

**VERTICALLY ALIGNED HIERARCHICAL
NANO-ARCHITECTURES FOR HIGHLY
EFFICIENT AND STABLE SOLUTION
PROCESSABLE SOLAR CELLS**

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DOCTOR OF PHILOSOPHY

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IRFAN AHMED

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for the award of the degree of
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For those who urge to know and explore the nature for the benefit of humanity.

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LIST OF SYMBOLS

C	Speed Light In Vacuum
cm	Centimetre
C_{μ}	Chemical Capacitance
D	Lattice Spacing
E_g	Band Gap
F	Frequency
H	Plank's Constant
I_{max}	Maximum Current
K	Kilo
L Or D	Photoelectrode Thickness
L_n	Diffusion Length
ms	Millisecond
mV	Millivolt
P_{max}	Maximum Power
P_{th}	Theoretical Power
R_{CT}	Recombination Resistance
R_s	Series Resistance
R_{SH}	Shunt Resistance
R_T	Charge Transport Resistance
V_{max}	Maximum Voltage
W	Watt
A	Absorption
T_d	Electron Transit Time
T_n	Electron Lifetime

ϵ	Molar Extinction Coefficient
η	Photoconversion Efficiency
η_{Cc}	Electron Collection Efficiency
η_{Inj}	Electron Injection Efficiency
λ	Wavelength
μ	Micrometer
μ_e	Electron Mobility

LIST OF ABBREVIATIONS

1D	One Dimensional
AM	Air Mass
APCE	Absorbed Photon to Current Efficiency
CB	Conduction Band
CE	Counter Electrode
DSCs	Dye-Sensitized Solar Cells
EIS	Electrochemical Impedance Spectroscopy
EQE	External Quantum Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FTO	Fluorine Doped Tin Oxide
FWHM	Full Width at Half Maxima
HOMO	Homo Highest Occupied Molecular Orbitals
IPCE	Incident Photon to Current Efficiency
I-V	Current-Voltage
J _{sc}	Short Circuit Current Density
LHE	Light Harvesting Efficiency
LUMO	Lowest Unoccupied Molecular Orbitals
MOS	Metal Oxide Semi-Conductor
NHE	Normal Hydrogen Electrode
NPs	Nanoparticles
NRNP	Nanorod nanoparticle
NRs	Nanorods
NRTLNP _s	Nanorod thin layer nanoparticles

NSCs	Nanostructures Solar Cells
NTs	Nanotubes
NWs	Nanowires
OCVD	Open Circuit Voltage Decay
PSCs	Perovskite Solar Cells
PV	Photovoltaic
SAED	Selection Area Electron Diffraction
TEM	Transmission Electron Microscopy
TNRs	TiO ₂ Nanorods
UV-VIS-NIR	Ultraviolet Visible near Infrared
VB	Valence Band
V _{oc}	Open Circuit Voltage
WE	Working Electrode
XRD	X-Ray Diffraction

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ABSTRACT

Intense research in the field of nanostructured solar cells (NSCs) brought them to a level of delivering photoconversion efficiency (PCE) $\sim 14.3\%$ and 20.2% (η) for dye sensitized solar cells (DSCs) and perovskite solar cells (PSCs), respectively. The state-of-the-art DSCs and PSCs typically employ a thin film of mesoporous TiO_2 nanoparticles (NPs) as an electron transport layer (ETL) due to its high specific surface area ($\sim 150 \text{ m}^2/\text{g}$). Despite the high efficiency achieved in both devices using TiO_2 NPs, there have been significant concerns regarding their inferior electronic mobility ($1 \times 10^{-7} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) that results in the loss of photogenerated electrons via recombination, inferior light harvesting properties and instability when exposed to UV-light. For a successful practical deployment of NSCs it is therefore crucial to overcome these intrinsic limitations by introducing suitable alternative morphologies. Towards this end, a vertically aligned TiO_2 nanorod provides two orders of magnitude higher electron mobility than their NPs analogues and therefore often demonstrates efficient charge collection in NSCs. However, due to their lower surface area, the performance of DSC and PSCs using pristine TiO_2 NRs has been far lower than NPs based analogues, $\sim 3\%$ and $\sim 9.4\%$, respectively. This thesis describe synthesis of vertically aligned TiO_2 NRs via a hydrothermal process on conducting glass substrates (FTO) and their usefulness as an ETL in DSCs and PSCs and also in perovskite solar modules (PSMs). The pristine TiO_2 NRs based DSCs resulted in PCE ($\sim 1.37\%$) which is far lower than the best performing DSCs due to the lower surface area. To overcome the low performance, layered NR architectures were introduced that employ TiO_2 NPs multi-layers over interface engineered NRs, resulting in a remarkable PCE ($\sim 11.2\%$) in the best performing device. The photovoltaic (PV) parameters of the layered NR DSC, i.e., short circuit density ($J_{sc} \sim 21.2 \text{ mA cm}^{-2}$), open circuit voltage ($V_{oc} \sim 764 \text{ mV}$) were far higher than a NP reference DSCs, i.e., 11.42 mA cm^{-2} , 720 mV and PCE $\sim 5.1\%$. The observed high PCE in layered photoanodes is due to their two times higher dye loading, improved light scattering and high surface area than the pristine analogues. The NRs were further investigated as a photoanode in PSCs resulting in PCE $\sim 6.4\%$ in pristine form, where a low PCE is attributed to poor surface roughness of the NRs that result in a weaker interaction with perovskite crystals. A post-treatment of TiO_2 NRs is carried out which doubled the PV performance of PSCs resulting in PCE as high as $\sim 12.2\%$, primarily due to efficient charge separation at ETL/Perovskite interface. In addition, the NRs based PSCs also showed durable PV performance compared to NPs counterparts when tested for a shelf-life of 60 days. Perovskite solar module (PSM, best and av. PCE 10.5% and 8.1%), which employs TiO_2 NRs as electron transport layer, that showed an increase in performance ($\sim 5\%$) even after shelf life investigation for 2500 h. Investigation shows that the active layer of perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) shows superior phase stability when incorporated in devices with TiO_2 NRs scaffold as compared their NPs counterpart. The results of this research provide directions to not only achieve high efficiency in NSCs but also, more importantly, to attain long term stability in these devices eventually paving ways for their commercial deployment.

