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Growth and characterization of magnesium in TiO₂ nanoparticles for dye sensitized solar cells

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ABSTRACT

Pristine and Mg- doped TiO₂ nanoparticles was prepared via sol-gel technique. The obtained products were characterized by powder XRD, FE-SEM, UV-vis spectroscopy and current-voltage characteristics. Experimental results indicated that magnesium doping inhibited the growth of crystalline size and most of the predominant phase was anatase form. The absorption edge of Mg doped TiO₂ shifted to longer wavelength. When Mg-TiO₂ was applied in DSSC, the energy conversion efficiency was enhanced considerably compared to that using pure TiO₂, it was approximately 4.69% with N719 dye under 100 mW/cm² of stimulated sunlight.

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KEYWORDS

TiO₂ nanomaterials;
Sol-gel technique;
Photoanode;
FTO glass;
Doctor blade method.

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have become an attractive alternative to conventional solar cells due to their low cost and high energy conversion efficiency. A dye-sensitized nanocrystalline semiconductor electrode is the main component of a DSSC and plays an important role in determining the DSSC performance^[1]. In order to develop DSSC with excellent photovoltaic properties, researchers have tried to control the nanostructure and morphology of TiO₂ photo-electrodes^[2]. TiO₂ is currently one of the most widely used materials due to its distinguished properties including wide optical band gap (~3.2 eV), strong ultraviolet absorptivity, non-toxicity, long-term chemical stability, good photocatalysis and high energy conversion effi-

ciency^[3-7]. However, the rather high recombination of photogenerated electron-hole pairs and the weak absorption in visible region are its main drawbacks^[8-9]. Therefore, various techniques have been proposed in order to modify TiO₂ to overcome these inferiorities. A number of research works have employed the advantage of comparably large surface area of TiO₂ nanostructures such as thin film structure, nanoparticles, nanorod, nanosheet and nanotube to improve its performance^[10-13]. Doping of TiO₂ nanomaterials has been investigated for more than 10 years^[14-16]. Doping a metal or nonmetal into TiO₂ could change the band edge or surface states of TiO₂^[17]. Until now, most of the doping for TiO₂ nanomaterials has been explored for photocatalysis. Since there are only a few papers reported in which doped TiO₂ nanomaterials were used as

photoanodes in DSSCs^[18-19]. The doping effects, however, do not seem so pronounced by comparison to the corresponding undoped TiO₂ photoanode. The energy conversion efficiency remained either unchanged or a little improvement. In the present work, we synthesized pristine and Mg-doped TiO₂ nanoparticles by sol-gel method, and then coated them onto bare-FTO substrate respectively and enhance the photovoltaic performance of N719 based DSSCs by modifying the TiO₂ electrode sensitized dye interface.

EXPERIMENTAL

The nano-TiO₂ powder was prepared with titanium isopropoxide solution as the raw material. In a typical experiment, 0.012 mol Magnesium nitrate were dissolved in 60 mL of deionized water at room temperature, followed by adding 5 mL of glacial acetic acid to obtain solution A. 14 mL titanium isopropoxide was dissolved in 40 mL of anhydrous ethanol with constant stirring to form solution B. Then, the solution B was added drop-wise into the solution A within 60 min under vigorous stirring. Subsequently, the obtained sol was stirred continuously for 2 h and aged for 48 h at room temperature. As-prepared TiO₂ gels was dried for 10h at 80 °C. The obtained solids were ground and finally calcined at 450 °C for 2 h (heating rate = 3 °C/min).

Fluorine doped tin oxide, (FTO, Solaronix) was washed with 2-propanol, ethanol, and distilled water several times to remove impurities and then dried. A dye-sensitized solar cell (effective area is 1cm X 1cm) was fabricated according to the following process. TiO₂ paste was prepared with certain proportions of nano-TiO₂ powder with distilled water, acetylacetone (A.R) and triton (X-100) in agate mortar^[20]. The photo anode was obtained using doctor blade method on the conductive glass and then sintered at 450° C for 30 min in air. After being cooled, the TiO₂ electrode was immersed into 0.5 mM N719 ethanol solutions for 24 hours at room temperature^[21]. Sensitized TiO₂ photoanode and the counter electrode were assembled and the liquid electrolyte, Idolyte TG 50 (Solaronix Corporation) was used as an electrolyte solution. One electrolyte solution drop penetrated into the working space and counter electrode via capillary action. The two electrodes were held with a binder clip^[22].

