SYNTHESIS AND CHARACTERIZATION OF Al_2O_3-SnO_2 COMPOSITE NANOFIBERS BY ELECTROSPINNING FOR DYE-SENSITIZED SOLAR CELLS

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Master of Science

Faculty of Industrial Sciences & Technology

UNIVERSITI MALAYSIA PAHANG

February 2019

ACKNOWLEDGEMENTS

First and foremost, thanks God for His grace and wisdom, leading me up until the completion of this study. Millions thanks to my supervisor, Professor Dr. Jose Rajan, and Associate Professor Dr. Chong Kwok Feng, for their unlimited and undivided support throughout the study. I greatly appreciate their kindness in facilitating my research work financially and for the great motivation as well as encouragement during my low in going through my research work. Their knowledge and expertise in nanostructured material do lots of helps and brought around lots of new insight that inspired me to learn more for knowledge, not only for a degree.

Secondly, my deepest gratitude for Dr Bhupender Pal, my supervisor Post-doctoral. His kindness in guiding me throughout the research work eased the completion of this study. Sharing of his experiences during his post-graduate study helped eliminating most of the mistakes that would had occurred during my research. His ideas on improving my research is an inspiration for me to think more innovatively and use my brain on a higher level. Not to forget my colleague from Nanostructured Renewable Energy Material Laboratory (NREML) for assisting me during my hardship throughout my study.

I am also thankful to the administration of Faculty of Industrial Sciences & Technology (FIST), especially Associate Professor Dr. Mohd Hasbi Ab Rahim, the Dean of faculty. I appreciate the helps poured out by our academic staffs and laboratory staffs in assisting me on chemical and apparatus purchasing, documentation works, as well as the usage of laboratory characterization instruments. Without their helps, it would be much harder for me to focus on my study and might get distracted by other stuff. I would also like to acknowledge the support from my family members, especially my parents. Their motivation had become my main backbone in supporting me, going through the highs and lows throughout my research.

I would like to mention the financial support from the GRS scholarship under Institution of Postgraduate Studies (IPS) and Flagship Leap 3 research grant (RDU172201) of Universiti Malaysia Pahang for financially support my study.

ABSTRAK

Tidak dapat dinafikan bahawa kejuruteraan bahan telah menjurus kepada kepada penumbuhan teknologi dimana kebanyakkan teknologi yang canggih dapat dihasilkan oleh sebab ketersediaan bahan yang berprestasi tinggi. Thesis ini akan menyiasat struktur, sifat optik dengan electrik bahan novel, iaitu komposit nanofiber dihasilkan daripada amorfus Al_2O_3 dan kristal SnO_2, dimana sifat komposit ini akan ditanda dengan *nanofiber* amorfus Al_2O_3, kristal SnO_2, dan Al-*doped* SnO_2. Sebab bahan ini dipilih adalah kerana Al_2O_3 merupakan bahan penebat tapi menawarkan kawasan permukaan spesifik yang tinggi dimana SnO_2 mempunyai kekonduksian yang tinggi tapi kawasan permukaannya dikompromi. Campuran kawasan permukaan spesifik yang tinggi dan kekonduksian yang tinggi akan menghasilkan komposit yang mempunyai impak besar dalam industri nanoeletrik. Sebagai contoh, komposit ini boleh digunakan sebagai anod fotovoltaik DSSCs kerana keupayaannya untuk beroperasi pada keamatan cahaya redup. Enam sampel akan disediakan, iaitu 5, 10, 25, dan 50% Al_2O_3 dalam SnO_2, termasuk juga *nanofiber* Al_2O_3 dan SnO_2, dengan mengunakan teknik elektrospinning. Hasil elektrospinning akan dikalsin 550 ^{o}C dan menghasilkan bahan komposit kristal-amorfus. Sampel yang disediakan akan dikaji dengan Mikroskop Pengimbasan Pelepasan Medan (FESEM), Difraksi X-ray (XRD), Spektroskopi Spektrum X-ray (XPS), Spektrofotometer UV-Vis, Analisis permukaan Brunauer-Emmett-Teller (BET) dan Spektroskopi Impedansi Elektrokimia. Stuktur *nanofiber* dikesah untuk semua sampel. Puncak Al_2O_3 tidak dapat ditemui dalam spektra XRD, menunjukkan Al_2O_3 amorfus sedangkan SnO_2 telah dihablur sepenuhnya. Spektra optik sampel menunjukkan pengurangan dalam pekali penyerapan dan penyebaran mencadangkan nisbah Al_2O_3 yang tinggi dalam SnO_2 tidak sesuai untuk dijadikan anod DSSCs. Pengiraan jurang tenaga menunjukkan jurang tenaga menyempit bila nisbah Al_2O_3 dalam SnO_2 meningkat. Analisis BET menunjukkan peningkatan dalam nisbah Al_2O_3 meluaskan kawasan permukaan, manakala analisis EIS mendedahkan penurunan dalam kekonduksian sampel. Penghasilan DSSCs dengan sampel dikaji bawa keadaan AM 1.5 dimana peningkatan operasi penukaran cahaya sinar dapat diperhatikan dari sampel 5-10% Al_2O_3 dalam SnO_2, dengan kecekapan 2% berbanding dengan SnO_2 (0.5%). Komposit SnO_2/Al_2O_3 menunjukkan kekonduksian yang sama dengan Al_2O_3 tapi menyampaikan operasi fotovoltaik yang bermagnitud tinggi berbanding dengan Al_2O_3, disebabkan oleh kesan lenturan jalur di permukaan *nanofibers* dan kluster, memudahkan aliran elektron. Pengajian ini menyediakan platform untuk mengaji hubungan antara struktur dengan sifat bahan dalam komposit amorfus-kristal.

