Influence of Metal Ion Doping of Zinc Oxide Photoanode on the Efficiency of Dye Sensitized Solar Cell

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Abstract

Doping zinc oxide nanoparticles (ZnO NPs) and doped with Niobium (Nb^{5+}) and Aluminium (Al^{3+}) ions were synthesized to use as a photoanode for the Dye Sensitized Solar Cells (DSSCs). The structural of the synthetized samples were examined via X-ray diffraction (XRD). The XRD patterns for all samples confirmed the hexagonal wurtzite structure. The DSSCs based on the undoped and doped ZnO NPs were fabricated and assembled. Scanning electron microscopic (SEM) images were measured for all fabricated devices. The doping Nb^{5+} and Al^{3+} ions influenced the performance of the DSSCs. ZnO NPs doped Nb^{5+} led to higher surface area and hence more dye loading and retard the recombination of charges, which enhanced the open circuit voltage.

1. Introduction:

The increasing global demands of clean renewable energy (CRE) is becoming one of the major scientific challenges for scientists, economists and politicians (Crabtree and Lewis, 2007), where the global warming coming from the combustion of fossil fuels have produced widespread environmental damage (Kerr, 2007). Therefore, the search for alternative source of CRE such as sun is one of the attractive research interests for many researchers. The sun is an abundant source of energy that has a solar flux deposited on the surface of the earth within one hour as much as the global power usage.

The dye-sensitized solar cells (DSSCs) (McConnell, 2002) are the third generation of solar cells after the silicon-based solar cell and the thin film solar cells (O'Regan and Gratzel, 1991). They are cost effective, easy to be fabricated and they are investigated widely for higher efficiency. The photovoltaic DSSCs is a mimic of the photosynthesis and a physical separation between photon absorption and charge percolation process, where the light is absorbed by a molecular dye, which is attached to the surface of semiconducting nanoparticles. The free charges are injected in the formed semiconducting photoanode, while the dye is regenerated via reduction by a redox shuttle electrolyte. The oxidized electrolyte is diffused to a counter electrode to complete the circuit. The recombination of the injected electron with the oxidized dye before it is regenerated, or the redox shuttle can intercept an electron from the photoanode before it is collected, causes a drop on the total performance of the conversion process. The developments of such cells are concentrated on the three main components of the cell, the photoanode, dye and the electrolyte and/or the interfaces between them. Conventional DSSCs require heating

the photoanode at higher temperature between 400 – 500 °C. This annealing step is needed for having good adherence on the substrate, eliminating the organic species present in the paste or colloid and to improve the connection between the nanocrystallites that constitute the film. Common photoanode materials in DSSCs are TiO_2, ZnO NPs film on transparent conducting oxide (TCO) layers (Graetzel, 2003). The popularity of such materials is due to their large surface area and chemical affinity for dye adsorption as well as their suitable energy band potential for charge transfer with dye and electrolytes (Bandara et al., 2005; Kuang,, 2007). The structure and morphology of the photoelectrode play a vital role in developing such materials (Zhang and Cao, 2011). The improvement of the conversion efficiency can be attributed to the larger surface area, which is a goal of most researchers. Using a doping element for ZnO may be enhanced the performance parameter of the DSSCs. In this work, is to investigate the impact of ZnO NPs doped metal ions, i.e. Nb^{5+} and Al^{3+}, on the performance of DSSCs. The structural and the electrochemical properties of the assembled solar cells were, also, investigated.

2. Experimental Set Up:

2.1. Synthesis of the Nanoparticle:

The undoped Zn NPs and doped $ZnO:Nb^{5+}$ 1.0 at.% and $ZnO:Al^{3+}$ 1.0 at.%. NPs were synthesized by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), in pure methanol under vigorous stirring for 30 min at 60 °C until a clear solution was obtained. Moreover, for the doped $ZnO:Nb^{5+}$ 1.0 at.% NPs, 1.0 at.% of Niobium chloride ($NbCl_5$) and for $ZnO:Al^{3+}$ 1.0 at.%. NPs, 1.0 at. % of Aluminum chloride ($AlCl_3$) were added to the starting zinc acetate solution. A 5M NaOH was added dropwise into the solution under vigorous stirring until the pH to adjust the solution to be 14 to get a milky white colloid. The obtained milky white colloid were washed five times with an absolute ethanol and then were centrifuged at 4000 rpm to removes the leftover unreacted materials. Finally, the produced powders were dried at 100 °C for 60 min, and then were sintered at 500 °C for 60 min in air. The collected powders were grinded, gently, and then were to be used for coating the photoanode.