ABSTRAK

Penyelidikan yang intensif di dalam bidang sel suria-berstruktur nano (NSC) telah menghasilkan kecekapan penukaran-foto (PCE) pada kadar ~14.3% dan 20.2% (η) untuk sel suria peka pewarna (DSCs) dan sel suria berdasarkan perovskite (PSCs). Pencapaian tersebut diperolehi dengan menggunakan filem nipis nanopartikal (NPs) TiO_2 berliang-meso sebagai lapisan pengangkutan elektron (ETL) berikutan luas permukaannya yang tinggi (~150 m^2/g). Walaubagaimanapun, disebalik rekod PCE yang tinggi di dalam peranti berdasarkan TiO_2 NPs, sifat mobiliti elektronik TiO_2 yang rendah ($1 \times 10^{-7} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) telah menyebabkan kehilangan elektron-teruja cahaya disebabkan penggabungan dengan lohong, kebolehan penuaan cahaya yang rendah dan ketidak-stabilan apabila terdedah kepada cahaya ultra-lembayung. Untuk menghasilkan peranti NSC berkecekapan yang lebih tinggi, had intrinsik ini perlu diatasi dengan menggunakan morfologi TiO_2 yang baru dan berlainan dengan morfologi sedia ada. Nanorod (NR) TiO_2 menegak-sejajar mampu memberikan dua kali ganda mobiliti elektron berbanding TiO_2 berliang-meso dan menunjukkan pengumpulan cas yang cekap di dalam NSC. Walaubagaimanapun, disebabkan luas permukaan NR yang rendah, PCE bagi peranti berdasarkan NR adalah lebih rendah (~3%) berbanding peranti berdasarkan NP (~9.4%). Tesis ini menerangkan sintesis nanorod TiO_2 menegak-sejajar di atas permukaan substrat gelas terkonduksi (FTO) menggunakan proses hidrotermal, dan kegunaannya sebagai ETL di dalam peranti DSC, PSC dan modul suria perovskite (PSM). Kecekapan (PCE) untuk DSC berdasarkan NR yang dihasilkan menggunakan proses hidrotermal adalah jauh lebih rendah (~1.37%) berbanding PCE peranti DSC yang tertinggi disebabkan keluasan permukaan yang rendah. Untuk mengatasi masalah ini, morfologi NR-berlapis telah digunakan; lapisan-lapisan NP telah ditindihkan di atas permukaan NR menghasilkan PCE ~11.2%. Parameter fotovoltaik (PV) bagi peranti DSC berdasarkan NR-berlapis iaitu ketumpatan arus litar-pintas ($J_{sc} \sim 21.2 \text{ mA cm}^{-2}$) dan voltan litar terbuka ($V_{oc} \sim 764 \text{ mV}$) adalah lebih tinggi berbanding DSC berdasarkan NP ($J_{sc} 11.42 \text{ mA cm}^{-2}$, $V_{oc} 720 \text{ mV}$ dan PCE ~5.1%). Nilai PCE yang tinggi bagi peranti DSC berdasarkan NR-berlapis ini adalah disebabkan peningkatan jumlah pewarna yang terjerap sebanyak dua kali ganda, penyerakan cahaya yang baik dan keluasan permukaan tinggi. Nanorod yang dihasilkan telah dikaji dengan lanjut sebagai foto-anod di dalam PSC, dan hanya menghasilkan PCE ~6.4% disebabkan kekasaran permukaan NR yang kurang baik lalu menghasilkan interaksi lemah antara kristal perovskite. Rawatan ke atas NR telah dijalankan, dan menghasilkan peranti PSC yang mencapai prestasi PV dua kali ganda berbanding yang asal (tanpa rawatan), PCE ~12.2%; disebabkan oleh pemisahan cas yang cekap di permukaan ETL/perovskite. Sebagai tambahan, PSC berdasarkan NR juga menunjukkan prestasi PV yang lebih tahan lama berbanding PSC berdasarkan NP, setelah diuji-simpan selama 60 hari. Modul suria perovskite berdasarkan NR sebagai ETL yang mempunyai PCE tertinggi (10.5%) dan purata (8.1%) telah menunjukkan peningkatan prestasi ~5% setelah diuji-simpan selama 2500 jam. Hasil siasatan menunjukkan lapisan aktif perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$) adalah sangat stabil apabila berada di dalam peranti yang diasaskan oleh NR sebagai perancah berbanding peranti berdasarkan NP. Hasil penyelidikan ini menyediakan hala tuju bukan sahaja untuk mencapai NSC berkecekapan tinggi, tetapi yang lebih utama adalah untuk mengekalkan kestabilan jangka panjang agar dapat digunakan secara komersil.

REFERENCES

- Ahmad, I., McCarthy, J.E., Bari, M., & Gun'ko, Y.K. (2014). Carbon nanomaterial based counter electrodes for dye sensitized solar cells. *Solar Energy*, 102, 152-161.
- Archana, P.S., Naveen Kumar, E., Vijila, C., Ramakrishna, S., Yusoff, M.M., & Jose, R. (2013). Random nanowires of nickel doped TiO₂ with high surface area and electron mobility for high efficiency dye-sensitized solar cells. *Dalton Transactions*, 42(4), 1024-1032. doi: 10.1039/C2DT31775C
- Armin, A., Velusamy, M., Wolfer, P., Zhang, Y., Burn, P.L., Meredith, P., & Pivrikas, A. (2014). Quantum efficiency of organic solar cells: Electro-optical cavity considerations. *ACS Photonics*, 1(3), 173-181. doi: 10.1021/ph400044k
- Badia, L., Mas-Marzá, E., Sánchez, R.S., Barea, E.M., Bisquert, J., & Mora-Seró, I. (2014). New iridium complex as additive to the spiro-ometad in perovskite solar cells with enhanced stability. *APL Materials*, 2(8), 081507.
- Ball, J.M., Lee, M.M., Hey, A., & Snaith, H.J. (2013). Low-temperature processed meso-superstructured to thin-film perovskite solar cells. *Energy & Environmental Science*, 6(6), 1739-1743.
- Bartesaghi, D., del Carmen Pérez, I., Kniepert, J., Roland, S., Turbiez, M., Neher, D., & Koster, L.J.A. (2015). Competition between recombination and extraction of free charges determines the fill factor of organic solar cells. *Nature communications*, 6.
- Baruah, S., & Dutta, J. (2009). Hydrothermal growth of ZnO nanostructures. *Science and Technology of Advanced Materials*, 10(1), 013001.
- Bavykin, D.V., Friedrich, J.M., & Walsh, F.C. (2006). Protonated titanates and TiO₂ nanostructured materials: Synthesis, properties, and applications. *Advanced Materials*, 18(21), 2807-2824.
- Beard, M.C., Luther, J.M., & Nozik, A.J. (2014). The promise and challenge of nanostructured solar cells. *Nature nanotechnology*, 9(12), 951-954.
- Berhe, S.A., Nag, S., Molinets, Z., & Youngblood, W.J. (2013). Influence of seeding and bath conditions in hydrothermal growth of very thin (~20 nm) single-crystalline rutile TiO₂ nanorod films. *ACS Applied Materials & Interfaces*, 5(4), 1181-1185. doi: 10.1021/am302315q
- Bi, D., Boschloo, G., Schwarzmüller, S., Yang, L., Johansson, E.M., & Hagfeldt, A. (2013). Efficient and stable CH₃NH₃PbI₃-sensitized ZnO nanorod array solid-state solar cells. *Nanoscale*, 5(23), 11686-11691.
- Bi, D., Yang, L., Boschloo, G., Hagfeldt, A., & Johansson, E.M. (2013). Effect of different hole transport materials on recombination in CH₃NH₃PbI₃ perovskite-sensitized mesoscopic solar cells. *The journal of physical chemistry letters*, 4(9), 1532-1536.
- Bierman, M.J., & Jin, S. (2009). Potential applications of hierarchical branching nanowires in solar energy conversion. *Energy & Environmental Science*, 2(10), 1050-1059. doi: 10.1039/B912095E

