Iraqi Journal of Science
ISSN: 0067-2904

Improving the efficiency of dye-sensitized solar cells with doping and co-doping titanium dioxide

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Abstract:
In this work, A new strategy for enhancing the efficiency of dye sensitized solar cells (DSSC) by doping foreign ion and co- doping TiO_2 / Fe and Cu (38 nm) was prepared by sol-gel method and successfully used as a photoanode for (DSSC). The samples were characterized by using X-ray diffraction (XRD) is used to calculate grain size, before and after Fe, Cu- doping and co- doping. Glass coating process with a thin layer on (Fluorine doped tin oxide) FTO glass by using doctor Blade technique .The optimum thickness utilized for TiO_2 paste is (15µm) on a conductive glass. The best experimental results for doping and co- doping TiO_2 with additive Copper (II) nitrate Cu $(NO_3)_2$ as improved it was V_{OC}=0.6 V, I_{SC}=1.92 mA, I_{max}=1.8 mA and V_{max}= 0.55 V with fill factor (FF) = 0.87. Power conversion efficiency of the cell became 2.5%.

Keywords: Sol- gel, Doping, (Metal) Co – doping semiconductor, N719, TiO_2, Efficiency.

تحسين كفاءة الخلايا الشمسية ذات الاصباغ بالتطعيم بمادة او اكثر لثنائي اوكسيد التيتانيوم

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الخلاصة:
في هذا العمل ،استخدمت استراتيجية جديدة لتحسين كفاءة الخلايا الشمسية الصبغية بواسطة التطعيم بايون او ايونات خارجية لثاني اوكسيد التيتانيوم (38 nm) من الحديد والنحاس ، تم اعدادها بطريقة سول- جل واستخدمت بنجاح لقطب الخلية الشمسية الصبغية . استخدم حيود الاشعة السينية لحساب الحجم الحبيبي قبل اضافة التطعيم بالحديد اوالنحاس . استخدمت تقنية doctor Blade في طلاء الزجاج الموصل بطبقة رقيقة وبعد الاختبار تم اختيار السمك الامثل (15µm) لعجينة ثاني اوكسيد التيتانيوم. تم الحصول على افضل النتائج التجريبية بوجود مادة مطعمة او مادتين عند اضافة نترات النحاس كمادة محسنة حيث كان (عامل التأثير (FF) = 0.87 ,V_{OC}=0.6 V, I_{SC}=1.92 mA, I_{max}=1.8 mA , V_{max}= 0.55 V) وبالتالي اصبحت كفاءة التحويل 2.5%.

1. Introduction

Due to the low price, easy fabrication process, high conversion efficiency and good stability, DSSC in 1991 have made progress. In recent years, doping TiO_2 with metal and nonmental elements has been considered as a promising way to tailor the electronic properties of TiO_2 photoanode in DSSC and has succeeded in improving photovoltaic performance of DSSC [1].

Conventional DSSC consist of mainly five components: (a) a conductive and transparent mechanical support, (b) a wide band gap semiconductor film, (c) a sensitizer, (d) redox couple (usually

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I_3^-/I^-) in an organic solvents and (e) a counter electrode [2]. When a DSSC is illuminated with sunlight, the dye absorbs incident light and becomes excited. The absorption of light by the dye is followed by the injection of an electron from the lowest unoccupied molecular orbital level of the excited dye to the conduction band of the semiconductor. The electrons in the conduction band of the semiconductor flow through the external circuit toward the counter electrode, which regenerates the redox electrolyte. Through these processes, radiant energy is converted into electricity [3]. The TiO_2 films prepared on Fluorine doped tin oxide glass annealing temperature 723 K (450^oC), the immersion time may be the uniquely influential factor to be analyzed at this stage sinc it is related to the dye concentration Ru (N719) $5x10^{-4}$M. The films that were immersed for 5.5 h yielded the highest efficiency, this gets in the first electrode [4].

The second counter electrode is coated with few atomic layers of carbon or platinum, in order to catalyze the red-ox reaction with the electrolyte [5]. Electrolytes play an important role in determining the cell performances. In general, a higher conversion efficiency of DSSC was obtained when an electrolyte was used together with proper additives. Additives are added to the electrolytes to enhance the open-circuit photovoltage (V_{oc}) and thus the conversion efficiency (η) of DSSC [6].

