



Resistive Switching in Diamondoid Counter Electrodes of Dye-Sensitized Solar Cells (DSSCs)

Sumeth Siroj [a], Seksan Lowpa [a], Dulyawat Doonyapisut [a], Suppanut Sangphet [a], Hideki Nakajima [b], Ratchadaporn Supruangnet [b], Santi Maensiri [a], Vittaya Amornkitbamrung [c] and Worawat Meevasana*[a]

[a] School of Physics and Research Network NANOTEC – SUT on Advanced Nanomaterials and Characterization, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

[b] Synchrotron Light Research Institute, Nakhon Ratchasima, 30000, Thailand

[c] Dept. of Physics and Integrated Nanotechnology Research Center, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

*Author for correspondence; e-mail: worawat@g.sut.ac.th

Received: 28 January 2021

Revised: 1 May 2021

Accepted: 6 May 2021

ABSTRACT

We have prepared diamondoid (adamantane) coated on a silicon substrate via a chemical vapor deposition (CVD) technique (ADA/Si: CVD) electrode. This electrode was used as a counter electrode of dye-sensitized solar cells (DSSCs) and this led to high short circuit current density (J_{sc}). The high J_{sc} can be explained by the resistive switching behavior of diamondoids films where the resistivity on the forward bias is lower than the reverse bias; this makes the transportation of electron at the interface between electrode and electrolyte become easier. By using ultraviolet/X-ray photoemission spectroscopy (UPS/XPS), it was found that ADA/Si: CVD film component of 81% SP^2 and 19% of SP^3 hybridization of carbon investigated film can conduct and still have the interesting properties of the diamond, such as negative electron affinity (NEA). The J_{sc} of the ADA/Si: CVD counter electrode is high as $22.1 \text{ mA} \cdot \text{cm}^{-2}$ compared to $19.8 \text{ mA} \cdot \text{cm}^{-2}$ of Pt reference counter electrode. However, the efficiency of the ADA/Si: CVD counter electrode is lower than the Pt reference counter electrode because the films are low conductive and resulting in the fill factor (FF) of only 0.36. It indicates that we can improve this electrode by optimizing the CVD process conditions. These findings should provide an attractive route to improve DSSC efficiency with lower production costs as well as for catalytic applications spanning perovskite solar cells, supercapacitors, and photocatalytic cells.

Keywords: diamondoid, adamantane, chemical vapor deposition (CVD), dye-sensitized solar cells (DSSCs), resistive switching

1. INTRODUCTION

Renewable energy development, especially solar cell technology, has attracted much attention recently because of the global warming problem and the coming of an electric vehicle (EV). Dye-sensitized solar cells (DSSCs) were originally

co-invented in 1988 by Brian O'Regan and Michael Grätzel in their first publication in 1991 [1]. It is easy to fabricate and has been expected to replace conventional silicon solar cells that require advanced manufacturing technology

[2]. However, the main trouble of DSSCs is the power conversion efficiency is still low. Thus, we must find a new route to develop and solve the problem [3]. There are three parts of DSSCs. The first one is the working electrode with a dye molecule as a sensitizer. When electrons in dye molecules absorb photons, they will be excited to exciton state, then transport through the metal oxide layer and load device and then go to counter electrode undergoing the redox reaction of an electrolyte. Platinum (Pt) is recognized as the best counter electrode although it is expensive. Besides Pt, there are also other materials used for the counter electrode, such as conductive polymers and carbon materials [4].

Carbon-based electrodes appear as promising candidates for DSSCs because carbon is much cheaper than platinum. Carbon films can be used as a counter electrode by many methods: lamination of nanotube paste [5], spraying of a CNT solution [6], a growth of a precursor or hydrothermal deposition [7]. Chemical vapor deposition (CVD) is one well-known method for growing carbon films. Normally, carbon film from CVD uses methane as a precursor [8]. However, in this work, we use diamondoid (nano molecule of a diamond which can be synthesized or extracted from the waste products of petroleum processing [9]) as a precursor. Because diamondoid has a negative electron affinity (NEA) [10-11] and can reduce the work function of the substrate [12] this can lead to having a resistive switching behavior (the conductive on forwarding bias or reverse bias better than another side) [13]. The CVD diamondoid films also exhibit strong ferromagnetism when the surface of the film is mechanically exfoliated. This interesting behavior likely comes from the broken of dangling bonds of exfoliated surface [14]. We are then motivated that these properties of the diamondoid films as counter electrodes may help to better transport electrons to the cell [15]. Generally, high short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) are significant parameters to obtain high power conversion

efficiency (PCE), which might be achieved by increasing the charge transfer at counter electrode interfaces [7]. The counter electrode undertakes to return the electrons from the external load back into the “circulation” within the cell [16]. So, it would have a diode behavior to give a one-way direction of electron flow.