- Bird, R.E., Hulstrom, R.L., & Lewis, L. (1983). Terrestrial solar spectral data sets. *Solar energy*, 30(6), 563-573.
- Bisquert, J. (2002). Theory of the impedance of electron diffusion and recombination in a thin layer. *The Journal of Physical Chemistry B*, 106(2), 325-333. doi: 10.1021/jp011941g
- Bisquert, J., Zaban, A., Greenshtein, M., & Mora-Seró, I. (2004). Determination of rate constants for charge transfer and the distribution of semiconductor and electrolyte electronic energy levels in dye-sensitized solar cells by open-circuit photovoltage decay method. *Journal of the American Chemical Society*, 126(41), 13550-13559. doi: 10.1021/ja047311k
- Blasco, J., García, J., Teresa, J.M.d., Ibarra, M.R., Algarabel, P.A., & Marquina, C. (1996). A systematic study of structural, magnetic and electrical properties of perovskites. *Journal of Physics: Condensed Matter*, 8(40), 7427.
- Boix, P.P., Nonomura, K., Mathews, N., & Mhaisalkar, S.G. (2014). Current progress and future perspectives for organic/inorganic perovskite solar cells. *Materials Today*, 17(1), 16-23.
- Boschloo, G., & Hagfeldt, A. (2009). Characteristics of the iodide/triiodide redox mediator in dye-sensitized solar cells. *Accounts of Chemical Research*, 42(11), 1819-1826.
- Burschka, J., Pellet, N., Moon, S.-J., Humphry-Baker, R., Gao, P., Nazeeruddin, M.K., & Grätzel, M. (2013). Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, 499(7458), 316-319.
- Burschka, J.A., Pellet, N., Nazeeruddin, M.K., Graetzel, M., & Ahmad, S. (2014). High performance perovskite-sensitized mesoscopic solar cells: Google Patents.
- Chu, S., & Majumdar, A. (2012). Opportunities and challenges for a sustainable energy future. *Nature*, 488(7411), 294-303.
- Cong, J., Yang, X., Kloo, L., & Sun, L. (2012). Iodine/iodide-free redox shuttles for liquid electrolyte-based dye-sensitized solar cells. *Energy & Environmental Science*, 5(11), 9180-9194.
- Cui, J., Yuan, H., Li, J., Xu, X., Shen, Y., Lin, H., & Wang, M. (2016). Recent progress in efficient hybrid lead halide perovskite solar cells. *Science and Technology of Advanced Materials*.
- Daeneke, T., Kwon, T.-H., Holmes, A.B., Duffy, N.W., Bach, U., & Spiccia, L. (2011). High-efficiency dye-sensitized solar cells with ferrocene-based electrolytes. *Nature chemistry*, 3(3), 211-215.
- Darling, S.B., & You, F. (2013). The case for organic photovoltaics. *RSC Advances*, 3(39), 17633-17648. doi: 10.1039/C3RA42989J
- De Angelis, F., Fantacci, S., Mosconi, E., Nazeeruddin, M.K., & Grätzel, M. (2011). Absorption spectra and excited state energy levels of the N719 dye on TiO₂ in dye-sensitized solar cell models. *The Journal of Physical Chemistry C*, 115(17), 8825-8831. doi: 10.1021/jp111949a

- De Angelis, F., Fantacci, S., Selloni, A., Nazeeruddin, M.K., & Grätzel, M. (2010). First-principles modeling of the adsorption geometry and electronic structure of ru (ii) dyes on extended TiO₂ substrates for dye-sensitized solar cell applications. *The Journal of Physical Chemistry C*, 114(13), 6054-6061.
- de Freitas, J.N., Nogueira, A.F., & De Paoli, M.-A. (2009). New insights into dye-sensitized solar cells with polymer electrolytes. *Journal of Materials Chemistry*, 19(30), 5279-5294.
- De Wolf, S., Holovsky, J., Moon, S.-J., Löper, P., Niesen, B., Ledinsky, M., Haug, F.-J., Yum, J.-H., & Ballif, C. (2014). Organometallic halide perovskites: Sharp optical absorption edge and its relation to photovoltaic performance. *The journal of physical chemistry letters*, 5(6), 1035-1039.
- Djurisic, A.B., Xi, Y.Y., Hsu, Y.F., & Chan, W.K. (2007). Hydrothermal synthesis of nanostructures. *Recent patents on nanotechnology*, 1(2), 121-128.
- Dualeh, A., Moehl, T., Tetreault, N., Teuscher, J., Gao, P., Nazeeruddin, M.K., & Grätzel, M. (2013). Impedance spectroscopic analysis of lead iodide perovskite-sensitized solid-state solar cells. *ACS nano*, 8(1), 362-373.
- Ecker, B., Egelhaaf, H.-J., Steim, R., Parisi, J., & von Hauff, E. (2012). Understanding s-shaped current-voltage characteristics in organic solar cells containing a tiox interlayer with impedance spectroscopy and equivalent circuit analysis. *The Journal of Physical Chemistry C*, 116(31), 16333-16337. doi: 10.1021/jp305206d
- Elumalai, N.K., & Uddin, A. (2016). Open circuit voltage of organic solar cells: An in-depth review. *Energy & Environmental Science*.
- Elumalai, N.K., Vijila, C., Jose, R., Zhi Ming, K., Saha, A., & Ramakrishna, S. (2013). Simultaneous improvements in power conversion efficiency and operational stability of polymer solar cells by interfacial engineering. *Physical Chemistry Chemical Physics*, 15(43), 19057-19064. doi: 10.1039/C3CP53352B
- Eperon, G.E., Burlakov, V.M., Docampo, P., Goriely, A., & Snaith, H.J. (2014). Morphological control for high performance, solution-processed planar heterojunction perovskite solar cells. *Advanced Functional Materials*, 24(1), 151-157.
- Even, J., Pedesseau, L., & Katan, C. (2014). Analysis of multivalley and multibandgap absorption and enhancement of free carriers related to exciton screening in hybrid perovskites. *The Journal of Physical Chemistry C*, 118(22), 11566-11572.
- Fabregat-Santiago, F., Bisquert, J., Palomares, E., Otero, L., Kuang, D., Zakeeruddin, S.M., & Grätzel, M. (2007). Correlation between photovoltaic performance and impedance spectroscopy of dye-sensitized solar cells based on ionic liquids. *The Journal of Physical Chemistry C*, 111(17), 6550-6560. doi: 10.1021/jp066178a
- Fabregat-Santiago, F., Garcia-Belmonte, G., Bisquert, J., Zaban, A., & Salvador, P. (2002). Decoupling of transport, charge storage, and interfacial charge transfer in the nanocrystalline TiO₂/electrolyte system by impedance methods. *The Journal of Physical Chemistry B*, 106(2), 334-339.