Recently, improving conversion efficiency of TiO_2 electrodes based DSSC by doping one kind of metal ion have been mostly investigated. However, there are few publications reporting the use of two kind of metal ions co-doped TiO_2 in DSSC [7]. Doping TiO_2 is a promising way to improve DSSC efficiency because it can easily shift the band edge and Fermi level of the material and thus change the electron transfer properties [8]. Aluminum is a group III metal (Al^{3+}) an interesting candidate for doping, with good optical quality, low resistivity and high conductance will have improve values of V_{OC} were reported, with largely unaffected J_{SC} [9].

There are two major reasons for introducing dopants into (TiO_2) in order to improve the photocatalytic activity. To increase the quantum efficiency, i.e. to increase the number of photons effectively used for the catalyzed redox reaction and to decrease the band gap energy (i.e. red shift of the optical absorption edge) enabling photocatalytic activity under visible light illumination. [10]. Fe doping has also been extensively studied for its effectiveness in reducing the TiO_2 bandgap making it suitable for visible light absorption and photocatalytic degradation of various organics.Fe^{3+} ionic radius is (0.055 nm hexacoordination) and the Ti^{4+} atomic radius (0.0605 nm) makes substitutional doping by Fe possible.[11,12].

Although, doping of transition metals ion (Fe and Cu) could increase photocatalytic efficiency of TiO_2 and the activity of this material also depends on various parameters related to the preparation method and the physical properties of the obtained catalyst. Several synthesis methods of TiO_2 have been proposed in literatures including sol-gel [13]. The sol-gel process is a most attractive method to introduce foreign metal ions into TiO_2 powders and films [14]. A wide range of metal ions such as iron [15], nickel [16], cupper [17] and cobalt [18] have been used as acceptor dopants into TiO_2 and the TiO_2 photocatalytic activity was improved to varying extents.

2. Experiment

2.1. Materials

Titanium dioxide powder anatase 38 nm was prepared Deionized water mixed with Nitric Acid (HNO_3), purity 65%, supplied from Merck Co. Titanium tetraisopropoxide (TTIP), Ti [OCH (CH3)2]4, purity 97%, from Sigma-Aldrich. Iron Chloride $FeCl_3$ and Copper Chloride $CuCl_2$ supplied from Merck Co. Conductive glass Fluorine doped tin oxide (FTO), sheet resistance (7 Ohm/sq) transmission (80%) and N719 ruthenium complex supplied by [Solaronix] .Solar Power Meter (TES-1333 Digital Radiation Detector-china). digital multimeter was utilized to measure the open-circuit photovoltage and short-circuit photocurrent of the DSSC - china. Ethylene glycol from Aldrich, acetic acid solution-from SCR-china, iodine (I_2) and potassium iodide (KI) was purchased from Erftstadt Germany. Cu $(NO_3)_2$ and $AlCl_3$ supplied from (G.P.R- England).

2.2. Preparation of doped and pure TiO_2 catalyst

Titanium dioxide (TiO_2) sol was prepared using the following procedure: deionized water was mixed with titanium tetraisopropoxide (TTIP) in terms of a molar ratio of Ti:H_2O =1:4. Nitric acid (HNO_3) was used to adjust the pH = 2 and for restrain the hydrolysis process of the solution. The solution was put on a magnetic stirrer for 24 hours. The resultant sol was aged for 6 hours at 55°C yielding a transparent sol [19].

Doped and pure TiO_2 samples were prepared by a simplest sol-gel technique. Deionized water (18.2MΩ.cm) Nitric Acid (HNO_3), purity 65%.Titanium tetraisopropoxide (TTIP), Ti [OCH $(CH_3)_2]_4$, purity 97% and Iron Chloride $FeCl_3$. Were used to get undoped and Fe doped thin films.

3. Band gap energy

The band gap energy of (TiO_2) samples could be obtained by applying Tauc law (αhv) n = $\mathcal{A}$ (hv – Eg), Where: Eg Absorption band gap energy, α Titania absorption coefficient ,hv Energy of the incident photons ,$\mathcal{A}$ Corresponding absorption constant ,n Value representing the optical transmission mode [20].