ABSTRACT

Materials engineering has been an inevitable part of technological advancements; many advanced technologies came in effect because of availability of new and high performing materials. This thesis investigates the structural, optical and electrical properties of a novel material, viz. a composite nanofiber containing amorphous Al_2O_3 and crystalline SnO_2; properties of this composite has been benchmarked with pure nanofibers of amorphous Al_2O_3, crystalline SnO_2, and Al-doped SnO_2. Rationale of selection of these materials is the fact that Al_2O_3 is an insulator but offer high specific surface area whereas SnO_2 is highly conducting but with compromised surface area – combining high specific surface area and high conductivity in one material would have potential impacts in nanoelectronics. For example, such materials are sought as photoanodes in dye-sensitized solar cells (DSSCs), which generated immense attention in clean energy research due to their capability of operating at dim light intensity. Six materials were prepared containing 5, 10, 25, and 50% of Al_2O_3 in SnO_2 in addition to pure Al_2O_3 and SnO_2 nanofibers by electrospinning technique. The as-spun polymeric fibrous cloths were calcined at 550 ^{o}C, which resulted in the crystallite –amorphous composite materials. The prepared samples were studied using Field Emission Scanning Electron Microscope, X-ray Diffraction, X-ray Photoelectron Spectroscopy, UV-Vis Spectrophotometer, Brunauer–Emmett–Teller (BET) surface analysis and Electrochemical Impedance Spectroscopy. Nanofiber structure was confirmed in all the samples. The XRD spectra showed no peak of Al_2O_3, indicating amorphous Al_2O_3 whereas SnO_2 was fully crystallized. The absorption spectroscopy showed decrease in sample's absorption and scattering coefficient indicating that higher ratio of Al_2O_3 in SnO_2 is not suitable for the DSSCs application. Energy gap calculated from the absorption spectroscopy resulted in a narrowed energy gap when more Al_2O_3 was added into SnO_2. The BET analysis showed an increase in sample's surface area with increase in the Al_2O_3 content in SnO_2 and electrochemical impedance spectroscopic analyses showed that the increase in surface area is at the expense of sample's conductivity. The DSSCs were fabricated using the nanofibers developed here and characterized their photovoltaic properties using current – voltage measurements at AM 1.5 conditions; the cells showed improved performance for the 5-10% of Al_2O_3 doped in SnO_2, with efficiency of 2% compared to SnO_2 (~0.5%). Interestingly, the 1:1 SnO_2/Al_2O_3 composite showed a conductivity similar to that of Al_2O_3; however, this composite when used as a photoanode showed orders of magnitude higher photovoltaic properties compared to that fabricated using pure Al_2O_3, due to the band bending effect at the nanofibers and cluster interface, facilitating the flow of electrons. This study opens up new opportunities in studying the structure – property correlations in amorphous – crystalline materials composites.

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LIST OF SYMBOLS

a	Crystal Lattice Parameter
α	Absorption Coefficient
A	Sample's Absorbance
Al^{3+}	Aluminium Ions with +3 Oxidation States
B_P	Peak Broadening
B_I	Peak Broadening Due to Instrumentation Factor
B_{hkl}	Peak Broadening Due to Sample
δ	Light Penetration Depth
d	Crystal Interplanal Distance
ε	Sample's Dielectric Constant
ε	Strain on Material
$e\varphi_b$	Flat-Band Potential
E	Modulus of Elasticity
E_C	Conduction Band Energy Level
E_F	Fermi Energy Level
E_g	Energy Gap
E_U	Urbach Energy
E_V	Valence Band Energy Level
Eff	Efficiency
FF	Fill Factor
h	Plank's Constant
hv	Light Photon Energy
Jsc	Closed-Circuit Current
k	Crystal Constant
k	Extinction Coefficient
K	Boltzmann Constant
λ	Electromagnetic Wavelength
L	Average Crystallite Size
m_e^*	Effective Mass of Electron
m_h^*	Effective Mass of Hole
η	Lattice Strain

n	Refractive Index
n	Type of Electron Transition
n	Electron Concentration
p	Hole Concentration
P	Pressure
R	Sample’s Reflectance
R_S	Sheet Resistance
R_{CT}	Charge Transport Resistance
R_{CR}	Charge Recombination Resistance
σ	Applied Stress
Sn^{4+}	Tin Ions with +4 Oxidation States
$\boldsymbol{\theta}$	XRD Illumination Angle
t	Sample Film’s Thickness
T	Temperature
V	Volume
Voc	Open-Circuit Voltage