- 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.
- Fakharuddin, A., Di Giacomo, F., Ahmed, I., Wali, Q., Brown, T.M., & Jose, R. (2015). Role of morphology and crystallinity of nanorod and planar electron transport layers on the performance and long term durability of perovskite solar cells. *Journal of Power Sources*, 283, 61-67.
- Fakharuddin, A., Jose, R., Brown, T.M., Fabregat-Santiago, F., & Bisquert, J. (2014). A perspective on the production of dye-sensitized solar modules. *Energy & Environmental Science*, 7(12), 3952-3981.
- Fakharuddin, A., Palma, A.L., Di Giacomo, F., Casaluci, S., Matteocci, F., Wali, Q., Rauf, M., Di Carlo, A., Brown, T.M., & Jose, R. (2015). Solid state perovskite solar modules by vacuum-vapor assisted sequential deposition on Nd: YVO₄ laser patterned rutile TiO₂ nanorods. *Nanotechnology*, 26(49), 494002.
- Feng, X., Shankar, K., Varghese, O.K., Paulose, M., Latempa, T.J., & Grimes, C.A. (2008). Vertically aligned single crystal TiO₂ nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis details and applications. *Nano letters*, 8(11), 3781-3786.
- Ferber, J., Stangl, R., & Luther, J. (1998). An electrical model of the dye-sensitized solar cell. *Solar Energy Materials and Solar Cells*, 53(1-2), 29-54. doi: [http://dx.doi.org/10.1016/S0927-0248\(98\)00005-1](http://dx.doi.org/10.1016/S0927-0248(98)00005-1)
- Gao, H., Bao, C., Li, F., Yu, T., Yang, J., Zhu, W., Zhou, X., Fu, G., & Zou, Z. (2015). Nucleation and crystal growth of organic-inorganic lead halide perovskites under different relative humidity. *ACS applied materials & interfaces*, 7(17), 9110-9117.
- Ghadiri, E., Taghavinia, N., Zakeeruddin, S.M., Grätzel, M., & Moser, J.-E. (2010). Enhanced electron collection efficiency in dye-sensitized solar cells based on nanostructured TiO₂ hollow fibers. *Nano letters*, 10(5), 1632-1638.
- Gonzalez-Pedro, V., Juarez-Perez, E.J., Arsyad, W.-S., Barea, E.M., Fabregat-Santiago, F., Mora-Sero, I., & Bisquert, J. (2014). General working principles of CH₃NH₃PbI₃ perovskite solar cells. *Nano letters*, 14(2), 888-893.
- Goodhew, P.J., Humphreys, J., & Beanland, R. (2000). *Electron microscopy and analysis*: CRC Press.
- Grätzel, M. (2001). Photoelectrochemical cells. *Nature*, 414(6861), 338-344.
- Grätzel, M. (2003). Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 4(2), 145-153.
- Grätzel, M. (2005). Solar energy conversion by dye-sensitized photovoltaic cells. *Inorganic Chemistry*, 44(20), 6841-6851. doi: 10.1021/ic0508371
- Grätzel, M. (2014). The light and shade of perovskite solar cells. *Nature materials*, 13(9), 838-842.
- Green, M.A., Emery, K., Hishikawa, Y., Warta, W., & Dunlop, E.D. (2015). Solar cell efficiency tables (version 45). *Progress in photovoltaics: research and applications*, 23(1), 1-9.