The phases and crystallite sizes of the prepared samples were characterized by X-ray diffraction (XRD), performed on (SHIMADZU-6000 Model) at room temperature using Cu K α radiation ($\lambda = 0.154056$ nm) with working voltage and current of 40 kV and 30mA, respectively. The optical properties were analyzed using a PerkinElmer Lamda-35 UV-vis spectrometer (UV-vis). The morphology of the prepared nanoparticles was characterized by using a field emission scanning electron microscope (FE-SEM, Model: FEI QUANTA 200F). The photovoltaic properties were measured with a computer-controlled digital source meter (Keithley, model 2400) under illumination with a Newport solar simulator (AM1.5, 100 mW/cm²).

RESULT AND DISCUSSION

Structural characterizations of TiO₂ nanopowders

The XRD pattern of pristine and Mg-doped nanopowders are illustrated in Figure 1 and it can be assigned to the body-centered tetragonal structure in accordance with the JCPDS card no.: 84-1286. The grain size of the pristine and Mg-doped nanoparticles were calculated with the Scherrer formula by the full width at half-maximum of the (1 0 1) diffraction peak of TiO₂ after subtraction of the equipment broadening. The diffraction peaks in the patterns of the samples are all contributed by the anatase phase and no other impurity phase can be detected. The doping elements did not affect the final TiO₂ powder crystalline phase. It was expected that doping elements would have an affect only on the dye-sensitized solar cell photovoltaic properties. However, estimated powder grain sizes of pristine and Mg (0.01, 0.03, 0.05 mol %) doped TiO₂ powders were 8.74nm, 8.90 nm, 9.54nm and 8.53nm. Figure 2 displays the FE-SEM micrographs of pristine and Mg doped TiO₂ nano powders. From FE-SEM analysis the pristine TiO₂ shows spherical particles with little agglomerate and having different dimensions. In the case of Mg doping, the layer exhibits high porosity due to the exothermal decomposition during the sintering process. The results suggest that the synthesized TiO₂ nanoparticle in the presence of magnesium leads to high crystallinity in agreement with the powder XRD data.

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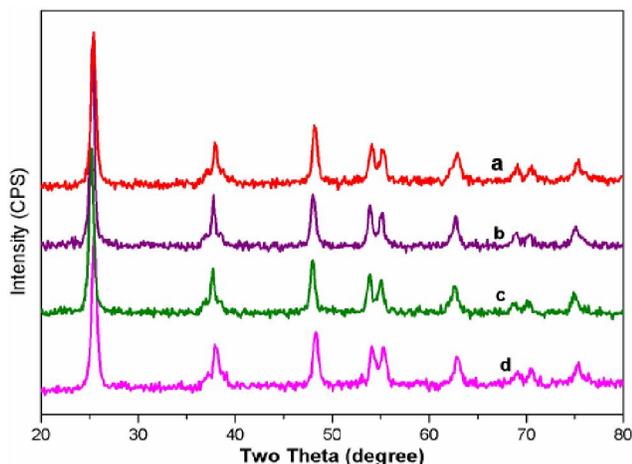


Figure 1: XRD powder diffraction patterns for (a) Pure TiO_2 , (b) Mg-TiO_2 (0.01 mol %), (c) Mg-TiO_2 (0.03 mol %), (d) Mg-TiO_2 (0.05 mol %).

Optical study

The UV-visible spectra of the Mg-TiO_2 nanopowders were obtained to determine the relationship between the solar energy conversion efficiency and spectroscopic property, as shown in Figure 3. It was shown that while TiO_2 has no absorption in the visible region ($>400\text{nm}$), Mg-TiO_2 had significant absorption between 400 and 500nm, which increase with the increase of magnesium ion content and the band gap decreases with increasing absorption wavelength. However, it is believed that the addition of Mg did alter the band gap of the TiO_2 semiconductor significantly. The broadened tail suggests that there was a low Mg concentration on the external surface in 0.05 mol% Mg-TiO_2 .