LIST OF ABBREVIATIONS

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3ET	Three Electrode Testing
APTES	3-Aminopropyltriethixysilane
AZO	Aluminium-Doped Zinc Oxide
BET	Brunauer-Emmett-Teller Measurement
CB	Conduction Band
CNT	Carbon Nanotube
CPE	Constant Phase Element
DFT	Density Functional Theory
DMF	N,N-dimethylformamide
DSSCs	Dye-Sensitized solar cells
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
FWHM	Full-Width at Half Maximum
FTO	Fluorine Doped Tin Oxide
GCMS	Gas-Chromatography Mass Spectroscopy
GW	Green's Function and Screened Coulomb Interaction
HOMO	Highest Occupied Molecular Orbital
LDPE	Low Density Polyethylene
LPMs	Lubricant Oil-Containing PUF Microcapsules
LSV	Linear Sweep Voltammetry
LUMO	Lowest Unoccupied Molecular Orbital
N3-dye	Cis-Bis(isothiocynato) bis(2,2'-bipyridyl-4,4'-dicarboxylato Ru(III)
NASA	National Aeronautics and Space Administration
PCE	Photo-electric Conversion Efficiency
P-123	Poly(ethylene glycol)-block-poly(propylene glycol)-polymer
PV	Photovoltaic
PVP	Polyvinylpyrrolidone

rGO	Reduced Graphene Oxide
SAN	Styrene Acrylonitrile
UN	United Nation
US	United States
UV-Vis	Ultra-violet Visible Light Spectroscopy
VB	Valence Band
WWII	World War II
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction Spectroscopy

REFERENCES

Afkham, Y., Khosroshahi, R.A., Rahimpour, S., Aavani, C., Brabazon, D. & Mousavian, R.T. (2018). Enhanced mechanical properties of in situ aluminium matrix composites reinforced by alumina nanoparticles. *Archives of Civil and Mechanical Engineering.* 18(1), 215-226. DOI: 10.1016/j.acme.2017.06.011.

Ahmed, Sk.F., Khan, S., Ghosh, P.K., Mitra, M.K. & Chattopadhyay, K.K. (2006). Effect of Al-doping on the conductivity type inversion and electro-optical properties of SnO_2 thin films synthesized by sol-gel technique. *Journal of Sol-Gel Science and Technology*. 39(3), 241-247. DOI: 10.1007/s10971-7808-x.

Ahn, H.-J., Choi, H.-C., Park, K.-W., Kim, S.-B. & Sung, Y.-E. (2004). Investigation of the structural and electrochemical properties of size-controlled SnO_2 nanoparticles. *Journal of Physical Chemistry B.* 108(28), 9815-9820. DOI: 10.1021/jp035769n.

Amit. Y., Li, Y., Frenkel, Al. & Banin, U. (2015). From impurity doping to metallic growth in diffusion doping: properties and structure of silver-doped InAs nanocrystals. *ACS Nano*. 9(11), 10790-800. DOI: 10.1021/acsnano.5b03044.

Anonymous. (2017). World Population Prospects: The 2017 Revision. *United Nations Population Division. 1*.

Anuchai,S., Phanichphant, S., Tantraviwat, D., Pluengphon, P., Bovornratanaraks, T. & Inceesungvorn, B. (2018). Low temperature preparation of oxygen-deficient tin dioxide nanocrystals and a role of oxygen vacancy in photocatalytic activity improvement. *Journal of Colloid and Interface Science.* 512, 105-114. DOI: 10.1016/j.jcis.2017.10.047.

Aragon, F.H., Coaquira, J.A.H., Villegas-Lelovsky, L., da Silva, S.W., Cesar, D.F., Nagamine, L.C.C.M., Cohen, R., Menendez-Proupin, E. & Morais, P.C. (2015). Evolution of the doping regimes in the Al-doped SnO_2 nanoparticles prepared by a polymer precursor method. *Journal of Physics: Condensed Matter*. 27(9), 095301.

Bakhshayesh, A.M., Mohammadi, M.R., Dadar, H. & Fray, D.J. (2013). Improved efficiency of dye-sensitized solar cells aided by corn-like TiO2 nanowires as the light scattering layer. *Electrochimica Acta.* 90, 302-308. DOI: 10.1016/j.electacta.2012.12.065.

