

Photovoltaic characterizations of nano-CdO based dye sensitized solar cells

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The synthesis of nano-CdO materials with two different types have been successfully achieved using additive-free, reproducible method by homogeneous precipitation from Cadmium acetate. Microwave heating method is used to synthesize nano-CdO materials. The X-ray diffraction (X-ray), scanning electron microscopy (SEM) and Atomic Force Microscopy have been provided for the characterization of two types nano-CdO materials. Two different morphologies are obtained for nano-CdO materials. Dye sensitized solar cells have been fabricated to test the efficiencies of nano-CdO materials. Sensitizations of nano-CdO electrodes have been carried out using Ruthenium (Z907) dye. Nano-CdO_1 material has been found that three times more efficient than Nano-CdO_2 material.

(Received April 28, 2012; accepted September 20, 2012)

Keywords: Dye Sensitized Solar Cell, Nano-CdO, SEM, AFM

1. Introduction

Energy is currently the most important problem facing mankind. In recent years, transparent conductive oxides (TCOs) have attracted much attention owing to their potential applications in electronics and photovoltaic devices [1]. CdO is one of the most important TCO materials; it is an n-type semiconductor and has a direct band gap of 2.2 eV at 300K [2]. It has many attractive properties such as high optical transmittance and low resistivity. CdO films have been used widely in many applications such as photodiodes, solar cells, phototransistors, and gas sensors [3–5]. Hydrothermal synthesis is therefore considered as an attractive route for producing nanocrystalline materials with low energy waste and high efficiency [6, 7]. Organic solar cells and dye-sensitized solar cells have been attracting considerable attention because of their high efficiency, simple fabrication process and low production cost [8-10]. Dye-sensitized solar cells are different from the conventional semiconductor solar cells in that they separate the function of light absorption from charge carrier transport. In conventional p–n junctions a long minority carrier diffusion length is essential, thus pure and well ordered semiconductors are required. The dye-sensitized solar cell consists of sensitizing dye, TiO₂ film (anode electrode), and electrolyte and opposite electrode (cathode electrode) such as graphite or platinum. When this cell is irradiated by sunlight, the electrons of dye are excited from ground state to excited state by absorbing photons. The excited electrons are injected to the conductive band of TiO₂ film, and then transfer to the indium doped tin oxide glass substrate through the TiO₂ film. The hydrothermal methods in aqueous solutions are recognized as excellent procedures for the preparation of metaloxide nanoparticles, as the resulting particles have narrow size

distribution, good crystallization, and high-quality growth orientation [11-14].

In this paper, an additive-free method has been developed to prepare nano-CdO materials from commercially available cadmium acetate precursor using solution-phase reactions. Two different types of nano-CdO materials are obtained. Nano-CdO materials are prepared using microwave oven. Also calcination effects on the morphology are discussed in this study. Two different morphologies for nano_CdO materials are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) measurements. Dye sensitized solar cells have been fabricated and characterized to test the efficiencies of nano-CdO materials using Ruthenium dye (Z907). Schematic illustration of dye sensitized solar cell is presented in Fig. 1.

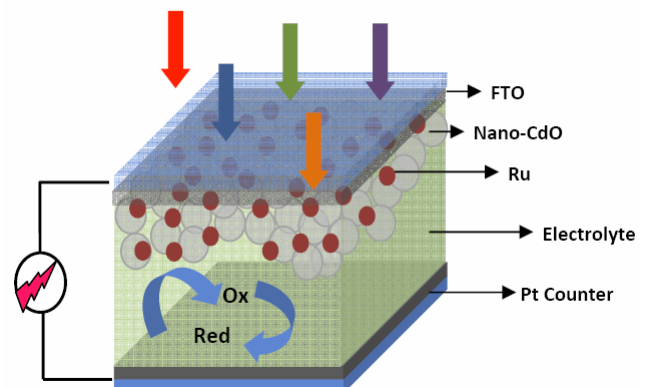


Fig. 1. Schematic Illustration of Dye Sensitized Solar Cell.