4. Assembling the Cell

Electrode and counter electrode were combined together keeping TiO_2 paste coated surface and the carbon coated surface face to face. 2-3 drops of electrolyte solution was given in the contact of two glasses and by the capillary action the electrolyte was uniformly distributed throughout the stained TiO_2 film. Excess electrolyte from the exposed area of the glass was wiped off by using cotton or tissue. The complete cell was then taken to sunlight for harvesting energy.

5. Cell efficiency

The conversion efficiency of the cell is the ratio of electrical output at power point and the power of incident radiations (Pin). The solar energy-to-electricity conversion efficiency (η) was determined by the equation (1).

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}} \times 100\% \quad (1)$$

6. Results and discussion

6.1 XRD Measurement of TiO_2

Figure -1 shows the XRD thin film of TiO_2 38 nm, paste sample deposited on Fluorine doped tin oxide conductive glass (FTO) after annealed at temperature 450 ^{0}C. It is clear that the X-ray diffraction pattern consists of characteristic diffraction peaks at 2θ. Which were assigned to (101), (004), (200), (105) and (211) respectively. It is observed that the film exhibited characteristic peaks of anatase crystal plane. The nearly sharp peak detected at (25.14º) can be related to anatase phase with crystal plane (101), while the intensity of the other peaks is very weak.

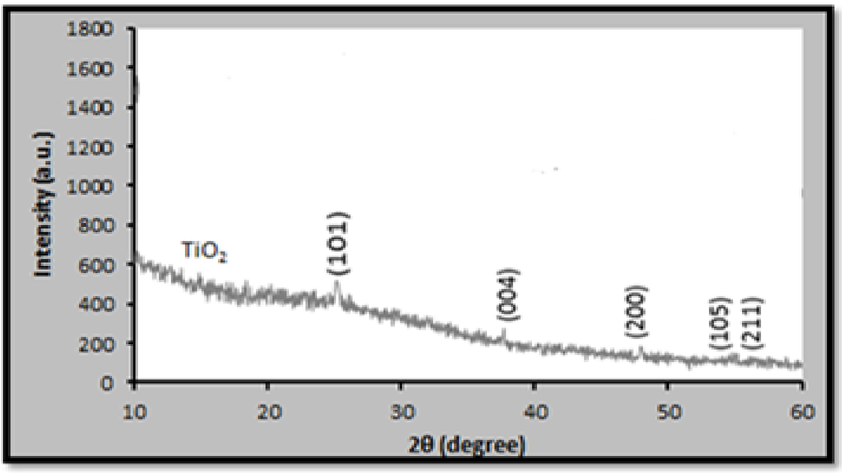

Figure 1- XRD thin film of TiO_2 38 nm

6.2. UV-VIS spectra analysis and Values of band gap energy

The absorbance of Fe/Cu- doped TiO_2 films deposited on commercial glass substrates in the spectral range of 200–500 nm is shown in Figure-2, The visible light photoabsorption of Fe- Cu-doped TiO_2 calcined at 450º C was the strongest. The energy gap (E_g) is determined by the formula, E_g = 1239.8/ λ where; λ (nm) is the wavelength of the absorption edge in the spectrum [21] .The energy gap for the CO-doping films of (TiO_2) pre-coated substrates was calculated by applying Tauc law = 3.34 eV are larger than that of the bulk TiO_2 (3.2 eV). This can be explained because the band gap energy of a doped semiconductor has been found to be dependent on the dopant. as explained in [20]. Figure-3 was shown The band gap energy of Fe - Cu -TiO_2 . The following equation represents the optimal result