Benouis, C.E., Benhaliliba, M., Mouffak, Z., Avila-Garcia, A., Tiburcio-Silver, A., Ortega Lopez, M., Romano Trujillo, R. & Ocak, Y.S. (2014). The low resistive and transparent Al-doped SnO_2 films: p-type conductivity, nanostructures and photoluminescence. *Journal of Alloys and Compounds.* 603, 213-223. DOI: 10.1016/j.jallcom.2014.03.046.

Besson, J.M., Itie, J.P., Polian, A., Weill, G., Mansot, J.L. & Gonzalez, J. (1991). High-pressure phase transition and phase diagram of gallium arsenide. *Physical Review B.* 44, 4214. DOI: 10.1103/PhysRevB.44.4214.

Beura, R., Pachaiappan, R. & Thangadurai, P. (2018). A detailed study on Sn4+ doped ZnO for enhanced photocatalytic degradation. *Applied Surface Science.* 433, 887-898. DOI: 10.1016/j.apsusc.2017.10.127.

Bhosale, N.Y., Mali, S.S., Hong, C.K. & Kadam, A.V. (2017). Hydrothermal synthesis of WO3 nanoflowers on etched ITO and their electrochromic properties. *Electrochimica Acta*. 246, 1112-1120. DOI: 10.1016/j.electacta.2017.06.142.

Biasi, R.S., Melo, G.B.M., Silva Figueiredo, A.B-H., Camarena, M.A. & Campos, J.B. (2018). Properties of manganese ferrite-paraffin composites. *Journal of Materials Research and Technology*. DOI: 10.1016/j.mrt.2017.09.010.

Caglar, Y., Gorgun, K. & Aksoy, S. (2015). Effect of deposition parameters on the structural properties of ZnO nanopowders prepared by microwave-assisted hydrothermal synthesis. 138, 617-622. DOI: 10.1016/j.saa.2014.12.008.

Cesar, M.G.M.M., Silveira, C.C., Paolinelli, S.C. & Cicale, S. (2018). Effect of Sn on the oxide subscale structure formed on a 3% Si steel. *Americal Institute of Physics Advances.* 8(4), 047610. DOI: 10.1063/1.4994051.

Demes, T., Ternon, C., Morisot, F., Riassetto, D., Legallais, M., Roussel, H. & Langlet, M. (2017). Mechanisms involved in the hydrothermal growth of ultra-thin and high aspect ratio ZnO nanowires. *Applied Surface Science*. 410, 423-431. DOI: 10.1016/j.apsusc.2017.03.086.

Dimroth, F. (2014). New world record for solar cells efficiency at 46% French-German cooperation confirms competitive advantage of European photovoltaic industry. *Fraunhofer ISE.* Retrieved from https://www.ise.fraunhofer.de/en/press-media/press-releases/2014/new-world-record-for-solar-cell-efficiency-at-46-percent.html.

Dubrovinskaia, N.A., Dubrovinsky, L.S., Ahuja, R., Prokopenko, V.B., Dmitriev, V., Weber, H.P., Osorio-Guillen, J.M. & Johansson, B. (2001). Experimental and theoretical identification of a new high-pressure TiO2 polymorph. *Physical Review Letters.* 87, 275501. DOI: 10.1103/PhysRevLett.87.275501.

Dudley, B. (2017). *BP Statistical Review of World Energy 2017*. Retrieved from https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html.

Fakharuddin, A., Ahmed, I., Khalidin, Z., Yusoff, M.M. & Jose, R. (2014). Channeling of electron transport to improve collection efficiency in mesoporous titanium dioxide dye sensitized solar cell stacks. *Applied Physics Letters.* 104(5), 053905. DOI: 10.1063/1.4864316.

Fang, H., Bai, S. & Wong, C.P. (2018). Microstructure engineering of graphene towards highly thermal conductive composites. *Composite Part A: Applied Science and Manufacturing.* 112, 216-238. DOI: 10.1016/j.compositesa.2018.06.010.

Ghafari, E., Feng, Y., Liu, Y., Ferguson, I. & Liu, N. (2017). Investigating process-structure relations of ZnO nanofiber via electrospinning method. *Composite Part B: Engineering.* 116, 40-45. DOI: 10.1016/j.compositesb.2017.02.026.

Graetzel, M. (1981). Artificial photosynthesis: water cleavage into hydrogen and oxygen by visible light. *Accounts of Chemical Research.* 14(12), 376-384. DOI: 10.1021/ar00072a003.

Haines, J., Leger, J.M. & Schulte, O. (1996). The high-pressure phase transition sequence from the rutile-type through to the cotunnite-type structure in PbO2. *Journal of Physics: Condensed Matter.* 8(11), 1631. DOI: 10.1088/0953-8984/8/11/009.