In this paper, by using chemical vapor deposition (CVD) technique and adamantane (smallest-nano molecule of a diamondoids series) as a precursor, we fabricate the counter electrodes of DSSCs and then measure their properties, including morphology and structural form, the NEA effect, conductivity (I-V loop), and current density (J_{sc}) of DSSC. We show that this counter electrode from CVD of adamantane on a silicon substrate (ADA/Si: CVD) shows significant provides such a high current density (J_{sc}) around $22.1 \text{ mA} \cdot \text{cm}^{-2}$ higher than the value of $19.8 \text{ mA} \cdot \text{cm}^{-2}$ measured in Pt reference electrode. The origin of this effect is then discussed.

2. MATERIALS AND METHODS

DSSCs were assembled using TiO_2 as scaffold working electrode via a screen-printing method [17]. TiO_2 pastes (PST-18NR and PST-400C from JGC, Japan) were coated on fluorine-doped tin oxide glass substrates (FTO) ($7 \Omega/\text{sq}$ sheet resistance, Solaronix) with an active area of $0.25 \text{ cm} \times 1 \text{ cm}$. TiO_2 films were sintered at 500°C for 1 h and then the surface was modified to improve dye adhesion by treated with UV radiation for 10 min [17]. Treated TiO_2 films were then immersed in 0.3 mM N-719 dye solution (Solaronix) for 24 h. The iodine electrolyte was synthesized by the standard method [18]. An I^-/I_3^- redox mediator switch mixture was prepared by mixing of 0.10 M LiI, 0.05 M I_2 , 0.50 M tert-butylpyridine (TBP), 0.0025 M Li_2CO_3 , and 0.60 M 1-methyl-3-popylimidazolium iodide (MPI) in acetonitrile to obtain iodine electrolyte. Pt counter electrode was prepared by sputtering technique on a tungsten (W) substrate with a thickness of about 50 nm. The CVD-diamondoid counter electrode (ADA/

Si: CVD) was prepared by evaporating the 0.025g of adamantane precursor in the CVD chamber at 1050 °C for 10 min on the silicon (Si) substrate (non-polishing sided silicon), under pressure 0.1 torr. The topography of films was observed using scanning electron microscopy (SEM, ZEISS Auriga) at 10 kV. To investigate the combination of carbon hybridization and NEA behavior at the surfaces of the diamondoid electrodes, ultraviolet/x-ray photoelectron spectroscopy (UPS/XPS) measurements, using Scienta R4000 analyzer, were performed at beamline 3.2a of the Synchrotron Light Research Institute (SLRI), Thailand. At SLRI, the photon energies were in the range of 60-600 eV (energy resolution < 100 meV) and the base pressure was at 2×10^{-10} torr; negative bias voltage from 2-8 V was also used to obtain the clearest spectra at low energy. DSSCs were fabricated and measure the efficiency at the Solid-state laboratory, faculty of science, Khon Kaen University (KKU), Thailand. The cell's efficiency was measured using a solar simulator (PEC-L11, Japan) under a light intensity of 100 mW/cm^2 . The electrical resistivity behavior of ADA/Si: CVD films were studied using the cat whisker setup (measured by B2901A Agilent Source meter) as shown in Figure 3a). The cat-whisker setup combines a source meter unit1 (SMU1) to apply a bias voltage (apply through a 200 μm diameter wire that lightly touches a sample surface) and measure the current by source meter unit2 (SMU2). The biasing voltage applies to a sample surface vertically by sweeping the bias voltage V from -1.0 to 1.0 V then back and repeat this full cycle [13].

