1(b). As the doping concentration of Mg element increases, the FWHM of (110) peak decreases due to the replacement of Sn⁴⁺ by Mg²⁺. To investigate the effect of doping concentration on the microstructure of SnO₂ nanoparticles, the effective average grain size was estimated from the FWHM of the first major peak (110) of pure SnO₂ and Mg-doped SnO₂ nanoparticles by using Scheller’s formula D=0.89λ/(βcosθ) [26]. Here β is the half-peak width in radians, θ is the Bragg diffraction angle, and λ is the wavelength of the X-ray. The grain size of SnO₂ nanoparticles gradually decreases as the concentration of Mg ions concentration increases. The grain size of SnO₂ nanoparticles decreased from 24.02 nm (pure SnO₂) to 22.24 nm (7 at% Mg-doped SnO₂).

![Figure 1](image-url)

Figure 1. (a) XRD patterns for five samples. (b) FWHM of peak (110) and grain size varies with doping concentration.

FESEM and EDS were used to analyze the morphology and element composition of SnO₂ photoanode films. Figure 2(a) and (b) show SEM images of pure and 3 at% Mg-doped SnO₂ photoanode film, respectively. The average size of SnO₂ nanoparticles is about 20 ~ 30 nm. Figure 2 (c) shows the cross section of the film doped with 3 at% Mg ion concentration. The thickness of SnO₂
film is about 14.98 um, which is consistent with the theoretical optimal range of photoanode film thickness. The EDS datum (figure 2(d)) shows that 3 at% Mg-doped SnO₂ film consists of Sn, Mg and O element. The doping concentration of Mg ions was found to be 3.09at% by EDS measurements.

3.2. Absorption Spectra
Figure 3(a) shows the absorption spectra of pure SnO₂ and 3 at% Mg-doped SnO₂. As shown in figure 3(b), the optical band gaps of pure SnO₂ and 3 at% Mg-doped SnO₂ are 3.76 and 3.65 eV, respectively, indicating that the doping of Mg ions can regulate the band gap of SnO₂, which makes it better match with dye molecules, and can improve the photoelectric performance of SnO₂ DSSCs.

3.3. Photovoltaic Performance and EIS Measurement
Figure 4 (a) and (b) are the J-V curves of five kinds of DSCs tested at fresh (0 day) and stable (18 days), respectively. The photovoltaic parameters are summarized in table 1. Compared with pure SnO₂,
the $V_{oc}$ of Mg-doped SnO$_2$ device is significantly improved, while $J_{sc}$ is almost unchanged. The detection of different concentrations of Mg doping shows that 3 at% Mg doping is optimal for its PCE of 4.38%, which is 57.8% higher than its corresponding pure SnO$_2$ DSCs after 18 days of storage.

![Figure 4](image)

*Figure 4. J-V curves of five kinds of DSCs. (a) fresh (0 day), (b) stable (18 days).*

| Sample          | $V_{oc}$(V) | $J_{sc}$(mA/cm$^2$) | FF(%)  | $\eta$(%) |
|-----------------|-------------|----------------------|--------|------------|
| Fresh undoped   | 0.45        | 10.17                | 37.11  | 1.72       |
| Fresh 1 at. % Mg| 0.51        | 11.55                | 39.46  | 2.35       |
| Fresh 3 at. % Mg| 0.57        | 11.03                | 42.68  | 2.68       |
| Fresh 5 at. % Mg| 0.61        | 9.43                 | 44.16  | 2.53       |
| Fresh 7 at. % Mg| 0.66        | 9.14                 | 30.07  | 1.82       |
| Stable undoped  | 0.72        | 10.79                | 52.67  | 4.10       |
| Stable 1 at. % Mg| 0.76       | 10.90                | 52.11  | 4.34       |
| Stable 3 at. % Mg| 0.78       | 10.76                | 51.88  | 4.38       |
| Stable 5 at. % Mg| 0.79       | 9.97                 | 50.48  | 3.98       |
| Stable 7 at. % Mg| 0.81       | 8.50                 | 54.33  | 3.74       |

After the preparation of the five DSCs, continuous measurements were made every 3 days. As shown in figure 5, with the change of time, the $V_{oc}$, FF and $PCE$ of the prepared DSCs would rise steadily, and the $J_{sc}$ would decrease to some degree. Finally, the performance of the DSCs would stabilize after 18 days. In this experiment, with the extension of time, the dye decomposition occurred and the production of photogenerated electrons decreased, resulting in the decline of $J_{sc}$. The reason for the slow growth of $V_{oc}$ may be that, with the passage of time, the contact between the DSCs components becomes better, which inhibits the charge recombination process and reduces the dark current. $FF$ is affected by the internal resistance of the DSCs. The increase of $FF$ indicates that the internal resistance gradually decreases during the stabilization of DSCs, leading to better performance of DSCs. This slow increase in $PCE$ observed in SnO$_2$ photoanode DSCs is consistent with the reported work [27].

In addition, charge accumulates in the photoanode semiconductor films and form capacitors at the various contact interfaces of the DSCs. Figures 6 (a) and (b) show the relationship between $C_{\mu}$, $R_{ct}$ and $V_F$ at steady state. Generally speaking, recombination resistance $R_{ct}$ is related to the barrier encountered in electron transfer, while the chemical capacitance $C_{\mu}$ is generally related to the local density of states. As the Mg doping concentration increases, the particle size becomes smaller and more surface states are formed on the photoanode film. However, as more Mg ions enter the SnO$_2$ crystalline lattice, the defects in the SnO$_2$ particles are reduced. Therefore, the chemical capacitance $C_{\mu}$ showed a trend of increasing and then decreasing with the increase of Mg ion concentration. At the same time, the $R_{ct}$ becomes larger and shifts toward higher bias, indicating that surface state electrons
pass through the SnO$_2$/Electrolyte interface more easily.

![Figure 5](image)

**Figure 5.** Changing curve of (a) PCE, (b) $V_{oc}$, (c) $J_{sc}$ and (d) FF with passage of time for the five kinds of DSCs.

![Figure 6](image)

**Figure 6.** (a) $C_{mu}$-$V_F$ and (b) $R_{ct}$-$V_F$ curves of five kinds of DSCs at stable (18 days).

### 4. Conclusions
In this study, Mg-doped SnO$_2$ materials with different molar ratios were synthesized by hydrothermal method, and characterized and analyzed by XRD, FESEM, EDS and UV-Vis absorption spectra. With the addition of Mg, the size of SnO$_2$ nanocrystals decreased, which was more conducive to the adsorption of dyes. The $E_g$ of the Mg-doped SnO$_2$ is adjusted from 3.76 eV to 3.65 eV via 3 at% concentrations. $PCE$ of 3 at% Mg-doped SnO$_2$ DSCs increases step by step and achieves 4.38% as the cell is tested after 18 days. Electrochemical impedance spectroscopy (EIS) analysis shows that Mg doping enhances light collection, increased the number of photogenerated electrons and inhibits charge recombination.

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