2.2. Thin Film Fabricated and Cell Assembly:

The pastes of ZnO, $ZnO:Nb^{5+}$ 1.0 at.% and $ZnO:Al^{3+}$ 1.0 at.%. NPs were prepared by mixing 0.3 g of with 0.6 g of Polyethylene glycol (PEG400) using a mortar and pestle for 10 minutes The pastes were deposited on

fluorine-doped SnO_2 (FTO) coated glass substrates, using the ''doctor blade'' technique forming 0.5 × 0.5 cm layers. The layers were dried at 100°C for 60 min followed by sintering them at 450 °C for 1 h in air. The obtained sintered layers had a thickness between 12 to 15 μm. The prepared films of ZnO, $ZnO:Nb^{5+}$ 1.0 at.% and $ZnO:Al^{3+}$ 1.0 at.%. NPs were immersed to sensitize them in 0.5 mM ruthenium-based N3 dye solution for 24 h. After that films were rinsed in ethanol and were dried in air at room temperature. A Pt-coated silicon substrate was used as the counter electrode and an iodide-based solution, consisting of 0.6M tetra-butylammonium iodide, 0.1M lithium iodide, 0.1M iodine and 0.5M 4-tert-butylpyridine in acetonitrile was used as the liquid electrolyte.

2.3. Characterization of DSSCs:

All powders obtained were analyzed using an X-ray Powder Diffractometer, SIEMENS Type D500 employing a CuKα radiation (λ = 1.5418 Å) source and equipped with a 25 kV power. The mean .crystallite size (d) can be evaluated from the line broadening of the XRD peaks using the Scherrer's equation. The morphology of the photoanode surfaces were measured by scanning electron microscopy (SEM, JEOL JSM-7000). Photovoltaic properties of DSSCs were characterized using simulated AM 1.5 sunlight illumination with an output power of 100 mW/cm². To measure the adsorbed N3 dye amount on the films, the dye was desorbed by immersing dye-sensitized films in a 0.1M NaOH solution in water and ethanol (1:1, v/v). An ultraviolet-visible-near infrared spectrophotometer (UV-Vis-NIR) was employed to measure the dye concentration of the desorbed-dye solution.

3. Results and Discussion:

3.1. Structural Properties:

Figure 1 shows the X-ray diffraction (XRD) patterns for the as-synthesised samples of ZnO, $ZnO:Nb^{5+}$ 1.0 at.% and $ZnO:Al^{3+}$ 1.0 at.%. NPs, which were measured at room temperature. The XRD patterns of ZnO, $ZnO:Nb^{5+}$ 1.0 at.% and $ZnO:Al^{3+}$ 1.0 at.% NPs was in agreement with the published pdf data number 01-070-2551 (ICDD 2009) for synthetic zincate, that was crystallized in the hexagonal wurtzite structure. The XRD patterns indicated that no traces were found from the dopants Nb^{5+} and Al^{3+} ions. The crystalline sizes of all as-prepared samples powders were calculated by the Scherrer formula. The crystalline sizes of ZnO, $ZnO:Nb^{5+}$ 1.0 at.% and $ZnO:Al^{3+}$ 1.0 at.% NPs are 24 nm, 31 nm and 38 nm, respectively.
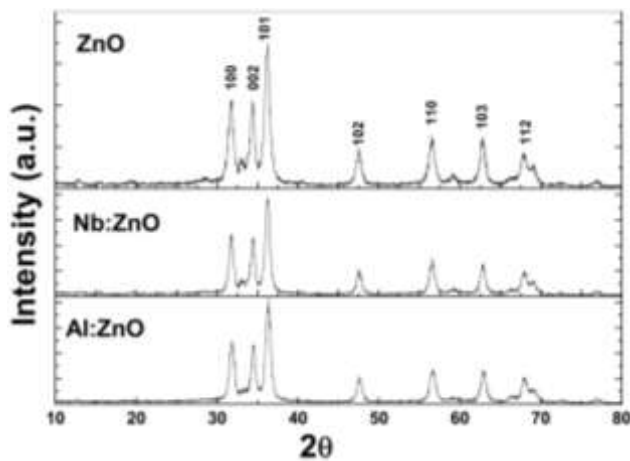
Figure 1 *XRD patterns of the ZnO, ZnO:Nb5+ 1.0 at.% and ZnO:Al3+ 1.0 at.% NPs*