3. RESULTS AND DISCUSSION

The CVD-grown diamondoid film's image (Figure 1b)) looks dark in contrast with the clear pristine sapphire and change the color of the silicon substrate (inset of Figure 1c) and 1d)). It is confirmed that the CVD-grown diamondoid film can cover the surface of a substrate as well. The scanning electron microscopy (SEM) shows

the difference surface topography between a clear and smooth surface of pristine silicon substrate (Figure 1c)) and the crystal structure of the carbon rod of CVD-grown diamondoid films as shown in Figure 1d). X-ray photoemission spectra (Figure 2) show how $\sim 81\%$ of the adamantane molecules (Figures 1a)) become transformed during this process to graphene-like (sp^2 -bonded), ensuring decent electrical contact with the conductive Si substrate. The remaining carbon in the ADA/Si: CVD film is sp^3 -bonded (like the adamantane precursor), and negative electron affinity (NEA) is shown by the film (see Figure 2a) and b)) suggests some diamondoid cage structures are preserved. This indicates that the CVD-grown diamondoid films can be improved by optimizing the process.

The electrical property of the electrode is necessary for this study because in the DSSC system, electrons go from the counter electrode to the electrolyte. This means that a counter electrode, which can give electrons better than receive them will be a good candidate [16]; in the other words, when we measure the resistivity under forwarding bias, it should have a lower resistivity compared to reverse bias, as explained in the previous study [13]. Figure 3a) shows an electrical resistivity measurement setup where a source measure unit (SMU) is connected to a 200 μm diameter copper wire. The wire was moved toward the sample surface (mounted on an adjustable micro-stage), by 10 μm increment step. The bias voltage V was applied (by SMU1) between the sample surface and the cat whiskers; the current was then measured by SMU2 from the sample through the wire. This experiment was swept V from -1.0 to 1.0 V and then back repeatedly. The voltage increment of 0.01 V was applied with time step of 0.02 s, with a complete cycle taking 9.2 s (including the 3 ms used to ramp up by V each step) [13]. As shown in Figure 3b), the ADA/Si: CVD electrode is observed to have lower resistivity in forward bias (black arrow direction) and vice versa in the reverse bias direction (blue arrow direction). The behavior resembles

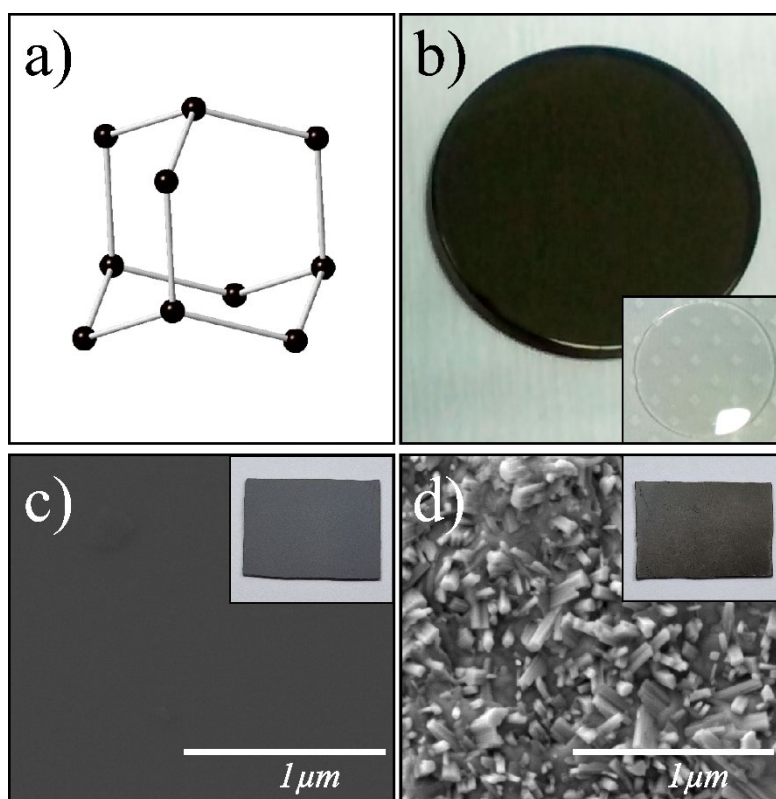


Figure 1. Image and topography: image of adamantane molecule structure (a); image of adamantane coated sapphire via the CVD technique darkness compared with pristine sapphire substrate (inset) (b); scanning electron microscopic (SEM) image of the pristine silicon substrate shown clear and smooth surface, inset of figure-shown picture of pristine silicon substrate (c) and SEM image of CVD adamantane on silicon substrate (ADA/Si: CVD) shown the crystal structure a carbon rod, inset of figure shown picture of ADA/Si: CVD (d).