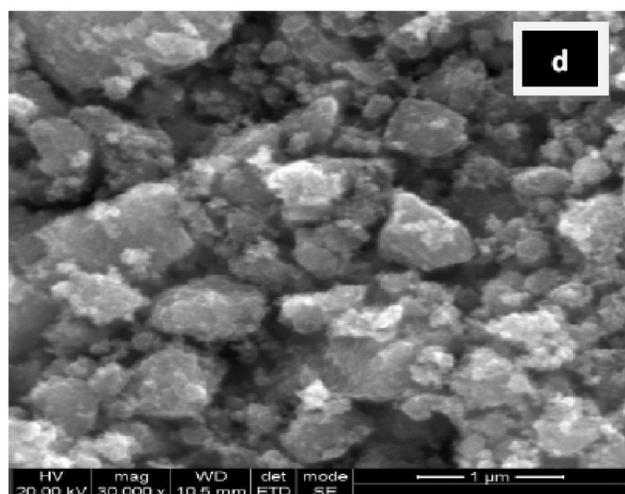
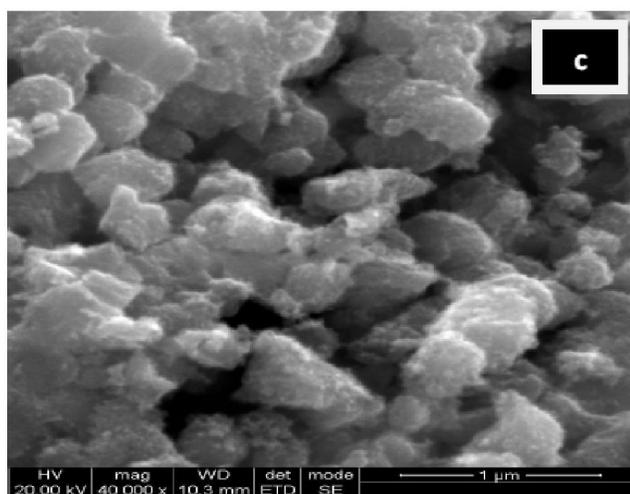
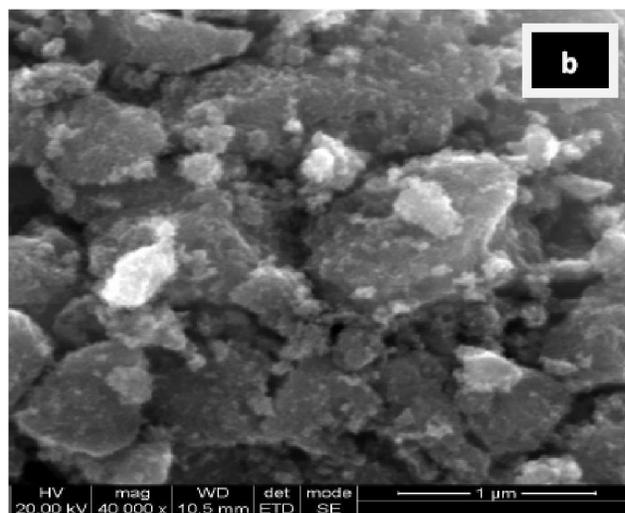
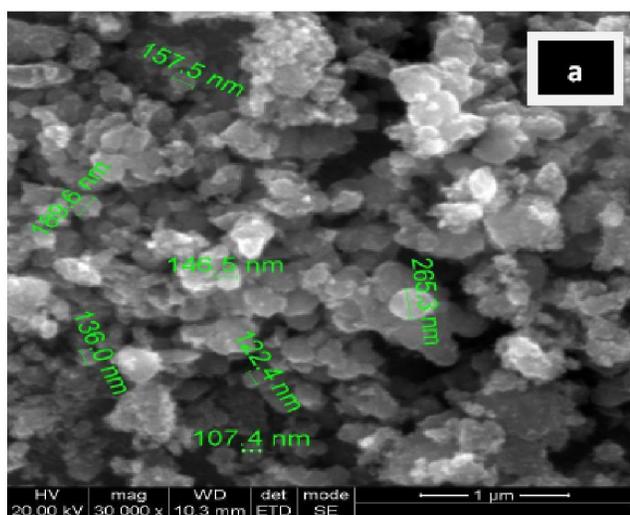


Figure 2: The FE-SEM micrographs and EDX analyses of TiO_2 nanopowders. (a) Pure (b) 0.01 Mg-TiO_2 mol% powder (c) 0.03 Mg-TiO_2 mol% powder (d) 0.05 Mg-TiO_2 mol%

which increased the light harvesting yield in the DSSCs.