2. Experimental section

2.1 Materials

Cadmium acetate is purchased from Sigma-Aldrich company and is used as starting material without further purification. Distilled water is used for all experiments.

2.1.1. Synthesis of Nano-CdO materials using Microwave Heating Method

Cadmium acetate is dissolved in 25 ml deionized water in a beaker. The concentration of cadmium acetate dehydrate is 0.7 M. The solution is stirred with magnetic bar at 100 °C for 1 hour until a transparent mixture is obtained. Subsequently, solution is loaded into a 100 ml Teflon-lined container. Then solution is irradiated by microwave energy in the microwave oven at 200 °C for 60 minutes (CEM MARS-5, frequency 2.45 GHz, maximum power 700 W, multimode oven). After 60 minutes irradiation, the solution is filtered. Afterwards, the white materials are calcined at different temperatures in order to investigate calcination effect on the morphology of the nano-CdO materials.

a) Synthesis of Nano-CdO_2 material;

White powder is calcined at 200 °C for 36 hours in a furnace and then calcined at 450 °C for 8 hours. Nano-CdO_2 materials are obtained with the two-step calcination procedure.

b) Synthesis of Nano-CdO_1 material;

White powder is calcined directly at 450 °C for 8 hours in a furnace. Nano-CdO_1 materials are obtained with one-step calcination procedure.

At the end of these two experiments, nano-CdO materials with two different morphologies are obtained and characterized.

2.2. Materials Characterization

The nano-CdO materials are characterized on a Rigaku X-Ray diffractometer (XRD) with Cu K α radiation (1.540 Å). The operation voltage and current are kept at 40 kV and 40 mA respectively. Scanning electron microscopy (SEM) images are obtained using a Philips XL 30S FEG. Dye sensitized solar cells are characterized by current-voltage ($J-V$) measurement.

All current-voltage ($J-V$) characterizations are done under 100 mW/cm² light intensity and AM 1.5 conditions. 450 W Xenon light source (Oriel) is used to give an irradiance of various intensities. $J-V$ data collection is made by using Keithley 2400 Source-Meter.

2.3 Photovoltaic Characterization

FTO (SnO₂:F, Pilkington TEC-15; SnO₂:F, TEC15, R_{sheet} : 15 ohm/square), electrically conductive oxide-coated glasses are used as transparent electrodes. The construction of the dye sensitized solar cell device requires first cleaning of the fluorine doped tin oxide (FTO) coated glass substrates. FTO glasses are cleaned using an ultrasonic bath with acetone, ethanol and distilled water for 15 minutes. The Nano-CdO pastes in ethanol are used to make thin films using doctor blading technique. Then Nano-CdO coated electrodes are immersed into the commercially available Ruthenium dye (Z907) [15] solution (0.5 mM) and kept at room temperature overnight. Platinized FTO glasses are used as counter electrode. Cells are prepared in a sandwich geometry. A drop of electrolyte solution (electrolyte of 1 M LiI, 0.044 M I₂, 0.25 M TBP in Acetonitrile/Valeronitrile (85/15 v/v)) is placed on the drilled hole in the counter electrode of the assembled cell and is driven into the cell. Finally, the hole is sealed using additional Bynel and a cover glass (0.1 mm thickness). Active areas of the cells are adjusted to 1 cm².

3. Results and discussion

3.1 X-ray diffraction

The Nano-CdO materials are characterized using X-ray diffraction analysis (XRD). X-ray powder diffraction pattern of nano-CdO materials is supplied in Fig. 2. This XRD pattern indicated that the peaks corresponding to the CdO phase are quite prominent compared to the Cd-related peaks. The XRD pattern shows the formation of nano-CdO materials. The diffraction peaks positioned at 2θ values of 32.9, 38.2, 55.2, 65.8, 69.2, 81.9° can be indexed to the phase of Cadmium oxide.