- Green, M.A., Ho-Baillie, A., & Snaith, H.J. (2014). The emergence of perovskite solar cells. *Nature Photonics*, 8(7), 506-514.
- Guo, W., Xu, C., Wang, X., Wang, S., Pan, C., Lin, C., & Wang, Z.L. (2012). Rectangular bunched rutile TiO_2 nanorod arrays grown on carbon fiber for dye-sensitized solar cells. *Journal of the American Chemical Society*, 134(9), 4437-4441.
- Habisreutinger, S.N., Leijtens, T., Eperon, G.E., Stranks, S.D., Nicholas, R.J., & Snaith, H.J. (2014). Carbon nanotube/polymer composites as a highly stable hole collection layer in perovskite solar cells. *Nano letters*, 14(10), 5561-5568.
- Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., & Pettersson, H. (2010). Dye-sensitized solar cells. *Chem. Rev.*, 110(11), 6595-6663.
- Hamad, H., El-latif, M.A., Kashyout, A.E.-H., Sadik, W., & Feteha, M. (2015). Optimizing the preparation parameters of mesoporous nanocrystalline titania and its photocatalytic activity in water: Physical properties and growth mechanisms. *Process Safety and Environmental Protection*, 98, 390-398.
- Hara, K., Sato, T., Katoh, R., Furube, A., Ohga, Y., Shinpo, A., Suga, S., Sayama, K., Sugihara, H., & Arakawa, H. (2003). Molecular design of coumarin dyes for efficient dye-sensitized solar cells. *The Journal of Physical Chemistry B*, 107(2), 597-606.
- Hendry, E., Wang, F., Shan, J., Heinz, T.F., & Bonn, M. (2004). Electron transport in TiO_2 probed by thz time-domain spectroscopy. *Physical Review B*, 69(8), 081101.
- Heo, J.H., Im, S.H., Noh, J.H., Mandal, T.N., Lim, C.-S., Chang, J.A., Lee, Y.H., Kim, H.-j., Sarkar, A., & Nazeeruddin, M.K. (2013). Efficient inorganic-organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors. *Nature Photonics*, 7(6), 486-491.
- Heo, J.H., Song, D.H., Patil, B.R., & Im, S.H. (2015). Recent progress of innovative perovskite hybrid solar cells. *Israel Journal of Chemistry*, 55(9), 966-977.
- Hore, S., Vetter, C., Kern, R., Smit, H., & Hinsch, A. (2006). Influence of scattering layers on efficiency of dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*, 90(9), 1176-1188.
- Hoshikawa, T., Yamada, M., Kikuchi, R., & Eguchi, K. (2005). Impedance analysis of internal resistance affecting the photoelectrochemical performance of dye-sensitized solar cells. *Journal of the Electrochemical Society*, 152(2), E68-E73.
- Hou, J.R. (2013). *Preparation of titania nanorod arrays by hydrothermal method*. Paper presented at the Advanced Materials Research.
- Huang, F., Chen, D., Zhang, X.L., Caruso, R.A., & Cheng, Y.B. (2010). Dual-function scattering layer of submicrometer-sized mesoporous TiO_2 beads for high-efficiency dye-sensitized solar cells. *Advanced Functional Materials*, 20(8), 1301-1305.
- Huber, B., Brodyanski, A., Scheib, M., Orendorz, A., Ziegler, C., & Gnaser, H. (2005). Nanocrystalline anatase TiO_2 thin films: Preparation and crystallite size-dependent properties. *Thin Solid Films*, 472(1), 114-124.

- Ito, S., Murakami, T.N., Comte, P., Liska, P., Grätzel, C., Nazeeruddin, M.K., & Grätzel, 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.
- J. Frank, A., Kopidakis, N., & Lagemaat, J.v.d. (2004). Electrons in nanostructured TiO₂ solar cells: Transport, recombination and photovoltaic properties. *Coordination Chemistry Reviews*, 248(13–14), 1165-1179.
- Jeng, J.-Y., Chen, K.-C., Chiang, T.-Y., Lin, P.-Y., Tsai, T.-D., Chang, Y.-C., Guo, T.-F., Chen, P., Wen, T.-C., & Hsu, Y.-J. (2014). Nickel oxide electrode interlayer in CH₃NH₃PbI₃ perovskite/PCBM planar-heterojunction hybrid solar cells. *Advanced Materials*, 26(24), 4107-4113. doi: 10.1002/adma.201306217
- Jeon, N.J., Noh, J.H., Yang, W.S., Kim, Y.C., Ryu, S., Seo, J., & Seok, S.I. (2015). Compositional engineering of perovskite materials for high-performance solar cells. *Nature*, 517(7535), 476-480.
- Jin, C., Huailiang, Y., Junpeng, L., Xiaobao, X., Yan, S., Hong, L., & Mingkui, W. (2015). Recent progress in efficient hybrid lead halide perovskite solar cells. *Science and Technology of Advanced Materials*, 16(3), 036004.
- Jose, R., Thavasi, V., & Ramakrishna, S. (2009). Metal oxides for dye-sensitized solar cells. *Journal of the American Ceramic Society*, 92(2), 289-301.
- Kakiage, K., Aoyama, Y., Yano, T., Oya, K., Fujisawa, J.-i., & Hanaya, M. (2015). Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. *Chemical Communications*, 51(88), 15894-15897.
- Kamat, P.V. (2013). Evolution of perovskite photovoltaics and decrease in energy payback time. *J. Phys. Chem. Lett*, 4(21), 3733-3734.
- Kashyout, A., Soliman, M., & Fathy, M. (2010). Effect of preparation parameters on the properties of TiO₂ nanoparticles for dye sensitized solar cells. *Renewable Energy*, 35(12), 2914-2920.
- Kim, H.-S., Lee, C.-R., Im, J.-H., Lee, K.-B., Moehl, T., Marchioro, A., Moon, S.-J., Humphry-Baker, R., Yum, J.-H., & Moser, J.E. (2012). Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Scientific reports*, 2.
- Kim, H.-S., Lee, J.-W., Yantara, N., Boix, P.-P., Kulkarni, S.-A., Mhaisalkar, S., Grätzel, M., & Park, N.-G. (2013). High efficiency solid-state sensitized solar cell-based on submicrometer rutile TiO₂ nanorod and CH₃NH₃PbI₃ perovskite sensitizer. *Nano Letters*, 13(6), 2412-2417. doi: 10.1021/nl400286w
- Kim, H.-S., Mora-Sero, I., Gonzalez-Pedro, V., Fabregat-Santiago, F., Juarez-Perez, E.J., Park, N.-G., & Bisquert, J. (2013). Mechanism of carrier accumulation in perovskite thin-absorber solar cells. *Nat Commun*, 4. doi: 10.1038/ncomms3242
- Kim, H.-S., & Park, N.-G. (2014). Parameters affecting i-v hysteresis of CH₃NH₃PbI₃ perovskite solar cells: Effects of perovskite crystal size and mesoporous TiO₂ layer. *The journal of physical chemistry letters*, 5(17), 2927-2934.
- Kim, M.-S., Kim, B.-G., & Kim, J. (2009). Effective variables to control the fill factor of organic photovoltaic cells. *ACS Applied Materials & Interfaces*, 1(6), 1264-1269. doi: 10.1021/am900155y