3.2. Scanning Electron Microscopic Study:

The surface morphology of the ZnO, ZnO:Nb^{5+} 1.0 at.% and ZnO:Al^{3+} 1.0 at.% NPs deposited on FTO glass substrate are show in Figure 2. The undoped ZnO NPs layer (Figure 2(a)) shows a fine structure with mesoporous form with a homogeneous distribution. The ZnO:Nb^{5+} 1.0 at.% NPs layer (Figure 2(b)) presents aggregated NPs forming sponge like structure, which accompanied with homogeneous pores. However, the ZnO:Al^{3+} 1.0 at.% layer (Figure 2(c)) iullstartes larger aggregates of loose packed NPs. The doped ZnO structure have a higher surface roughness and is expected to have larger pores that is more convenient for electrolyte transportation, which enhances the regeneration of the oxide dye allowing rapid injection of the charge effectively into the photoanode.
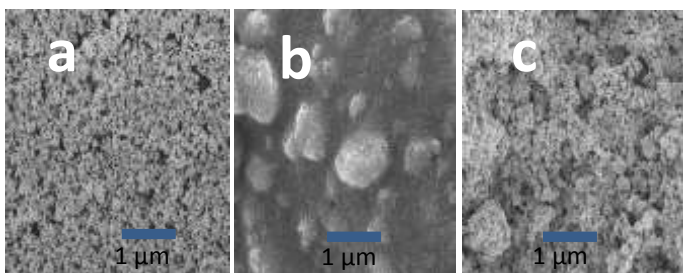

Figure 2 *SEM of a) ZnO, b) ZnO:Nb^{5+} 1.0 at.% and c) ZnO:Al^{3+} 1.0 at.% NPs layers on FTO substrate*

3.3. Cell Performance:

The performance of the fabricated DSSCs using ZnO, ZnO:Nb^{5+} 1.0 at.% and ZnO:Al^{3+} 1.0 at.% NPs at AM 1.5 simulated solar lights (100 mW/cm^2) were measured as shown in Figure 3 and tabulated in Table 1. From

Table 1, the undoped ZnO NPs shows a highest value of the short circuit current density (J_{sc}) and lowest value of the open circuit voltage (V_{oc}). The photocurrent density (J) of undoped ZnO based DSSCs is higher than ZnO:Nb^{5+} 1.0 at.% and ZnO:Al^{3+} 1.0 at.%. However, a significant increase to higher V_{oc} was observed for the doped ZnO based DSSCs. The V_{oc} for undoped ZnO NPs photoanode was 530 mV, which increased by doping with Al^{3+} ions to 580 mV and to 635 mV by doping with Nb^{3+} ions. This had a better impact on the overall efficiency of the fabricated DSSCs. The increasing in the V_{oc} of the doped ZnO photoanode may be attributed to a shift of the flat band potential of the ZnO to negative value. The increasing of the V_{oc} could be due to the band bending which might be occured by creating oxidizing sites inhibit the charge recombination [Jafry et al, 2011]. The fabricated DSSCs based ZnO:Nb^{5+} 1.0 at.% displays an efficiency of 2.76 %, which is 57 % larger than of ZnO and ZnO:Al^{3+} 1.0 at.% NPs. The ZnO:Nb^{5+} 1.0 at.% NPs layer exhibits a significant enhancment of the filling factor (FF) from 0.43 to 0.67. The increasing in FF can be attributed to the faster electron transport and regeneration.
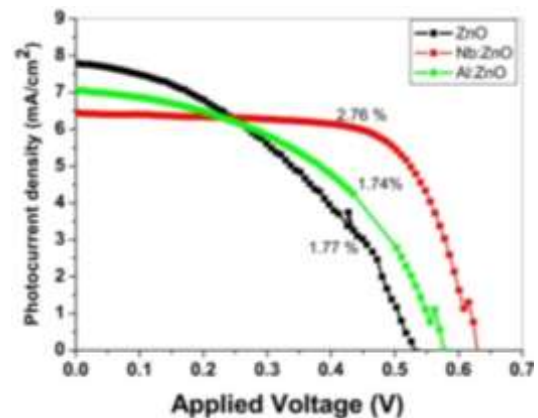