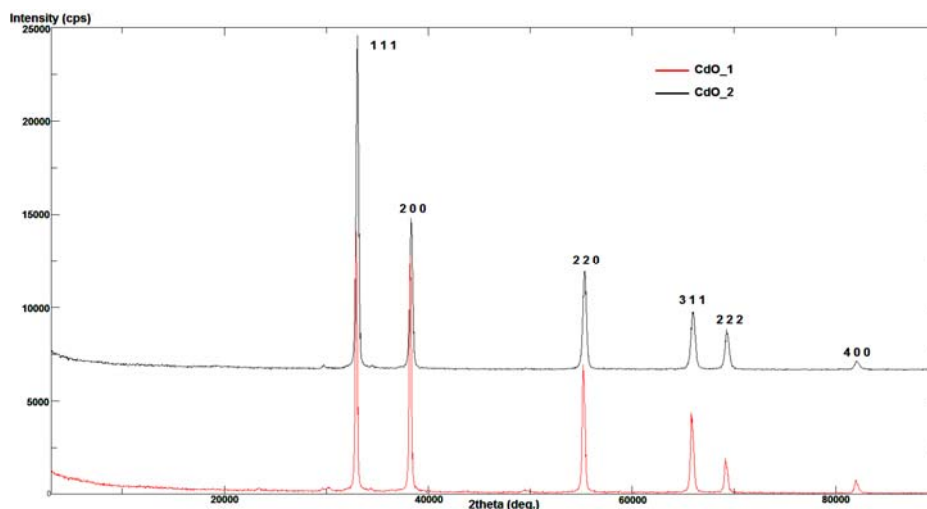


Fig. 2. XRD pattern of nano-CdO materials.

3.2. SEM images of nano-CdO materials

After the reaction is finished in microwave oven, calcination temperatures and calcination times are investigated to obtain nano-CdO materials. Firstly, white powders are calcined at 200 °C for 36 hours. And calcined products are analysed using X-ray diffraction. The X-ray results show that some Cd(OH)₂ and Cadmium peroxides species are occurred at 200 °C calcination temperature. The colour of material is obtained as yellowish and pale brown. The calcination temperature is increased to 450 °C for 8 hours to obtain nano-CdO materials. And then nano-CdO materials are characterized using X-Ray diffraction and SEM image. X-ray diffraction is shown in Fig. 2 for Nano-CdO₂ material. The diffraction peaks are corresponded to CdO peaks. It shows the formation of CdO materials after the calcinations of 450 °C. The SEM image is shown in Fig. 3 (b) of this type of CdO material. The morphology is different because calcinations is carried out at different temperatures with two steps. The CdO is formed at 450 °C after the formation of Cadmium hydroxides and cadmium peroxides species at 200 °C. Fig. 3 (b) is shown the SEM images of nano-CdO₂ materials and the morphology seems as CdO small wafers. The AFM image of nano-CdO₂ material is shown in Fig. 4 (b) with the rms value of 13 nm. After obtaining nano-CdO materials at 450 °C, the role of calcination temperature and calcinations time are investigated for the dimension and degree of orientation of the nano-CdO materials. After this experiment, white product is calcined directly at 450 °C for 8 hours. SEM images show the result of this experiment in Fig. 3 (a). The characterization of nano-CdO₁ material is supplied using also X-ray diffraction analysis. X-ray analysis shows the formation of CdO materials. The SEM images of nano-CdO₁ material is so different from the nano-CdO₂ material. The morphology looks like nano CdO bundles and spherical CdO nanoparticles. The AFM image of nano-CdO₁ material is shown in Fig. 4 (a) with the rms value of 14 nm. The film morphology is very smooth and homogeneous surface. These results show that CdO material forms at 450 °C

calcination temperatures as dark brown particles. In our experiments, two different morphologies are obtained using different calcination temperatures and calcination times as nano-CdO₁ and nano-CdO₂ materials. The length of CdO₁ nanoparticles are in between 360-610 nm and the length of CdO₂ nanoparticles are in between 1410-2290 nm.