the “resistive switching behavior”, similar to the previous study from diamondoids with preparation from self-assembled monolayers (SAMs) technique [13]. The origin of this behavior can come from a unique property called ‘ionized radical cation’ when diamondoids are formed on metal substrates according to explained from the previous study [12]. This behavior acts as a local electrostatic gating that the accumulation of relatively positive charges on metal surfaces and hence assists in the improvement of electron transfer better in the one-way direction [12]. This shows that electrons can move better in one direction over the other

one and reduce the chance of the backflow of electronics. However, the resistivity of ADA/Si: CVD films are not uniform, depending on the position of the measuring point on the surface as shown in Figure 3c), this may be due to a non-homogenous topography of the surface as shown in Figure 1d). The resistance of the electrodes was measured using a multimeter. The resistance of ADA/Si: CVD across 1 cm in length is 15 Ω while the resistance of the pristine Si substrate is 50 Ω compared to 0.01 Ω of the Pt/W reference electrode.

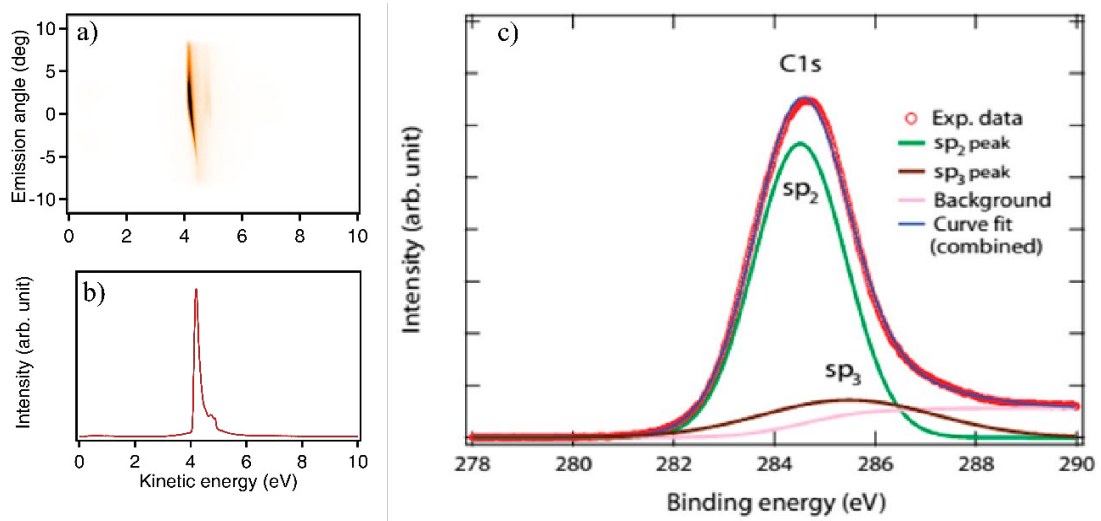


Figure 2. The result of C1s from the X-ray photoemission (XPS) data of the ADA/Si: CVD substrate, measured at SLRI Beamline 3.2a; the angle-resolved photoemission spectrum of the adamantane film on Si substrate as a function of emission angle from the perpendicular direction of the film surface with the negative bias of -4 V (a); the corresponding energy distribution curve as a function of photoelectron kinetic energy. The large peak of low-energy threshold suggests the negative electron affinity of the adamantane film (b); the carbon peaks of both sp^2 and sp^3 with the ratio of 81% and 19%, respectively (c).

The efficiency of DSSCs was then measured under 1 sun illumination. The Pt counter electrodes were set as reference cells. The power conversion efficiency (PCE) of our reference cells is calculated to be 9.21% (red lines in Figure 4). We then replaced the Pt reference cell with ADA/Si: CVD cells and immediately performed the efficiency measurements. As shown in Figure 4, the photocurrent versus voltage (J-V) curve of ADA/Si: CVD cells (green curve) presents the short circuit current density (J_{sc}) around $22.1 \text{ mA} \cdot \text{cm}^{-2}$ higher than the value of $19.8 \text{ mA} \cdot \text{cm}^{-2}$ measured in Pt reference electrode. The high J_{sc} in the ADA/Si: CVD film can come from the resistive switching behavior with help the counter electrode to return electron into the electrolyte and block the recombination of the electron at the counter surface. As a previous study on improving the photovoltaic effect of resistive switching [19],