- Kojima, A., Teshima, K., Shirai, Y., & Miyasaka, T. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, 131(17), 6050-6051.
- Kroeze, J.E., Hirata, N., Schmidt-Mende, L., Orizu, C., Ogier, S.D., Carr, K., Grätzel, M., & Durrant, J.R. (2006). Parameters influencing charge separation in solid-state dye-sensitized solar cells using novel hole conductors. *Advanced Functional Materials*, 16(14), 1832-1838.
- Kumar, A., Madaria, A.R., & Zhou, C. (2010). Growth of aligned single-crystalline rutile TiO₂ nanowires on arbitrary substrates and their application in dye-sensitized solar cells. *The Journal of Physical Chemistry C*, 114(17), 7787-7792.
- Law, C., Miseikis, L., Dimitrov, S., Shakya-Tuladhar, P., Li, X., Barnes, P.R., Durrant, J., & O'Regan, B.C. (2014). Performance and stability of lead perovskite/TiO₂, polymer/pcbm, and dye sensitized solar cells at light intensities up to 70 suns. *Advanced Materials*, 26(36), 6268-6273.
- Lee, B.H., Song, M.Y., Jang, S.-Y., Jo, S.M., Kwak, S.-Y., & Kim, D.Y. (2009). Charge transport characteristics of high efficiency dye-sensitized solar cells based on electrospun TiO₂ nanorod photoelectrodes. *The Journal of Physical Chemistry C*, 113(51), 21453-21457. doi: 10.1021/jp907855x
- Lee, M.M., Teuscher, J., Miyasaka, T., Murakami, T.N., & Snaith, H.J. (2012). Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science*, 338(6107), 643-647.
- Li, D., Qin, D., Deng, M., Luo, Y., & Meng, Q. (2009). Optimization the solid-state electrolytes for dye-sensitized solar cells. *Energy & Environmental Science*, 2(3), 283-291.
- Li, Y., Zhang, M., Guo, M., & Wang, X. (2010). Hydrothermal growth of well-aligned tio2 nanorod arrays: Dependence of morphology upon hydrothermal reaction conditions. *Rare metals*, 29(3), 286-291.
- Listorti, A., O'Regan, B., & Durrant, J.R. (2011). Electron transfer dynamics in dye-sensitized solar cells. *Chemistry of Materials*, 23(15), 3381-3399.
- Liu, B., & Aydil, E.S. (2009). Growth of oriented single-crystalline rutile TiO₂ nanorods on transparent conducting substrates for dye-sensitized solar cells. *Journal of the American Chemical Society*, 131(11), 3985-3990.
- Liu, M., Johnston, M.B., & Snaith, H.J. (2013). Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature*, 501(7467), 395-398.
- Lu, K. (2014). *Materials in energy conversion, harvesting, and storage*: John Wiley & Sons.
- Lv, M., Zheng, D., Ye, M., Xiao, J., Guo, W., Lai, Y., Sun, L., Lin, C., & Zuo, J. (2013). Optimized porous rutile TiO₂ nanorod arrays for enhancing the efficiency of dye-sensitized solar cells. *Energy & Environmental Science*, 6(5), 1615-1622.
- Ma, T., Fang, X., Akiyama, M., Inoue, K., Noma, H., & Abe, E. (2004). Properties of several types of novel counter electrodes for dye-sensitized solar cells. *Journal of Electroanalytical Chemistry*, 574(1), 77-83.

- Maçaira, J., Andrade, L., & Mendes, A. (2013). Review on nanostructured photoelectrodes for next generation dye-sensitized solar cells. *Renewable and Sustainable Energy Reviews*, 27, 334-349. doi: <http://dx.doi.org/10.1016/j.rser.2013.07.011>
- Martínez-Ferrero, E., Albero, J., & Palomares, E. (2010). Materials, nanomorphology, and interfacial charge transfer reactions in quantum dot/polymer solar cell devices. *The Journal of Physical Chemistry Letters*, 1(20), 3039-3045. doi: 10.1021/jz101228z
- Mathew, S., Yella, A., Gao, P., Humphry-Baker, R., Curchod, B.F., Ashari-Astani, N., Tavernelli, I., Rothlisberger, U., Nazeeruddin, M.K., & Grätzel, M. (2014). Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nature chemistry*, 6(3), 242-247.
- Matteocci, F., Cinà, L., Di Giacomo, F., Razza, S., Palma, A.L., Guidobaldi, A., D'Epifanio, A., Licoccia, S., Brown, T.M., & Reale, A. (2014). High efficiency photovoltaic module based on mesoscopic organometal halide perovskite. *Progress in Photovoltaics: Research and Applications*.
- Matteocci, F., Razza, S., Di Giacomo, F., Casaluci, S., Mincuzzi, G., Brown, T., D'Epifanio, A., Licoccia, S., & Di Carlo, A. (2014). Solid-state solar modules based on mesoscopic organometal halide perovskite: A route towards the up-scaling process. *Physical Chemistry Chemical Physics*, 16(9), 3918-3923.
- McCusker, L., & Baerlocher, C. (2013). Electron crystallography as a complement to x-ray powder diffraction techniques. *Zeitschrift für Kristallographie-Crystalline Materials*, 228(1), 1-10.
- Mei, A., Li, X., Liu, L., Ku, Z., Liu, T., Rong, Y., Xu, M., Hu, M., Chen, J., & Yang, Y. (2014). A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. *Science*, 345(6194), 295-298.
- Mitzi, D.B. (2007). Synthesis, structure, and properties of organic-inorganic perovskites and related materials. *Progress in Inorganic Chemistry, Volume 48*, 1-121.
- Mohammad, N., Quamruzzaman, M., Hossain, M.R.T., & Alam, M.R. (2013). Parasitic effects on the performance of dc-dc sepic in photovoltaic maximum power point tracking applications.
- Moser, J. (1887). Notiz über verstärkung photoelektrischer ströme durch optische sensibilisirung. *Monatshefte für Chemie/Chemical Monthly*, 8(1), 373-373.
- Murakami, T.N., Ito, S., Wang, Q., Nazeeruddin, M.K., Bessho, T., Cesar, I., Liska, P., Humphry-Baker, R., Comte, P., & Péchy, P. (2006). Highly efficient dye-sensitized solar cells based on carbon black counter electrodes. *Journal of the Electrochemical Society*, 153(12), A2255-A2261.
- Murray, A.T., Frost, J.M., Hendon, C.H., Molloy, C.D., Carbery, D.R., & Walsh, A. (2015). Modular design of spiro-ometad analogues as hole transport materials in solar cells. *Chemical Communications*, 51(43), 8935-8938.
- Nazeeruddin, M.K., De Angelis, F., Fantacci, S., Selloni, A., Viscardi, G., Liska, P., Ito, S., Takeru, B., & Grätzel, M. (2005). Combined experimental and dft-tddft computational study of photoelectrochemical cell ruthenium sensitizers. *Journal of the American Chemical Society*, 127(48), 16835-16847.