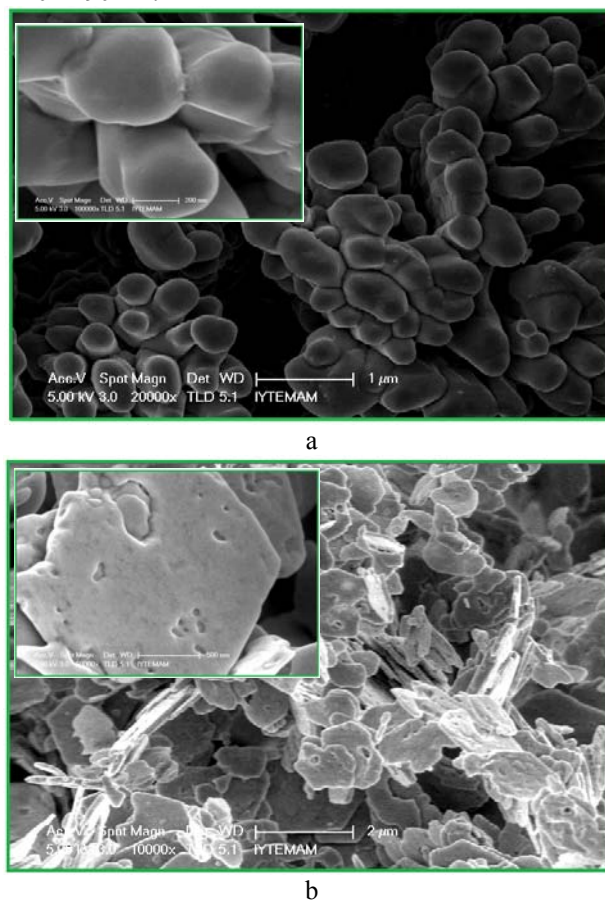


Fig. 3. Scanning Electron Microscopy Images (SEM) of CdO₁ (a) and CdO₂ (b).

