Dye sensitized solar cell efficiency improvement using TiO₂/nanodiamond nano composite

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Abstract. This paper aims to demonstrate the efficiency and recombination improvement of Dye-sensitized solar cells (DSSCs) by introducing of a Nanodiamond (NDs)-TiO₂ nano composite. The main challenge in the proposed application is to find the optimal wt.% of ND in TiO₂. The experimental tests were conducted to compare the developed NDs/TiO₂ cell with one of pure TiO₂ nanoparticles prepared in the same conditions. It was observed that short circuit current density, power conversion efficiency, fill factor and electron life time enhanced with increasing ND content. The best performance was obtained with 1 wt.% ND content; with a current density of 12.11 mA/cm² and light-to-electricity conversion efficiency of 4.95%. The improvement in efficiency of 18.7% was obtained as the standard DSSC was compared with that of pure TiO₂.

Keywords. Dye sensitized solar cells; nanodiamond / TiO₂ nano composite; charge carrier; electron life time; photovoltaic.

1. Introduction

Dye-sensitized solar cell (DSSC) has a number of attractive features; it is semi-flexible and semi-transparent which offers a variety of uses, and most of the materials used are of low-cost. In a search for alternative materials to be used in the solar cells systems, carbon seems to have a high potential due to its high stability. Different stable carbon allotropes possess a number of properties with potential applications in the photovoltaic industry [1]. Fullerenes, carbon nanotubes, nanodiamond and hraphene have various applications in the development of solar cells, including dye sensitized solar cells. Nanocarbons can be used as an active light-absorbing component, current collector, photo-anode additive and counter electrode [2]. Incorporation of low-dimensional carbon nanostructures such as carbon nanotubes (CNTs) and graphene sheets into semiconductor electrodes is a common approach to improve charge collection and photovoltaic performance of DSSCs [3]. The relatively inexpensive large scale production of nanodiamonds (NDs) have made them commercially viable for a broad range of applications. NDs have tetrahedral network structures; large grain boundary density and low negative electron affinity which makes them attractive for electronic applications such as field emission [4]. The wide band gap ($E_g \sim 5.4$ to 5.6 eV) makes ND a semiconductor material with a wide range of applications. The combination of high mechanical strength, stiffness, light

weight, and low coefficient of friction make ND attractive for the fabrication of structural composites [5]. NDs comprise of a diamond core (sp^3), a middle core (sp^{2+x}) and a graphitic outer core (sp^2). The highest occupied molecular orbital and lowest unoccupied molecular orbital energies of NDs are quite uniform ~ 5.5 eV and ~ 3.0 eV, respectively [6, 7]. NDs also have charge mobility properties which increase with temperature, possibly by carrier hopping between localized states introduced by the inhomogeneity, with the coulomb blockade playing a role. Charge transport takes place mainly within this inter particle carbon [8]. Mesoporous TiO₂ nanoparticle films are used as photo-anodes for high-efficiency DSSCs. In spite of excellent photovoltaic power conversion efficiencies (PCEs) displayed by titanium dioxide nanoparticle structures, the transport rate of electrons is known to be low due to low electron mobility [9], while the same for ND is known to be orders of higher magnitude [10]. Based on these considerations, it is conceivable that NDs can serve as charge material in DSSCs. The objective of this paper is to study the implementation of NDs in TiO₂ and investigate its effects on dye solar cell performance.

2. Experimental

2.1 Preparation of TiO₂ paste mixed with ND powder

As received ND powder aggregates (ALIT co.) result in too large particles in the order of micron size, it is necessary to

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Table 1. The composition of NDs in TiO₂ paste for 7 different samples (wt.%).

SHOT count	Solution weight that mixed with TiO ₂ [mg]	Nano diamond weight [mg]	Nano diamond in TiO ₂ paste wt. [%]	Sample number
1	63.56	.2	0.1	1
5	317.8	1	0.5	2
10	635.6	2	1	3
15	922.5	3	1.5	4
20	1270	4	2	5
25	1587.5	5	2.5	6
—	—	0	0	7

disaggregate these particles to make their use in solar cell fabrication possible. Thus, the 250 mg ND powder was dispersed in 100 cc methanol (CH₃OH, 99%; Merck) followed by tip sonication (Bandelin Sonopuls HD 3200 Ultrasonic Homogenizer, Germany) for 1 h (Vincent *et al* 2007 [11]; Lin *et al* 2014 [12]). As illustrated in table 1, different shots (each shot equal to 85.9 micro liter or 63.56 mg of ND-methanol solution) were mixed with 200 mg standard transparent TiO₂ paste (PST-20T, composed of 20 nm TiO₂ nanoparticles; Sharif Solar), dispersed by ultrasonic bath. For all samples, 20 cc methanol was added for easier stirring and then it was stirred for 1 h. Then methanol was removed by rotary evaporator [13].