Hassan, M.S., Amna, T., Al-Deyab, S.S., Kim, H.C. & Khil, M.S. (2015). Monodispersed 3D MnWO4-TiO2 composite nanoflowers photocatalysts for environmental remediation. *Current Applied Physics.* 15(6), 753-758. DOI: 10.1016/j.cap.2015.03.022.

Hijazi, M., Rieu, M., Stambouli, V., Tournier, G., Viricelle, J.P. & Pijolat, C. (2018). Ambient temperature selective ammonia gas sensor based on SnO2-APTES modifications. *Sensors and Actuators B: Chemical.* 256, 440-447. DOI: 10,1016/j.snb.2017.10.036.

Hu, X., Sun, Z., Zhang, C., Wang, X. & Wu, K. (2018). Microstructure and mechanical properties of bio-inspired Cf/Ti/Mg laminated composites. *Journal of Magnesium and Alloys.* 6(2), 164-170. DOI: 10.1016/j.jma.2018.04.005.

Ito, S., Murakami, T.N., Comte, P., Liska, P., Gratzel, C., Nazeeruddin, M.K. & Gratzel, M. (2008). Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. *Thin Solid Films*. 516(14), 4613-4619. DOI: 10.1016/j.tsf.2007.05.090.

Jang, K.S. (2018). Mechanics and rheology of basalt fiber-reinforced polycarbonate composites. *Polymer*. 147, 133-141. DOI: 10.1016/j.polymer.2018.06.004.

Jayalakshmi, M., Venugopal, N., Phani Raja, K. & Mohan Rao, M. (2005). Nano SnO_2-Al_2O_3 mixed oxide and SnO_2-Al_2O_3-carbon composite oxides as new and novel electrodes for supercapacitor applications. *Journal of Power Sources*. 158, 1538-1543. DOI: 10.1016/j.powsour.2005.10.091.

Jin, H., Xu, Y., Pang, G., Dong, W., Wan, Q., Sun, Y. & Feng, S. (2003). Al-doped SnO_2 nanocrystals from hydrothermal systems. *Materials Chemistry and Physics.* 84, 58-62. DOI: 10.1016/j.matchemphys.2003.12.006.

Jo, C.H., Jo, J.H. & Myung, S.T. (2018). Confinement of nanosized tin(IV) oxide particles on rGO sheets and its application to sodium-ion full cells as a high capacity anode material. *Journal of Alloys and Compounds.* 731, 339-346. DOI: 10.1016/j.jallcom.2017.10.048.

Karabay, S., Erturk, A.T., Zeren, M., Yamanoglu, R. & Karakulak, E. (2018). Failure analysis of wire-breaks in aluminium conductor production and investigation of early failure reasons for transmission lines. *Engineering Failure Analysis.* 83, 47-56. DOI: 10.1016/j.engfailanal.2017.09.007.

Kawakita, J. (2010). Trends of research and development of dye-sensitized solar cells. *Science and Technology Trends Quaterly Review*. 35, 70-82. Available from: http://hdl.handle.net/11035/2834.

Keisuke, N., Takaya, K. & Yoshinori, N. (2008). Electrophoretically deposited TiO_2 nanotube light-scattering layers of dye-sensitized solar cells. *Japanese Journal of Applied Physics.* 47(8R), 6610. DOI: 10.1143/JJAP.47.6610.

Khaled, U., Alzahrani, S. & Khan, Y. (2016). Dielectric properties improvement of LDPE based on nano fillers. *2016 IEEE International Conference on High Voltage Engineering and Application (ICHVE)*. DOI: 10.1109/ICHVE.2016.7800822.

Kim, J.H., Kim, J.M., Jerng, D.W., Kim, E.Y. & Ahn, H.S. (2018). Effect of aluminium oxide and reduced graphene oxide mixtures on critical heat flux enhancement. *International Journal of Heat and Mass Transfer.* 116, 858-870. DOI: 10.1016/j.ijheatmasstransfer.2017.09.063.

Kowano, H., Morii, K. & Nakayama, Y. (1998). Effects of crystallization on structural and dielectric properties of thin amorphous films of (1-x)$BaTiO_3$-x$SrTiO_3$ (x=0-0.5,1.0). *Journal of Applied Physics*. 73, 5141. DOI: 10.1063/1.353788.

Kumar, P.N., Mary, J.S.S., Chandrakala, V., Jeyarani, W.J. & Shyla, J.M. (2017). Investigation of superior electro optical properties of SnO2/SiO2 nanocomposite over its individual counterpart SnO2 nanoparcticles. *Materials and Solar Cells.* 193, 234-243. DOI: 10.1016/j.matchemphys.2017.02.039.

Lee, J.H., Ahn, K., Kim, S.H., Kim, J.M., Jeong, S.Y., Jin, J.S., Jeong, E.D. & Cho, C.R. (2014). Thickness effect of the TiO2 nanofiber scattering layer on the performance of the TiO2 nanoparticle/TiO2 nanofiber-structured dye-sensitized solar cells. *Current Applied Physics.* 14(6), 856-861. DOI: 10.1016/j.cap.2014.04.001.