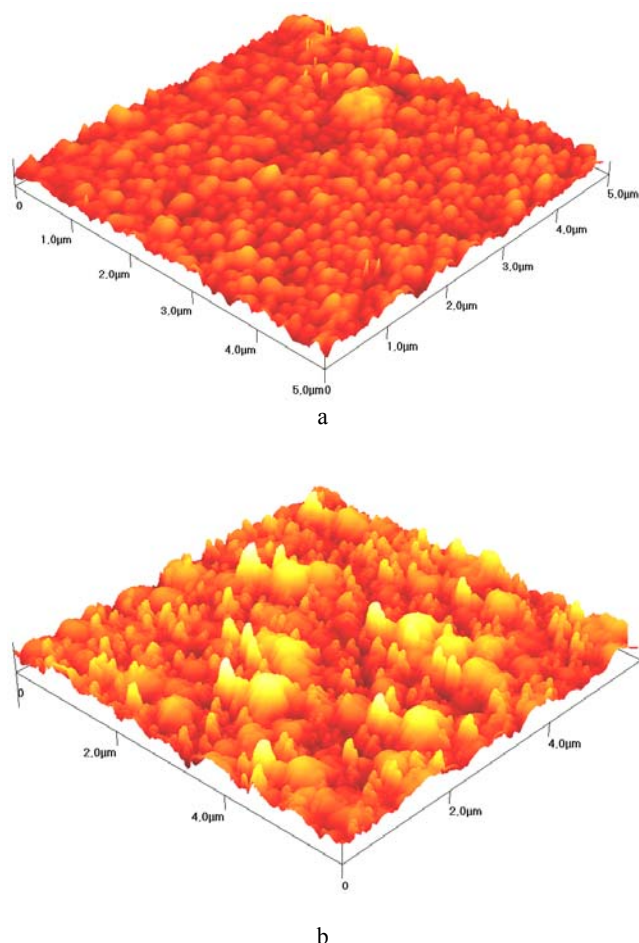


Fig. 4. Atomic Force Microscopy Images of CdO_1 (a) and CdO_2 (b) films

4.3. The evaluation of the performance of nano-CdO structured dye sensitized solar cell

Dye sensitized solar cells have been fabricated to test the efficiencies of nano-CdO₁ and nano-CdO₂ materials. Sensitizations of nano-CdO electrodes are carried out using commercially available Ru dye (Z907). J–V data collection is made using Keithley 2400 Source-Meter. J–V characteristics of dye sensitized solar cell in dark and under illumination are shown in Fig. 5 and Table 1. Under standard global AM 1.5 solar conditions, nano-CdO₁ material is three times more efficient than nano-CdO₂ material. Nano-CdO₁ structured dye sensitized solar cell devices using Z-907 dye gave a short-circuit photocurrent density (J_{sc}) of 0.1 mA/cm², an open-circuit voltage (V_{oc}) of 350 mV, and a fill factor (ff) of 0.37, corresponding to an overall conversion efficiency η , derived from the equation $\eta = J_{sc} V_{oc} ff / \text{light intensity}$, of 0.012 % (see Table 1). Our results show that CdO₁ nanoparticles are exhibited enhanced electron transport properties compared to CdO₂ nanowafers using hydrothermal synthesis method without using any surfactant and additives. Because the lengths and morphologies of CdO materials are so different and these parameters effect the efficiency of dye sensitized solar

cells. The individual bright objects that exhibit a spherical morphology of CdO₁ can be attributed to the strong hydrogen bond formation ability of the functional groups of the ligands, such as –COOH (Ruthenium dye). To achieve high performance, the photoanode needs to possess a good electron transport capability. In CdO₁ nanoparticle film, electron transport is easier than CdO₂ because of electrons can be transferred by hopping process to neighboring nanoparticles. The lengths of CdO₁ nanoparticle are in between 360-610 nm. The lengths of CdO₂ nanowafers are in between 1410-2290 nm. The CdO₁ electrode in dye sensitized solar cell serve as direct pathways for fast electron transport. In addition, CdO₁ nanoparticles have smaller surface-to-volume ratio compared to nanowafers, thus possessing fewer surface defect states that trap electrons. Therefore, electrons have a much higher mobility and can travel through nanoparticles faster than that through thin films composed of nanowafers. Efficient electron transport helps shorten the time needed for electron to travel to the electrode, thus lowering probability of the recombination loss of electrons.

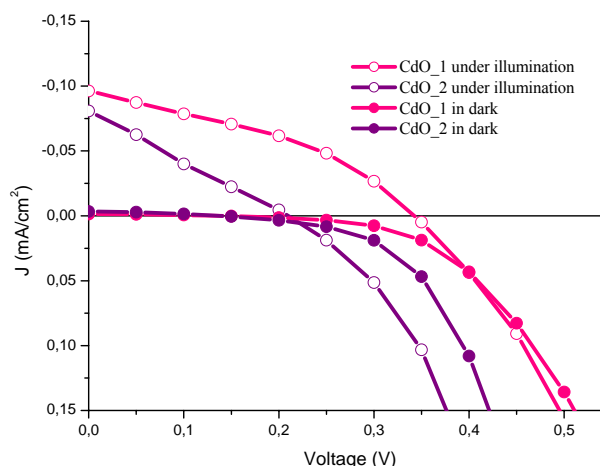


Fig. 5. I-V curve of nano-CdO based dye sensitized solar cells

Table 1. Photovoltaic characterization of Nano-CdO based dye sensitized solar cell using Z907 dye

	I_{sc} (mA/cm ²)	V_{oc} (mV)	FF	η (%)
CdO ₁	0.10	350	0.37	0.012
CdO ₂	0.08	200	0.25	0.004

5. Conclusion

Two different nano-CdO materials are obtained using microwave method at different calcination temperatures and calcination times. Different morphologies are obtained from the SEM images. The size of nanoparticles are measured and added to the text. The length of CdO₁ nanoparticles are in between 360-610 nm and the length of CdO₂ nanoparticles are in between 1410-2290 nm.