2.2 Fabrication process of DSCs

The fluorine doped tin oxide substrates (FTO; Dyesol) were sequentially cleaned with acetone, ethanol and deionized water via ultra-sonication for 10 min to remove contaminants [14]. ND/TiO₂ paste was prepared according to the above procedure. It was printed onto FTO and then dried at 100°C for 5 min. The above process was repeated 3 times, then annealed according to a standard programmed procedure [15]. After annealing, the films were cooled to 80°C for dye sensitization. Dye sensitization was performed by immersing ND/TiO₂ films in 0.3 mM N719 ruthenium dye (Dyesol) ethanol solution (using 7 different containers for different samples base of table 1) for 18–20 h at room temperature to complete the sensitizer uptake then washed with ethanol.

For counter electrode pt-paste (PST-Pt; Sharif Solar) was used. The paste was printed onto a clean FTO (with a drilled hole) and then heated at 460°C for 15 min. The dye-sensitized working electrode was assembled with the Pt-coated counter electrode into a cell of sandwich type by heating at 120°C using a hot-melt film (Surlyn, Dyesol) as spacer between electrodes. Then, a drop of electrolyte solution (standard iodine based electrolyte, sharif solar) was placed on the hole in the counter electrode and it was driven into the cell via vacuum back. Finally, the hole was sealed using additional Surlyn and a cover glass. For a better understanding of the constructed cell structure, schematic views of standard and ND/TiO₂ cells are shown in figure 1.

Figure 1. Schematic view of (a) standard and (b) ND/TiO₂ cells.

3. Results and discussion

NDs have a high band gap of 5.5 eV, which gives excellent dielectric properties [16]. Also, diamond films have negative electron affinity characteristics, that makes them promising for electron field emission devices and related emission properties. Further, strong mechanical properties, chemical inertness and good carrier mobility make NDs ideal for high power switches and fast field effect transistors for electronic devices. The optical transparency over a wide spectral range can be utilized in making diamond lasers, optical sensors and

Figure 2. FE-SEM picture of ND powder: (a) before, (b) after, (c) disaggregation, (c) 1 wt.% ND/TiO₂ film's surface and (d) ND/TiO₂ EDAX.

light emitting diodes [16, 17]. Because of these unique properties and also low electron mobility of TiO₂ when compared with NDs, investigating ND/TiO₂ nanocomposite and its effect on DSSCs efficiency have encouraged the study. Figure 2 shows the FE-SEM images ND powder before and after disaggregation and 1 wt.% ND/TiO₂ film's surface. The top-view of SEM pictures after ND powder deposition on glass is shown in figure 2a, where large particles in the order of micron size is observed. Figure 2b shows the disaggregated NDs after tip sonication process. This picture confirmed that the disaggregation process was successful. These aggregates are polydisperse in size with diameters ranging from several tens to several hundreds of nanometers. The film therefore presents a highly disordered structure [18]. The FE-SEM images of 1 wt.% ND aggregates embedded in the mesoporous layer are shown in figure 2c, illustrating that ND aggregates are uniformly mixed in the paste [13].

The effect of ND in composition with TiO₂ on the photovoltaic behavior was analyzed. Current-voltage plots were recorded using a Palmsens potentiostat under simulated AM1.5G light (Sharif Solar). Overall 7 cells were fabricated for characterization. Six of them were embedded with a ND and the last (standard reference cell) was used as reference. The results are summarized in table 2. The conversion efficiency (η) and fill factor (FF) are calculated from $\eta = P_{\text{out,max}}/P_{\text{in}}$ and $FF = P_{\text{out,max}}/(V_{\text{OC}} \times J_{\text{SC}})$, where $P_{\text{out,max}}$ is the maximum output power density, P_{in} is the incident light power density, V_{OC} is the photovoltage at open circuit and J_{SC} is short-circuit current density.

The J_{SC} increased from 10.54 mA/cm² (reference sample) to 12.11 mA/cm² with 1 wt.% of ND-TiO₂ nano composite. As a result, the energy conversion efficiency (η) also increased from 4.17% to 4.95% (18.7% improvement). Figure 3 shows current density-voltage characteristics of all

Table 2. Photovoltaic properties of investigated DSSCs composed with ND (sample 1 through 6) and Standard reference cell (sample 7) at various concentrations.