(Eg) Fe , Cu > (Eg) Fe > (Eg) Cu

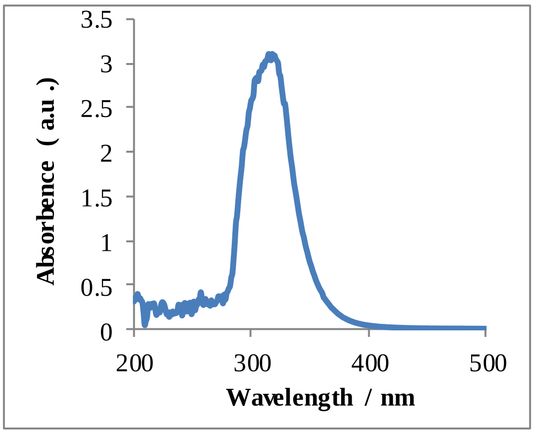

Figure 2- Absorption spectra of (Fe - Cu) – doped TiO_2

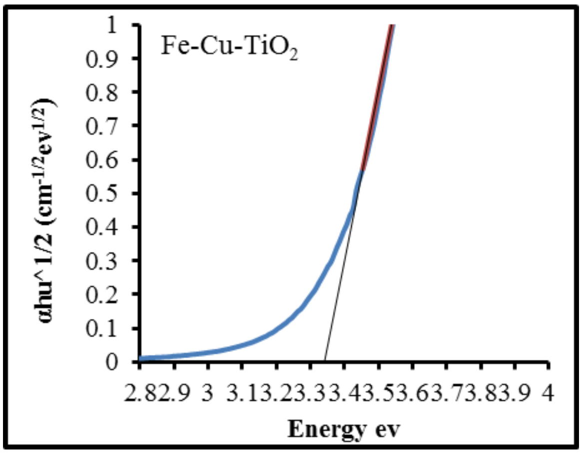

Figure 3- Band gap energy for (Fe - Cu) - doped TiO_2

6.3. Effect of Different Ion-Doped and co- doping

In the present investigation, it was observed that doping of titania by metal (Fe) and metal (Cu) has increased the photocatalytic activity of semiconductor in visible light and simultaneously maintain strong redox potential .The performance of cell was improved, as compared to pure TiO_2. The results shows a faster electron transport in the Fe - cu -doped TiO_2 films, which contributes to a higher J_{sc} of DSSCs. A positive shift of the flat band is also responsible for the significant improvement of J_{sc}. This finding demonstrates the feasibility of improvement of conversation efficiency with two kinds of elements doped in the DSSC and thus efficiency increased means that the last model is the best of everything. As shown in Table-1.

Table 1- Doping and co-doping without additives Vs efficiency

Type	I_{sc}	V_{oc}	I_{max}	V_{max}	%FF	%η
$TiO_{2\ pure}$	1.6	0.55	1.3	0.5	73	1.6
TiO_2/cu	1.8	0.54	1.5	0.49	76	1.85
TiO_2/Fe	1.85	0.6	1.65	0.52	77	2.14
TiO_2/Fe/ cu	1.88	0.57	1.7	0.54	86	2.30

6.4. Effect of light intensity

Light intensity may also affect the electrical parameters of DSSC and therefore, light intensity was changed from 20 to 60 mW/cm^2 to observe the effect of light intensity on electrical output of the cell. The results are reported in Figure-4. It shows an increasing trend with increasing light intensity because an increase in light intensity increases the photons per unit area. Higher light intensities were avoided as an adverse effect was observed with higher intensities. This may be due to the evaporation very fast of electrolyte at higher intensities.