they said that the resistive switching might be applied to photovoltaic devices in two possible manners. One is that defects can be removed from the inner light-absorptive layer to the interface by applying a sufficiently large electric field, which may decrease the recombination centers of light-generated electrons and holes. The other is that the barrier height at the interface can be lowered by the accumulation of defects, which may facilitate the transport of electrons or holes [19]. In this case, they applied the BiFeO_3 base to TiO_2 to act as a resistive switching light-absorptive layer and can increase J_{sc} about 2.3 times. On the other hand, our system uses a resistive switching electrode as a counter electrode, which may facilitate the transport of charge at the counter electrode surface.

However, the calculated efficiency of ADA/Si: CVD is only around 6.26%, lower than the Pt

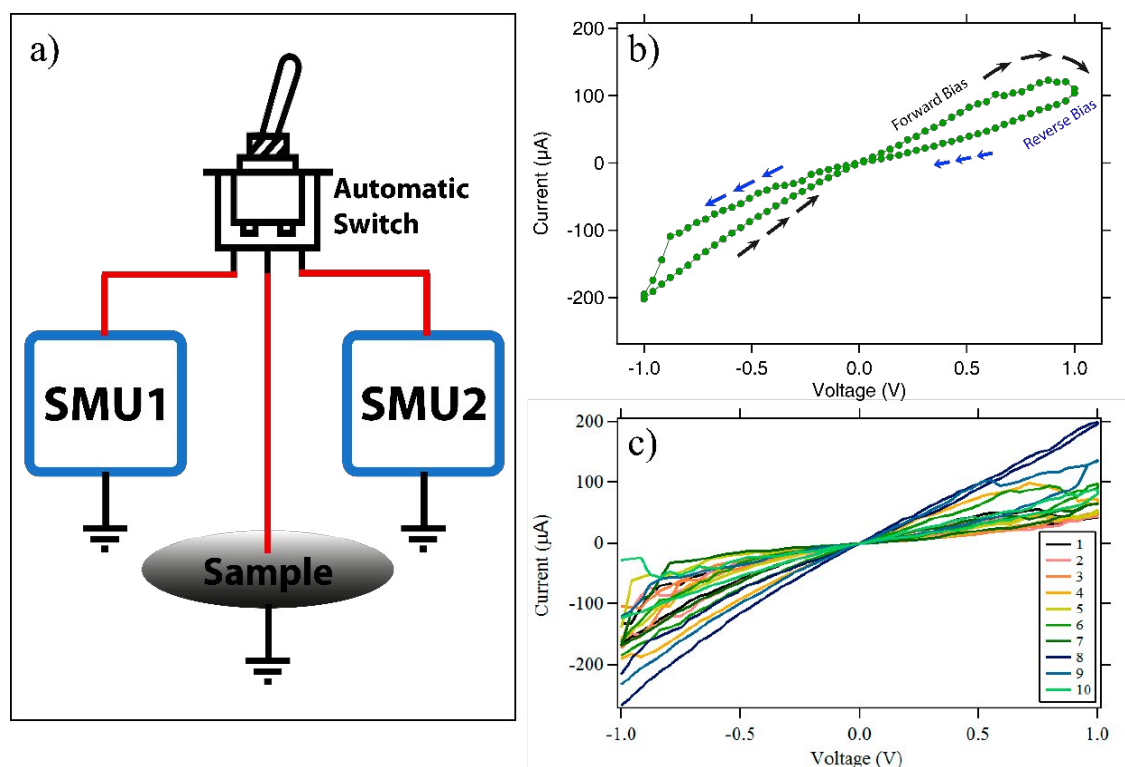


Figure 3. Resistivity measurement. Schematic of the cat-whisker setup (a); The current-voltage curve I-V measured for the ADA/Si: CVD electrode is shown forward bias (black arrow direction) has resistivity lower than the reverse bias direction (blue arrow) (b); I-V measured 10 points on the sample, it shows the electrical properties of this sample spread (c).

electrode. This could be explained by its low fill factor ($FF = 0.36$), which might be caused by its high series resistance (R_s) [20]. The main impact of series resistance is to reduce the fill factor as the previous study [21-23] and descriptive in equation (1):

$$FF = FF_{ref} \left(1 - R_s \frac{I_{sc}}{V_{oc}} \right) \quad (1)$$

where, FF_{ref} is the reference fill factor of the Pt reference electrode. Equation (1) shows that, when R_s increases the FF will decrease; this is consistent with the experiment.