Figure 3 *J-V characteristics curve for DSSCs based on ZnO, ZnO:Al^{3+} 1.0 at.% and ZnO:Nb^{5+} ZnO:Al^{3+} 1.0 at.% NPs photoanodes*

Table 1 *PV performance of DSSCs based on ZnO, ZnO:Al^{3+}1.0 at.% and ZnO:Nb^{5+} 1.0 at.% NPs photoanodes*

	J_{sc} (mAcm^{-2})	V_{oc} (mV)	FF	η%
ZnO	7.84	531	0.43	1.77
ZnO:Al^{3+}	7.1	577	0.42	1.74
ZnO:Nb^{5+}	6.46	630	0.68	2.76

Figure 4 exhibits the UV-Vis absorption of the dye uptake from the different photoanodes made from ZnO, ZnO:Nb^{5+} 1.0 at.% and ZnO:Al^{3+} 1.0 at.% NPs. As shown in Figure 4, the larger absorption spectra in the visible

region for undoped ZnO NPs. This implies to a larger surface area for dye loading from undoped ZnO NPs which may be expected due to the homogeneous multiparous structure achieved. The obtaining of higher J requires larger dye loading adsorption onto the surface of the photoanode. Larger amount of dye adsorbed on the mesoporous titania (TiO_2) NPs is a consequence of the larger surface area, which also implies a larger exposed active region for electrochemical reaction.
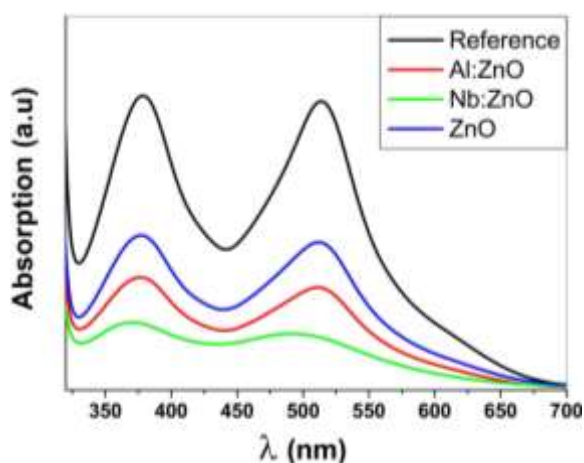

Figure 4 *Dye Uptake of cells made using the ZnO, ZnO:Al^{3+} 1.0 at.% and ZnO:Nb^{5+} ZnO:Al^{3+} 1.0 at.% NPs photoanodes*

4. Conclusion:

ZnO, ZnO:Nb^{5+} 1.0 at.% and ZnO:Al^{3+} 1.0 at.% NPs were successfully synthesised and used to fabricate DSSCs. The undoped ZnO NPs showed a higher short circuit current density, however a lower open circuit voltage. ZnO:Nb^{5+} 1.0 at.% and ZnO:Al^{3+} 1.0 at.% NPs resulted in slight decrease of the short circuit current, however a remarkable increase of the open circuit voltage. An increase of the overall light to current conversion efficiency from 1.77 to 2.76 % was observed by using ZnO:Nb^{5+} 1.0 at.%, due to a significant increase of the open circuit voltage from 531 to 630 mV.

5. Acknowledgement:

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تأثير تطعيم حبيبات أكسيد الزنك النانونية بأيونات معدنية المستخدم كأنود ضوئي علي كفاءة الخلايا الشمسية الصبغية

كلمات مفتاحية:
الخلايا الشمسية الصبغية،
حبيبات اكسيد الزنك النانونية،
التطعيم،
الطاقة المتجددة.

تم تخليق أكسيد الزنك على مستوى النانو وتطعيمه بأيونات الألمونيوم والنيوبيوم ودراسة الخصائص التركيبية للمكونات بواسطة حيود أشعة أكس والميكروسكوب الالكتروني المسحي. وتم استخدام هذه المواد النانونية لتكون الأنود الضوئي للخلايا الشمسية الصبغية. وبعد دراسة فاعلية الخلايا الشمسية الصبغية وحساب كفاءتها تبين تأثير عملية التطعيم لأكسيد الزنك على كفاءة الخلايا الشمسية الصبغية وتحسينها نتيجة تحسن في شدة كثافة التيار الضوئي بالإضافة إلى زيادة واضحة في جهد الدائرة المفتوحة مما أدى إلى زيادة واضحة بمقدار 56% في حالة التطعيم بعنصر النيوبيوم.

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