- Nazeeruddin, M.K., Humphry-Baker, R., Liska, P., & Grätzel, M. (2003). Investigation of sensitizer adsorption and the influence of protons on current and voltage of a dye-sensitized nanocrystalline TiO_2 solar cell. *The Journal of Physical Chemistry B*, 107(34), 8981-8987.
- Nazeeruddin, M.K., Zakeeruddin, S., Lagref, J.-J., Liska, P., Comte, P., Barolo, C., Viscardi, G., Schenk, K., & Grätzel, M. (2004). Stepwise assembly of amphiphilic ruthenium sensitizers and their applications in dye-sensitized solar cell. *Coordination chemistry reviews*, 248(13), 1317-1328.
- Niu, G., Li, W., Meng, F., Wang, L., Dong, H., & Qiu, Y. (2014). Study on the stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells. *Journal of Materials Chemistry A*, 2(3), 705-710.
- Noh, S.I., Ahn, H.-J., & Riu, D.-H. (2012). Photovoltaic property dependence of dye-sensitized solar cells on sheet resistance of fto substrate deposited via spray pyrolysis. *Ceramics International*, 38(5), 3735-3739.
- O'regan, B., & Grifitzeli, M. (1991). A low-cost, high-efficiency solar cell based on dye-sensitized. *nature*, 353(6346), 737-740.
- Ogomi, Y., Kukihara, K., Qing, S., Toyoda, T., Yoshino, K., Pandey, S., Momose, H., & Hayase, S. (2014). Control of charge dynamics through a charge-separation interface for all-solid perovskite-sensitized solar cells. *ChemPhysChem*, 15(6), 1062-1069.
- Park, N.-G. (2013). Organometal perovskite light absorbers toward a 20% efficiency low-cost solid-state mesoscopic solar cell. *The Journal of Physical Chemistry Letters*, 4(15), 2423-2429.
- Park, N.-G., Van de Lagemaat, J., & Frank, A. (2000). Comparison of dye-sensitized rutile-and anatase-based TiO_2 solar cells. *The Journal of Physical Chemistry B*, 104(38), 8989-8994.
- Perkampus, H.-H., Grinter, H.-C., & Threlfall, T. (1992). *Uv-vis spectroscopy and its applications*: Springer.
- Pitarch, Á., Garcia-Belmonte, G., Mora-Seró, I., & Bisquert, J. (2004). Electrochemical impedance spectra for the complete equivalent circuit of diffusion and reaction under steady-state recombination current. *Physical Chemistry Chemical Physics*, 6(11), 2983-2988.
- Polman, A., Knight, M., Garnett, E.C., Ehrler, B., & Sinke, W.C. (2016). Photovoltaic materials: Present efficiencies and future challenges. *Science*, 352(6283). doi: 10.1126/science.aad4424
- Pottier, A., Chanéac, C., Tronc, E., Mazerolles, L., & Jolivet, J.-P. (2001). Synthesis of brookite TiO_2 nanoparticles by thermolysis of TiCl_4 in strongly acidic aqueous media. *Journal of Materials Chemistry*, 11(4), 1116-1121.
- Privalov, T., Boschloo, G., Hagfeldt, A., Svensson, P.H., & Kloo, L. (2008). A study of the interactions between i-/i3- redox mediators and organometallic sensitizing dyes in solar cells. *The Journal of Physical Chemistry C*, 113(2), 783-790.
- Qiu, J., Qiu, Y., Yan, K., Zhong, M., Mu, C., Yan, H., & Yang, S. (2013). All-solid-state hybrid solar cells based on a new organometal halide perovskite sensitizer and one-dimensional TiO_2 nanowire arrays. *Nanoscale*, 5(8), 3245-3248.

- Qu, J., Li, G.R., & Gao, X.P. (2010). One-dimensional hierarchical titania for fast reaction kinetics of photoanode materials of dye-sensitized solar cells. *Energy & Environmental Science*, 3(12), 2003-2009. doi: 10.1039/C003646C
- Reese, M.O., Gevorgyan, S.A., Jørgensen, M., Bundgaard, E., Kurtz, S.R., Ginley, D.S., Olson, D.C., Lloyd, M.T., Morville, P., & Katz, E.A. (2011). Consensus stability testing protocols for organic photovoltaic materials and devices. *Solar Energy Materials and Solar Cells*, 95(5), 1253-1267.
- Robertson, N. (2006). Optimizing dyes for dye-sensitized solar cells. *Angewandte Chemie International Edition*, 45(15), 2338-2345.
- Saito, M., & Fujihara, S. (2008). Large photocurrent generation in dye-sensitized ZnO solar cells. *Energy & Environmental Science*, 1(2), 280-283.
- Saliba, M., Orlandi, S., Matsui, T., Aghazada, S., Cavazzini, M., Correa-Baena, J.-P., Gao, P., Scopelliti, R., Mosconi, E., & Dahmen, K.-H. (2016a). A molecularly engineered hole-transporting material for efficient perovskite solar cells. *Nature Energy*, 1, 15017.
- Saliba, M., Orlandi, S., Matsui, T., Aghazada, S., Cavazzini, M., Correa-Baena, J.-P., Gao, P., Scopelliti, R., Mosconi, E., & Dahmen, K.-H. (2016b). A molecularly engineered hole-transporting material for efficient perovskite solar cells. *Nature Energy*, 15017.
- Schmidt-Mende, L., & Grätzel, M. (2006). TiO₂ pore-filling and its effect on the efficiency of solid-state dye-sensitized solar cells. *Thin Solid Films*, 500(1), 296-301.
- Schulz, P., Edri, E., Kirmayer, S., Hodes, G., Cahen, D., & Kahn, A. (2014). Interface energetics in organo-metal halide perovskite-based photovoltaic cells. *Energy & Environmental Science*, 7(4), 1377-1381. doi: 10.1039/C4EE00168K
- Shao, Y., Xiao, Z., Bi, C., Yuan, Y., & Huang, J. (2014). Origin and elimination of photocurrent hysteresis by fullerene passivation in CH₃NH₃PbI₃ planar heterojunction solar cells. *Nature communications*, 5.
- Shen, Q., Ogomi, Y., Chang, J., Toyoda, T., Fujiwara, K., Yoshino, K., Sato, K., Yamazaki, K., Akimoto, M., Kuga, Y., Katayama, K., & Hayase, S. (2015). Optical absorption, charge separation and recombination dynamics in Sn/Pb cocktail perovskite solar cells and their relationships to photovoltaic performances. *Journal of Materials Chemistry A*, 3(17), 9308-9316. doi: 10.1039/C5TA01246E
- Singh, J., Gusain, A., Saxena, V., Chauhan, A.K., Veerender, P., Koiry, S.P., Jha, P., Jain, A., Aswal, D.K., & Gupta, S.K. (2013). XPS, UV-Vis, FTIR, and EXAFS studies to investigate the binding mechanism of N719 dye onto oxalic acid treated TiO₂ and its implication on photovoltaic properties. *The Journal of Physical Chemistry C*, 117(41), 21096-21104. doi: 10.1021/jp4062994
- Sivakumar, R., Ramkumar, J., Shaji, S., & Paulraj, M. (2016). Efficient TiO₂ blocking layer for TiO₂ nanorod arrays-based dye-sensitized solar cells. *Thin Solid Films*, 615, 171-176.