4. CONCLUSIONS

Our ADA/Si: CVD films are fabricated by using the CVD technique. These films can conduct and still have the interesting properties of diamond, such as negative electron affinity (NEA), which leads to exhibit the resistive switching behavior. This behavior can significantly improve the J_{sc} of DSSCs. The J_{sc} of the ADA/Si: CVD counter electrode is high as $22.1 \text{ mA} \cdot \text{cm}^{-2}$ compared to $19.8 \text{ mA} \cdot \text{cm}^{-2}$ of Pt reference counter electrode. However, the efficiency of the ADA/Si: CVD counter electrode is lower than the Pt reference counter electrode because of the low fill factor (FF) of only 0.36 which likely comes from the high

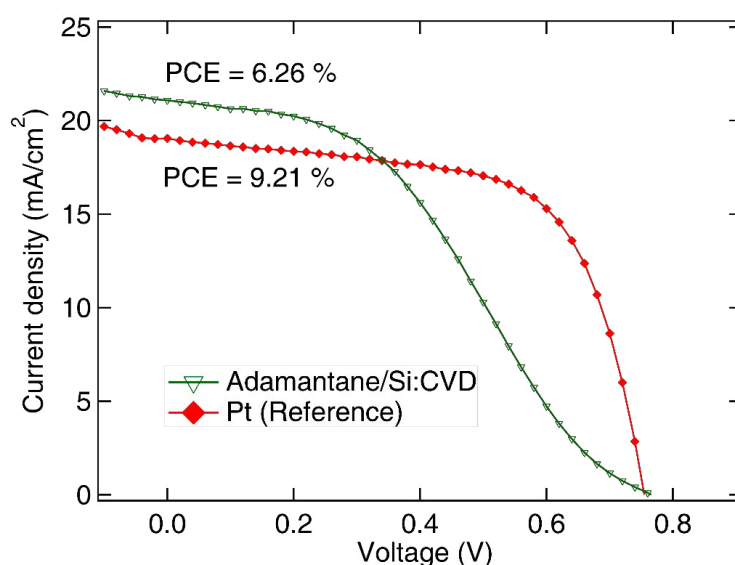


Figure 4. J-V curve and efficiency of DSSCs, green line is a curve of adamantane coated on silicon via the CVD technique (ADA/Si: CVD) and the red line is Pt reference counter electrode.

series resistance (R_s), compared to the Pt electrode. It indicates that we can improve this electrode by optimization of the CVD-processing condition. We believe that, besides DSSC, our findings may offer an attractive route to facilitate diamondoids in other applications such as photocatalytic water splitting, supercapacitors, and batteries.

ACKNOWLEDGEMENTS

This work was supported by Suranaree University of Technology, the Research Network NANOTEC (RNN) program of the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology and Thailand Science Research and Innovation (TSRI). SS acknowledges TRF (TSRI) and SUT through the Royal Golden Jubilee Ph.D. Program (Grant no. PHD/0007/2555) for financial support.

REFERENCES

- [1] O'Regan B. and Grätzel M., *Nature*, 1991; **353**: 737-740. DOI 10.1038/353737a0.
- [2] Gong J., Sumathy K., Qiao Q. and Zhou Z., *Renew. Sust. Energ. Rev.*, 2017; **68**: 234-246. DOI 10.1016/j.rser.2016.09.097.
- [3] Mustafa M.N. and Sulaiman Y., *Sol. Energy*, 2021; **215**: 26-43. DOI 10.1016/j.solener.2020.12.030.
- [4] Imoto K., Takahashi K., Yamaguchi T., Komura T., Nakamura J.I. and Murata K., *Sol. Energ. Mat. Sol. C.*, 2003; **79**: 459-469. DOI 10.1016/S0927-0248(03)00021-7.
- [5] Hwang S., Moon J., Lee S., Kim D.-H., Lee D., Choi W. and Jeo M., *Electron. Lett.*, 2007; **43**: 1455-1456. DOI 10.1049/el:20072867.
- [6] Lee W.J., Ramasamy E., Lee D.Y. and Song J.S., *ACS Appl. Mater. Inter.*, 2009; **1(6)**: 1145-1149. DOI 10.1021/am800249k.
- [7] Siriroj S., Pimanpang S., Towannang M., Maiaugree W., Phumying S., Jarernboon W., et al., *Appl. Phys. Lett.*, 2012; **100(24)**: 243303. DOI 10.1063/1.4726177.