Li, H., Cheng, L., Sun, X., Li, Y., Li, B., Liang, C., Wang, H. & Fan, J. (2018). Fabrication and properties of magnesium matrix composite reinforced by urchin-like carbon nanotube-alumina in situ composite structure. *Journal of Alloys and Compounds.* 746, 320-327. DOI: 10.1016/j.jallcom.2018.02.273.

Li, H., Ma, Y., Li, Z., Cui, Y. & Wang, H. (2018). Synthesis of novel multilayer composite microcapsules and their application in self-lubricating polymer composites. *Composite Science and Technology*. 164, 120-128. DOI: 10.1016/j.compscitech.2018.05.042.

Li, X., Sun, X., Gao, Z., Hu, X., Guo, J., Cai, S., Guo, R., Ji, H., Zheng, C. & Hu, W. (2018). Fabrication of porous carbon sphere@SnO2@carbon layer coating composite as high performance anode for sodium-ion batteries. *Applied Surface Science.* 433, 713-722. DOI: 10.1016/j.apsusc.2017.10.107.

Li, Y. (2018). A novel snowflake-like SnO2 hierarchical architecture with superior gas sensing properties. *Physica E: Low-Dimensional Systems and Nanostructures.* 96.54-56. DOI: 10.1016/j.physe.2017.10.009.

Li, Z., Qin, X., Zhu, Z., Fu, H., Wang, A., Li, H., Zhang, H., Li, Y. & Zhang, H. (2018). Laminar TiZr-based bulk metallic glass composites with improved mechanical properties. *Materials Science and Engineering: A.* 726, 231-239. DOI: 10.1016/j.msea.2018.04.089.

Liu, R., Tan, M., Zhang, X., Xu, L., Chen, J., Chen, Y., Tang, X. & Wan, L. (2018). Solution-processed composite electrodes composed of silver nanowires and aluminium-doped zinc oxide nanoparticles for thin-film solar cells applications. *Solar Energy Materials and Solar Cells.* 174, 584-592. DOI: 10.1016/j.solmat.2017.09.042.

Liu, X., Fang, J., Liu, Y. & Lin T. (2016). Progress in nanostructured photoanodes for dye-sensitized solar cells. *Frontiers of Materials Science*. 10(3), 225-237. DOI: 10.1007/s11706-016-0341-0

Mattesini, M., Almeida, J.S., Dubrovinsky, L., Dubrovinskaia, N., Johansson, B. & Ahuja, R. (2004). High pressure and high-temperature synthesis of the cubic TiO2 polymorph. *Physical Review B*. 70, 212101. DOI: 10.1103/PhysRevB.70.212101.

Miao, R., Zeng, W. & Gao, Q. (2017). Hydrothermal synthesis of novel NiO nanoflowers assisted with CTAB and SDS respectively and their gas-sensing properties. *Materials Letters.* 186, 175-177. DOI: 10.1016/j.matlet.2016.09.127.

Mohamad, M., Haq, B.U., Ahmed, R., Shaari, A., Ali, N. & Hussain, R. (2015). A density functional study of structural, electronic and optical properties of titanium dioxide: Characterization of rutile, anatase and brookite polymorphs. *Materials Science in Semiconductor Processing.* 31, 405-414. DOI: 10.1016/j.mssp.2014.12.027.

Mahmoud, S.A. & Fouad, O.A. (2015). Synthesis and application of zinc/tin oxide nanostructures in photocatalysis and dye sensitized solar cells. *Solar Energy Materials and Solar Cells.* 136, 38-43. DOI: 10.1016/j.solmat.2014.12.035.

Miyauchi, M., Nakajima, A., Watanabe, T. & Hashimoto, K. (2002). Photocatalysis and photoinduced hydrophilicity of various metal oxide thin films. *Chemistry of Materials.* 14(6), 2812-2816. DOI: 10.1021/cm020076p.

Moharrami, F., Bagheri-Mohagheghi, M-M., Azimi-Juybari, H. & Shokooh-Saremi, M. (2012). Structural, electrical, optical, thermoelectrical and photoconductivity properties of the SnO_2-Al_2O_3 binary transparent conducting films deposited by the spray pyrolysis method. *Physica Scripta*. 85(1), 015703.

Muchuweni, E., Sathiaraj, T.S. & Nyakotyo, H. (2017). Hydrothermal synthesis of ZnO nanowires on rf sputtered Ga and Al co-doped ZnO thin films for solar cell application. *Journal of Alloys and Compounds*. 721, 45-54. DOI: 10.1016/j.jallcom.2017.05.317.

Neisiany, R.E., Khorasani, S.N., Lee, J.K.Y., Naeimirad, M. & Ramakrishna, S. (2018). Interfacial toughening of carbon/epoxy composite by incorporating styrene acrylonitrile nanofibers. *Theoretical and Applied Fracture Mechanics.* 95, 242-247. DOI: 10.1016/j.tafmec.2018.03.006.