Characterization

Figure 4 shows the photovoltaic properties of DSSCs

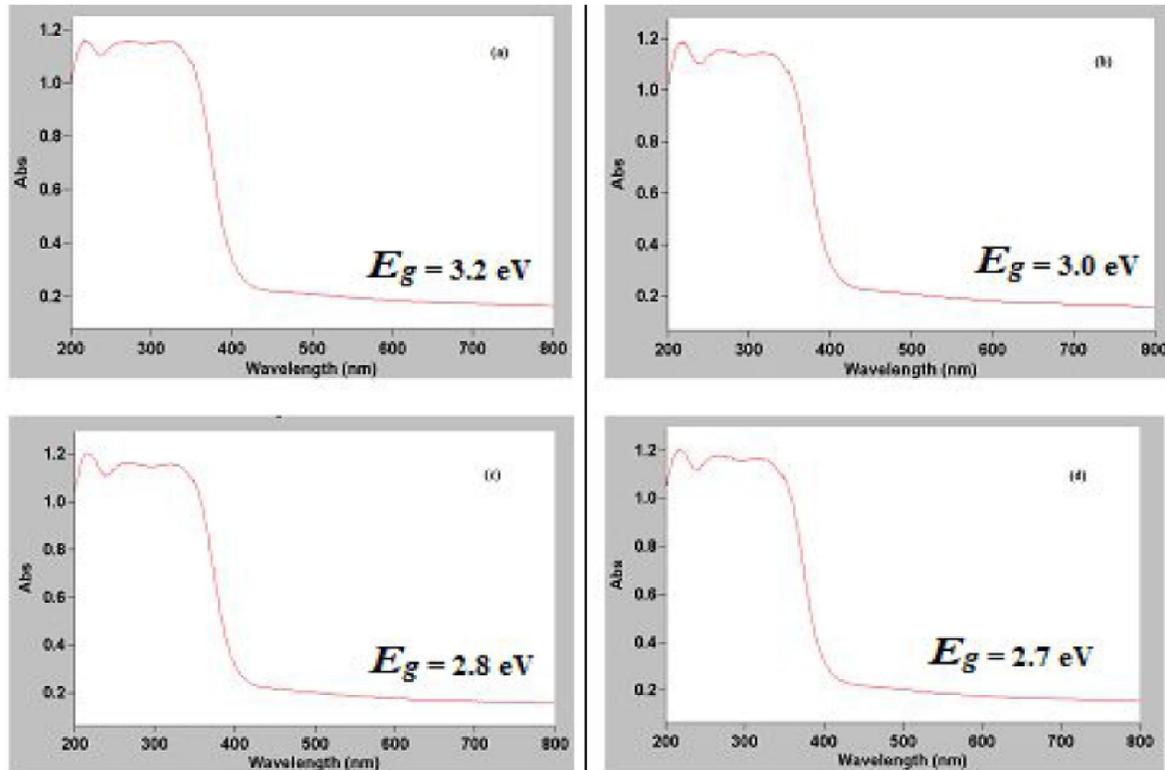


Figure 3 : UV-vis absorption spectra for (a) Pure (b) 0.01 Mg- TiO₂ mol% powder (c) 0.03 Mg- TiO₂ mol% powder d) 0.05 Mg- TiO₂ mol%

based on modified TiO₂ photoelectrodes. TABLE 1 summarizes the photovoltaic parameters of N719 dye based DSSCs. The fill factor (FF) and the light-to-electric energy conversion efficiency (η) of DSSC were calculated according to the following equations^[23].

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \quad (1)$$

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100\% \quad (2)$$

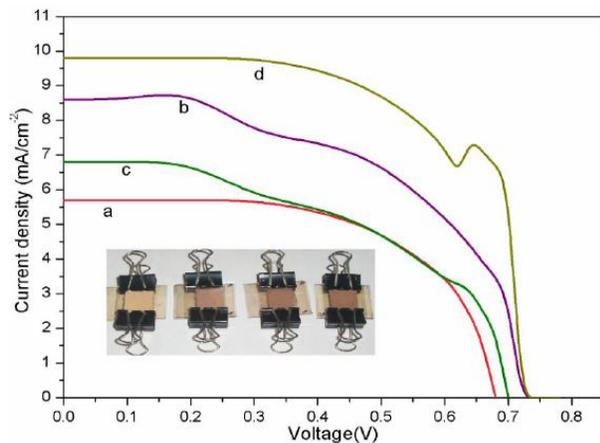


Figure 4 : I-V curves of the pristine and modified TiO₂ nanoparticles

TABLE 1 : Performance of the DSSCs based on Mg-doped and pristine electrodes

Solar cells	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill Factor (FF)	Efficiency (η in %)
a- Pure TiO ₂	0.67	5.70	0.613	2.34
b- Mg-TiO ₂ (0.01 mol%)	0.72	8.60	0.563	3.48
c- Mg-TiO ₂ (0.03mol%)	0.69	6.81	0.571	2.68
d- Mg-TiO ₂ (0.05mol%)	0.73	9.87	0.648	4.69

CONCLUSIONS

Pristine and Mg-doped dye solar cell were successfully prepared on glass substrate by doctor blade method at room temperature. The J_{sc} and V_{oc} values were increased by 9.87, 0.73 respectively. It was confirmed that the J_{sc} improvement was attributed to the increase in the dye adsorption. This improvement DSSC from (0.05 mol %) Mg- doped nanoparticles has low cost, low resistance, high reflectance and simple fabrication processes which can improve obviously photoelectric conversion efficiency from 2.34% to 4.69%.

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