- [8] Hernadi K., Fonseca A., Nagy J.B., Bernaerts D. and Lucas A.A., *Carbon*, 1996; **34**(10): 1249-1257. DOI 10.1016/0008-6223(96)00074-7.
- [9] Schwertfeger H., Fokin A.A. and Schreiner P.R., *Angew. Chem. Int. Edit.*, 2008; **47**(6): 1022-1036. DOI 10.1002/anie.200701684.
- [10] Yang W.L., Fabbri J.D., Willey T.M., Lee J.R.I., Dahl J.E., Carlson R.M.K., et al., *Science*, 2007; **316**(5830): 1460-1462. DOI 10.1126/science.1141811.
- [11] Roth S., Leuenberger D., Osterwalder J., Dahl J.E., Carlson R.M.K., Tkachenko B.A., et al., *Chem. Phys. Lett.*, 2010; **495**: 102-108. DOI 10.1016/j.cplett.2010.06.063.
- [12] Narasimha K.T., Ge C., Fabbri J.D., Clay W., Tkachenko B.A., Fokin A.A., et al., *Nat. Nanotechnol.*, 2016; **11**: 267-272. DOI 10.1038/nnano.2015.277.
- [13] Jantayod A., Doonyapisut D., Eknapakul T., Smith M.F. and Meevasana W., *Sci. Rep.*, 2020; **10**: 19009. DOI 10.1038/s41598-020-76093-3.
- [14] Sangphet S., Siriroj S., Sriplai N., Doonyapisut D., Thila S., Lowpa S., et al., *Appl. Phys. Lett.*, 2018; **112**(24): 242406. DOI 10.1063/1.5027450.
- [15] Meevasana W., Supruangnet R., Nakajima H., Topon O., Amornkitbamrung V. and Songsiriritthigul P., *Appl. Surf. Sci.*, 2009; **256**(4): 934-936. DOI 10.1016/j.apsusc.2009.05.113.
- [16] Wu J., Lan Z., Lin J., Huang M., Huang Y., Fan L., et al., *Chem. Soc. Rev.*, 2017; **46**: 5975-6023. DOI 10.1039/C6CS00752J.
- [17] Saekow S., Maiakgree W., Jarernboon W., Pimanpang S. and Amornkitbamrung V., *J. Non-Cryst. Solids*, 2012; **358**: 2496-2500. DOI 10.1016/j.jnoncrsol.2012.01.050.
- [18] Pimanpang S., Maiaugree W., Jarernboon W., Maensiri S. and Amornkitbamrung V., *Synthetic Met.*, 2009; **159**(19-20): 1996-2000. DOI 10.1016/j.synthmet.2009.07.008.
- [19] Biao X., Guangyu W., Yong Z., Qi L. and Qingyu X., *Appl. Phys. Lett.*, 2018; **113**: 133901. DOI 10.1063/1.5039590.
- [20] William A., Vallejo L., Cesar A., Quiñones S., Johann A. and Hernandez S., The Chemistry and Physics of Dye-Sensitized Solar Cells, Solar Cells: in Leonid A. K., ed., *Dye-Sensitized Devices*, InTech Europe, Rijeka, Croatia, 2011.
- [21] Mallajosyula A. T., Srivastava N., Iyer S. S. K., and Mazhari B., *Sol. Energ. Mat. Sol. C.*, 2010; **94**: 1319-1323. DOI 10.1016/j.solmat.2008.09.027.
- [22] Muhammad F.F. and Sulaiman K., *Thin Solid Films*, 2011; **519**(15): 5230-5233. DOI 10.1016/j.tsf.2011.01.165.
- [23] Muhammad F.F., Yahya M.Y., Hameed S.S., Aziz F., Sulaiman K., Rasheed M.A., et al., *PLoS One*, 2017; **12**: e0182925. DOI 10.1371/journal.pone.0182925.