Dye sensitized solar cell consisting of Z907 dye and nano-CdO electrodes have been fabricated and characterized. The solar cell efficiency under standard conditions obtained for Z907 using nano-CdO₁ electrode that shows the open circuit voltage of 350 mV, short-circuit current density of 0.1 mA/cm², filling factor of 0.37 and overall conversion efficiency of 0.012 %. Electron transport in CdO₁ nanoparticle film is easier than CdO₂ nanowafers film because of electrons can be transferred by hopping process to neighboring nanoparticles. The CdO₁ electrode in dye sensitized solar cell serve as direct pathways for fast electron transport

Acknowledgements

We acknowledge financial support from Scientific and Technological Research Council of Turkey (TUBITAK) and Alexander von Humboldt Foundation of Germany (AvH). I thank Mechanical Engineer MSc. Cagatay Ela for proofreading and his big support to my scientific career.

References

- [1] M. V. Madsen, K. O. Sylvester-Hvid, B. Dastmalchi, K. Hingerl, K. Norrman, T. Tromholt, M. Manceau, D. Angmo, and Krebs FC. *J. Phys. Chem. C* **115**, 10817 (2011)
- [2] M. Ortega, G. Santana, A. M. Acevedo, *Solid State Electronics* **44**, 1765 (2000).
- [3] F. C. Krebs, T. Tromholt, M. Jørgensen, *Nanoscale* **2**, 873-86 (2010).
- [4] D. Ma, Z. Ye, L. Wang, J. Huang, B. Zhao, *Materials Letters* **58**, 128 (2003).
- [5] R. S. Mane, H. M. Pathan, C. D. Lokhande, S. H. Han. *An Solar Energy* **80**, 185 (2006).
- [6] a) S. Erten-Ela, S. Cogal, G. Turkmen, S. Icli, *Curr Appl Phys* **10**, 187 (2010).
b) S. Erten-Ela, S. Cogal, S. Icli, *Inorg Chim Acta* **362**, 1855 (2009).
c) A. C. Cakir, P. Guloglu, M. Bilgin, S. Erten-Ela, *Journal of Optoelectronics and Advanced Materials*, **14**, 230 (2012).
- d) S. Erten Ela, S. Cogal, S. Icli, *Optoelectronics and Advanced Materials, OAM-RC*, **3**, 459 (2009).
- [7] a) S. Erten-Ela, J. Brendel, M. Thelakkat, *Chemical Physics Letters*, **510**, 93 (2011).
b) D. Rana Bekci, Sule Erten-Ela, *Renewable Energy*, **43**, 378 (2012).
c) A. Cagatay Cakir, Sule Erten-Ela, *Advanced Powder Technology*, **23**, 655 (2012).
- [8] F. C. Krebs, T. D. Nielsen, J. Fyenbo, M. Wadstrøm, M. S. Pedersen, *Energy Environ. Sci* **3**, 512 (2010).
- [9] F. C. Krebs, J. Fyenbo, M. Jørgensen, *J. Mater. Chem* **20**, 8994 (2010).
- [10] O. Brian, M. Graetzel, *Nature* **353**, 737 (1991).
- [11] S. Kolemen, A. Bozdemir, Y. Cakmak, G. Barin, S. Erten-Ela, M. Marszalek, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Graetzel, E. U. Akkaya, *Chemical Science* **2**, 949 (2011).
- [12] a) S. Kolemen, Y. Cakmak, S. Erten-Ela, Y. Altay, J. Brendel, M. Thelakkat, E. U. Akkaya, *Organic Letters* **12**, 3812 (2010).
b) S. Erten-Ela, M. D. Yilmaz, B. Icli, Y. Dede, S. Icli, E. U. Akkaya, *Organic Letters* **10**(15), 3299 (2008)
- [13] T. R. Andersen, T. T. Larsen-Olsen, B. Andreasen, A. P. L. Bottiger, J. E. Carlé, M. Helgesen, E. Bundgaard, K. Norrman, J. W. Andreasen, M. Jørgensen, F. C. Krebs, *ACS Nano* **5**, 4188 (2011).
- [14] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, Cevey L, Costa E, Shklover V, Spiccia L, G.B. Deacon, C.A. Bignozzi, M. Gratzel, *J. Am. Chem. Soc.* **123**, 1613 (2011).
- [15] M. Graetzel, *J. Photochem. Photobiol. A: Chemistry*, **164**, 3 (2004).

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