Nozawa, T. (2013). EPFL develops dye-sensitized solar cell with 15% conversion efficiency. *Solar Power Plant Business*. Retreived from https://tech.nikkeibp.co.jp/dm/english/NEWS_EN/20130716/292380/

Nozik, A.J. (2002). Quantum dot solar cells. *Physica E: Low-dimensional Systems and Nanostructures.* 14(1-2), 115-120. DOI: 10.1016/S1386-9477(02)00374-0.

Nozik, A.J., Beard, M.C., Luther, J.M., Law, M., Ellingson, R.J. & Johnson, J.C. (2010). Semiconductor quanum dots and quantum dot arrays and application of multiple exciton generation to third-generation photovoltaic solar cells. *Chemical Reviews.* 110(11), 6873-6890. DOI: 10.1021/cr900289f.

Perween, S. & Ranjan. A. (2017). Improved visible-light photocatalytic activity in ZnTiO3 nanopowder prepared by sol-electrospinning. *Solar Energy Materials and Solar Cells.* 163, 148-156. DOI: 10.1016/j.solmat.2017.01.020.

Phuruangrat, A., Thongtem, S. & Thongtem, T. (2017). Microwave-assisted hydrothermal synthesis and characterization of CeO2 nanowires for using as a photocatalytic material. *Materials Letters.* 196, 61-63. DOI: 10.1016/j.matlet.2017.03.013.

Poudel, P. & Qiao, Q. (2012). One dimensional nanostructure/nanoparticle composites as photoanodes for dye-sensitized solar cells. *Nanoscale*. 4(9), 2826-2838. DOI: 10.1039/C2NR30347G.

Prasittichai, C. & Hupp, J.T. (2010). Surface modification of SnO_2 photoelectrodes in dye-sensitized solar cells: Significant improvements in photovoltage via Al_2O_3 atomic layer deposition. *The Journal of Physical Chemistry Letters.* 1(10), 1611-1615. DOI: 10.1021/jz100361f.

Qurashi, A., Zhang, Z., Asif, M. & Yamazaki, T. (2015). Template-less surfactant-free hydrothermal synthesis NiO nanoflowers and their photoelectrochemical hydrogen production. *International Journal of Hydrogen Energy.* 40(45), 15801-15805. DOI: 10.1016/j.ijhydene.2015.07.114.

Rana, M.M., Lee, C.K., Al-Deen, S. & Zhang, Y.S. (2018). Flexural behaviour of steel composite beams encased by engineered cementitious composites. *Journal of Constructional Steel Research.* 143, 279-290. DOI: 10.1016/j.jcsr.2018.01.004.

Raga, S.R., Barea, E.M. & Fabregat-Santiago, F. (2012). Analysis of the origin of open circuit voltage in dye solar cells. *The Journal of Physical Chemistry Letters.* 2(12), 1629-1634. DOI: 10.1021/jz3005464.

Ryu, J.H., Kongsy, P., Lim, D.Y., Cho, S.B. & Song, J.H. (2016). Facile glycothermal synthesis of ZnO nanopowder at low temperature. *Ceramic International.* 42(15), 17565-17570. DOI: 10.1016/j.ceramint.2016.08.070.

Saravanan, P., Gnanawelbabu, A. & Pandiaraj, P. (2018). Effect of pre-annealing on thermal and optical properties of ZnO and Al-ZnO thin films. *International Journal of Nanoscience.* 17(1-2), 1760017. DOI: 10.1142/S0219581X17600171.

Sengupta, D., Das, P., Kasinadhuni, U., Mondal, B. & Mukherjee, K. (2014). Morphology induced light scattering by zinc oxide polydisperse particles: Promising for dye sensitized solar cell application. *Journal of Renewable and Sustainable Energy*. 6, 063114. DOI: 10.1063/1.4904435.

Shakeel Ahmad, M., Pandey, A.K. & Abd Rahim, N. (2017). Advancements in the development of TiO_2 photoanodes and its fabrication methods for dye sensitized solar cells (DSSC) applications. A review. *Renewable and Sustainable Energy Reviews.* 77, 89-108. DOI: 10.1016/j.rser.2017.03.129.

Sharma, S., Siwach, B., Ghoshal, S.K. & Mohan, D. (2017). Dye sensitized solar cells: From genesis to recent drifts. *Renewable and Sustainable Energy Reviews.* 70, 529-537. DOI: 10.1016/j.rser.2016.11.136.

Shi, L. & Lin, H. Facile fabrication and optical property of hollow SnO_2 spheres and their application in water treatment. *ACS Langmuir*. 26(24), 18718-18722. DOI: 10.1021/la103769d.