Sample	Wt. [%]	η [%]	η Improvement [%]	Voc [mV]	Jsc [mA/cm ²]	FF [%]
1	0.1	4.24	1.6	655	11.26	57.4
2	0.5	4.52	8.3	675	11.64	57.5
3	1	4.95	18.7	650	12.11	62.8
4	1.5	4.34	4	665	11.50	57.6
5	2	2.43	—	690	7.58	46.4
6	2.5	1.93	—	625	6.62	46.6
7 (ref)	0	4.17	—	640	10.54	61.8

Figure 3. J-V curves for DSSCs composed with ND (sample 1 through 6) and standard reference cell (sample 7) at various concentrations.

7 samples measured under an illumination intensity of 100 mW cm⁻².

Open-circuit voltage decay (OCVD) was further employed to investigate the electron recombination process in the DSSCs based on TiO₂ photo-anodes with different wt.% of ND (figure 4). To measure the electron lifetime in DSSCs, the OCVD technique was used for OCVD measurement, a stationary light was illuminated on the DSSCs and abruptly switched off [19]. Then, the decay of the steady-state photovoltage induced by the stationary light was monitored [20]. The OCVD technique is a powerful tool to study interfacial recombination processes in TiO₂ DSSCs between photo injected electrons and the electrolyte

Figure 4. Open-circuit voltage decay curves of the DSSCs based on various concentrations.

in the dark. It can provide some quantitative information on the electron recombination rate [21].

As voltage decay reflects the decrease in electron concentration, which is mainly caused by the charge recombination, electron lifetime (τ_n) proposed to quantify the extent of electron recombination with the redox electrolyte, which previously has been proven to be effective. τ_n Was calculated with the OCVD using the following equation and the results are presented in figure 5.

$$\tau_n = -\frac{k_B T}{e} \left(\frac{dV_{OC}}{dt} \right)^{-1} \quad (1)$$

where k_B is the Boltzmann constant, T is absolute temperature, e is the electronic charge, and dV/dt is the derivative of the transient open-circuit voltage [21].

Figures 4 and 5 compare simplified results of τ_n dependence on the open-circuit voltage for DSSCs based on various concentrations. For greater clarity, figures 3 and 5 demonstrate that ND improves the current density and also recombination rate for concentrations up to 1 wt.%. The short-circuit photocurrent density increased with the added amount of ND and reaches its maximum value at 1 wt.% of ND. Further, it is observed that an increase in ND concentration from 1 wt.% up to 2.5 wt.% reduces the cell efficiency, due to increased haziness arising from the aggregates and the roughness, acting as light-scattering centers [22] and

Figure 5. Comparison of the electron lifetime as a function of open-circuit voltage of DSSCs based on 3 various concentrations.

also antireflection properties of ND particles [23]. The low mobility of electrons in TiO_2 affects the electron transport rate in the photo-anode film, leading to a decrease in the photo generated electron collection efficiency. NDs have good electron mobility which lead to faster electron transport. The ND mobility is orders of magnitude higher than TiO_2 [9]. Generally, electrons captured by TiO_2 molecules are transferred to ND, which is energetically favored. This is followed by faster electron transport than what could be achieved by hopping among TiO_2 molecules. The largest electron lifetime was found for the sample with 1 wt.% ND concentration, in agreement with TiO_2 for both dark and light conditions. The addition of a large amounts of ND (1.5 wt% to 2.5 wt.%) result in very short electron lifetime, due to very fast electron transfer from the photo-anode to the electrolyte, resulting in very large electron recombination, which in turn negatively affects the cell performance. It can thus be conclude that the addition of moderate quantities of ND highly improves the PCE, but an excessive amount of ND induces an electrochemical short circuit, in which electrons are massively injected into the electrolyte and no longer collected at the anode [24].

4. Conclusions

It is demonstrated in this work that ND- TiO_2 is an effective photo-anode composition for DSSCs applications. The effects of embedding ND in composition with TiO_2 on DSSC photovoltaic behavior have been experimentally analyzed. For this purpose, a total of 7 cells were fabricated for characterization. Six of the cells were embedded with ND and the seventh (standard reference cell) was used as reference. Optimum ratio of ND content in TiO_2 was 1 wt.%. The ND was found to form a good composite with TiO_2 and led to an 18.7% (1 wt.%) increase in power conversion efficiency in comparison with the standard pure TiO_2 DSSC. It is seen that 1 wt.% ND in combination with DSSC photo-anode increased the short-circuit current density from 10.54 to 12.1 mA/cm^2 by using the screen printing method. Further increase in ND concentration does not lead to improvement in efficiency and recombination rate because of optical difference between layers of pure transparent TiO_2 up to 2.5 wt. % (hazy). OCVD was further employed to investigate the electron recombination process and the largest electron lifetime was also found for the 1 wt. % ND concentration which in agreement with TiO_2 in the dark and under light.

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