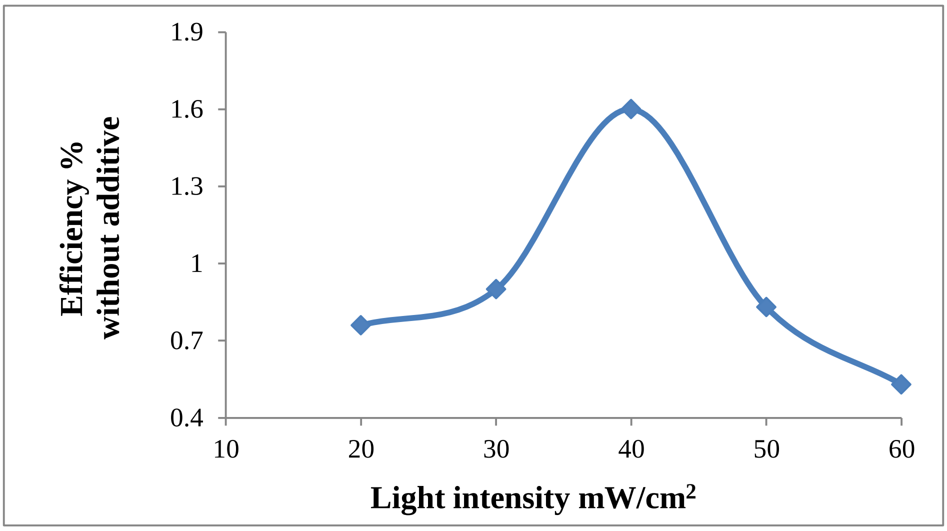

Figure 4- Light intensity Vs efficiency

6.5. Effect of additives on current density and efficiency

Additives play an important role to enhance the photovoltaic parameters in liquid electrolyte-based DSSC. In addition to a redox couple, two types of additives are normally introduced into the liquid electrolytes Cu $(NO_3)_2$ and $AlCl_3$. Cu doped TiO_2 thin films were lower, Fe doped TiO_2 thin film photovoltaic best performance, and cell power was highest, indicating that the effect of doping of Fe was the best in these two kinds of ions. The first additives type, it showed high efficiency for enhancing both the open-circuit voltage and short-circuit current density of DSSC when the suitable amount. Figure-5 shows the effect of added solar cell in the case of glass in case TiO_2 (38nm).

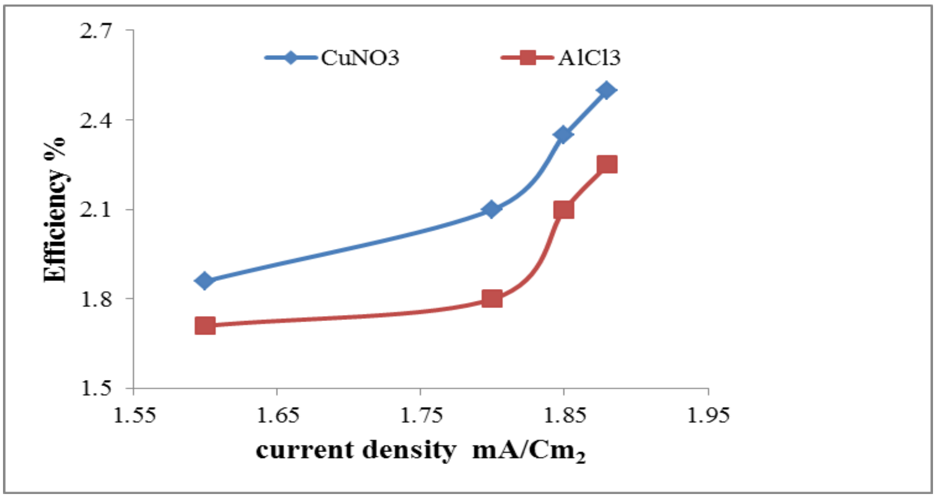

Figure 5- Efficiency vs current density

Consequently we get the ideal values in Table -2.

Table 2- The final exemplary values in the search

Type	η% Without additive	η% $Cu(NO_3)_2$	η% $Alcl_3$
$TiO_{2\ pure}$	1.6	1.86	1.71
TiO_2/cu	1.85	2.1	1.8
TiO_2/Fe	2.14	2.35	2.1
TiO_2/Fe, cu	2.30	2.5	2.25

7. Conclusions

In the present investigation undoped ,Fe-doped TiO_2 nanoparticles and Cu-doped TiO_2 nanoparticles were successfully synthesized via Sol-gel method using Titanium tetraisopropoxide (TTIP) as precursor., it was observed that doping of titanium by metal (Fe) and metal (Cu) has increased the power conversion efficiency. The solar cell fabricated with co-doped titanium was more efficient from the solar cells pure titanium and doping; therefore The band gap energy increases with increasing the Fe doping TiO_2,Cu doping TiO_2 and mix (Fe-Cu doping TiO_2) weight percentage and the absorption edge is shifted to a higher energy (blue shift), considering the blue shift of the absorption position from the bulk TiO_2.

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