Sivakumar, M., Sundaram, N.S., Kumar, R.R. & Thasthagir, M.H.S. (2018). Effect of aluminium oxide nanoparticles blended pongamia methyl ester on performance, combustion and emission characteristics of diesel engine. *Renewable Energy*. 116(A), 518-526. DOI: 10.1016/j.renene.2017.10.002.

Soltan, W.B., Ammar, S., Olivier, C. & Toupance, T. (2017). Influence of zinc doping on the photocatalytic activity of nanocrystaline SnO2 particles synthesized by the polyol method for enhanced degradation of organic dyes. *Journal of Alloys and Compounds.* 729, 638-647. DOI: 10.1016/jallcom.2017.09.155.

Tavakoli, A.H., Maram, P.S., Widgeon, S.J., Rufner, J., van Benthem, Klaus, Ushakov, S., Sen, S. & Navrotsky, A. (2013). Amorphous alumina nanoparticles: Structure, surface energy, and thermodynamic phase stability. *The Journal of Physical Chemistry C.* 117(33), 17123-17130. DOI: 10.1021/j.p405820g.

Tiwana, P., Docampo, P., Johnston, M.B., Snaith, H.J. & Herz, L.M. (2011). Electron mobility and injection dynamics in mesoporous ZnO, SnO2, and TiO2 films used in dye-sensitized solar cells. *American Chemical Society Nano.* 5(6), 5158-5166. DOI: 10.1021/nn201243y.

Wali, Q., Fakharuddin, A., Yasin, A., Rahim, M.H., Ismail, J. & Jose, R. (2015). One pot synthesis of multi-functional tin oxide nanostructures for high efficiency dye-sensitized solar cells. *Journal of Alloys and Compounds.* 646, 32-39. DOI: 10.1016/j.jallcom.2015.05.120.

Wang, G., Zhu, X. & Yu, J. (2015). Bilayer hollow/spindle-like anatase TiO2 photoanode for high efficiency dye-sensitized solar cells. *Journal of Power Sources.* 278, 344-351. DOI: 10.1016/j.jpowsour.2014.12.091.

Wang, Y., Sun, J., Fan, X.Y. & Yu, X. (2011). A CTAB-assisted hydrothermal and solvothermal synthesis of ZnO nanopowders. *Ceramics International.* 37(8), 3431-3436. DOI: 10.1016/j.ceramint.2011.04.134.

Xiao, J., Tao, R., Costa, B.F.O. & Paixao, J.A. (2015). Nanostructured Titania Photoanodes for Dye Solar Cells. *Materialstoday: Proceedings*. 2(1), 141-146. DOI: 10.1016/j.matpr.2015.04.041.

Yalcinkaya, F. (2016). Preparation of various nanofiber layers using wire electrospinning system. *Arabian Journal of Chemistry.* DOI: 10.1016'j.arabjc.2016.12.012.

Yin, X.T. & Tao, L. (2017). Fabrication and gas sensing properties of Au-loaded SnO2 composite nanoparticles for low concentration hydrogen. *Journal of Alloys and Compounds.* 727, 254-259. DOI: 10-1016/j.allcom.2017.08.122.

Zhang, X., Zhang, P., Wang, L., Gao, H., Zhao, J., Liang, C., Hu, J. & Shao, G. (2016). Template-oriented synthesis of monodispersed SnS2@SnO2 heterp-nanoflowers for Cr(VI) photoreduction. *Applied Catalysis B: Environmental.* 192, 17-25. DOI: 10.1016/j.apcatb.2016.03.035.

Zhao, F., Lu, Q., Liu, S., Zhu, C. & Sun, H. (2015). Fabrication and characterization of the enhanced photocatalytic CuO/In2O3 heterpstructured nanobelts by electrospinning process. *Materials Letters*. 139, 19-21. DOI: 10.1016/j.matlet.2014.10.028.

Zhao, J., Yang, Y., Cui, C., Hu, H., Zhang, Y., Xu, J., Lu, B., Xu, L., Pan, J. & Tang, W. (2016). TiO2 hollow spheres as light scattering centers in TiO2 photoanodes for dye-sensitized solar cells: the effect of sphere diameter. *Journal of Alloys and Compounds.* 663, 211-216. DOI: 10.1016/j.jallcom.2015.12.118.

Zhou, Y., Xia, C., Hu, X., Huang, W., Aref, A.A., Wang, B., Liu, Z., Sun, Y., Zhou, W. & Tang, Y. (2014). Dye-sensitized solar cells based on nanoparticle-decorated ZnO/SnO2 core/shell nanoneedle arrays. *Applied Surface Science.* 292, 111-116. DOI: 10.1016/j.apsusc.2013.11.095.

Zhu, T. & Gao, S.-P. (2014). The Stability, Electronic Structure, and Optical Property of TiO_2 Polymorphs. *Journal of Physical Chemistry C*. 118(21), 11385-11396. DOI: 10.1021/jp412462m.