- Snaith, H.J. (2013). Perovskites: The emergence of a new era for low-cost, high-efficiency solar cells. *The Journal of Physical Chemistry Letters*, 4(21), 3623-3630.
- Snaith, H.J., Abate, A., Ball, J.M., Eperon, G.E., Leijtens, T., Noel, N.K., Stranks, S.D., Wang, J.T.-W., Wojciechowski, K., & Zhang, W. (2014). Anomalous hysteresis in perovskite solar cells. *The journal of physical chemistry letters*, 5(9), 1511-1515.
- Snaith, H.J., Humphry-Baker, R., Chen, P., Cesar, I., Zakeeruddin, S.M., & Grätzel, M. (2008). Charge collection and pore filling in solid-state dye-sensitized solar cells. *Nanotechnology*, 19(42), 424003.
- Snaith, H.J., & Schmidt-Mende, L. (2007). Advances in liquid-electrolyte and solid-state dye-sensitized solar cells. *Advanced Materials*, 19(20), 3187-3200.
- Sommeling, P., O'regan, B., Haswell, R., Smit, H., Bakker, N., Smits, J., Kroon, J., & Van Roosmalen, J. (2006). Influence of a $TiCl_4$ post-treatment on nanocrystalline TiO_2 films in dye-sensitized solar cells. *The Journal of Physical Chemistry B*, 110(39), 19191-19197.
- Su, J., Feng, X., Sloppy, J.D., Guo, L., & Grimes, C.A. (2010). Vertically aligned WO_3 nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis and photoelectrochemical properties. *Nano letters*, 11(1), 203-208.
- Sun, P., Zhang, X., Liu, X., Wang, L., Wang, C., Yang, J., & Liu, Y. (2012). Growth of single-crystalline rutile TiO_2 nanowire array on titanate nanosheet film for dye-sensitized solar cells. *Journal of Materials Chemistry*, 22(13), 6389-6393.
- Suryanarayana, C., & Norton, M.G. (2013). *X-ray diffraction: A practical approach*: Springer Science & Business Media.
- Tavakoli, A., Sohrabi, M., & Kargari, A. (2007). A review of methods for synthesis of nanostructured metals with emphasis on iron compounds. *Chemical Papers*, 61(3), 151-170.
- Tiwana, P., Docampo, P., Johnston, M.B., Snaith, H.J., & Herz, L.M. (2011). Electron mobility and injection dynamics in mesoporous ZnO , SnO_2 , and TiO_2 films used in dye-sensitized solar cells. *ACS nano*, 5(6), 5158-5166.
- Toivola, M., Ahlskog, F., & Lund, P. (2006). Industrial sheet metals for nanocrystalline dye-sensitized solar cell structures. *Solar energy materials and solar cells*, 90(17), 2881-2893.
- Vesce, L., Riccitelli, R., Soscia, G., Brown, T.M., Di Carlo, A., & Reale, A. (2010). Optimization of nanostructured titania photoanodes for dye-sensitized solar cells: Study and experimentation of $TiCl_4$ treatment. *Journal of Non-crystalline solids*, 356(37), 1958-1961.
- Vincent, B., Robertson, K., Cameron, T., & Knop, O. (1986). Isolated PbI_6 4-ions in $(CH_3NH_3)4PbI_6 \cdot 2H_2O$. *Can. J. Chem.*, 65, 1042-1046.
- Vogel, R., Hoyer, P., & Weller, H. (1994). Quantum-sized PbS , CdS , Ag_2S , Sb_2S_3 , and Bi_2S_3 particles as sensitizers for various nanoporous wide-bandgap semiconductors. *The Journal of Physical Chemistry*, 98(12), 3183-3188.

- Vougioukalakis, G.C., Konstantakou, M., Pefkianakis, E.K., Kabanakis, A.N., Stergiopoulos, T., Kontos, A.G., Andreopoulou, A.K., Kallitsis, J.K., & Falaras, P. (2014). A ruthenium-based light-harvesting antenna bearing an anthracene moiety in dye-sensitized solar cells. *Asian Journal of Organic Chemistry*, 3(9), 953-962.
- Vougioukalakis, G.C., Philippopoulos, A.I., Stergiopoulos, T., & Falaras, P. (2011). Contributions to the development of ruthenium-based sensitizers for dye-sensitized solar cells. *Coordination Chemistry Reviews*, 255(21), 2602-2621.
- Wang, H.-E., Chen, Z., Leung, Y.H., Luan, C., Liu, C., Tang, Y., Yan, C., Zhang, W., Zapien, J.A., & Bello, I. (2010). Hydrothermal synthesis of ordered single-crystalline rutile TiO₂ nanorod arrays on different substrates. *Applied Physics Letters*, 96(26), 263104.
- Wang, H.E., Chen, Z., Leung, Y.H., Luan, C., Liu, C., Tang, Y., Yan, C., Zhang, W., Zapien, J.A., Bello, I., & Lee, S.T. (2010). Hydrothermal synthesis of ordered single-crystalline rutile TiO₂ nanorod arrays on different substrates. *Applied Physics Letters*, 96(26).
- Wang, J., & Lin, Z. (2012). Dye-sensitized TiO₂ nanotube solar cells: Rational structural and surface engineering on TiO₂ nanotubes. *Chemistry—An Asian Journal*, 7(12), 2754-2762.
- Wang, K.-C., Jeng, J.-Y., Shen, P.-S., Chang, Y.-C., Diau, E.W.-G., Tsai, C.-H., Chao, T.-Y., Hsu, H.-C., Lin, P.-Y., & Chen, P. (2014). P-type mesoscopic nickel oxide/organometallic perovskite heterojunction solar cells. *Scientific reports*, 4.
- Wang, M., Grätzel, C., Zakeeruddin, S.M., & Grätzel, M. (2012). Recent developments in redox electrolytes for dye-sensitized solar cells. *Energy & Environmental Science*, 5(11), 9394-9405.
- Wang, Q., Ito, S., Grätzel, M., Fabregat-Santiago, F., Mora-Sero, I., Bisquert, J., Bessho, T., & Imai, H. (2006). Characteristics of high efficiency dye-sensitized solar cells. *The Journal of Physical Chemistry B*, 110(50), 25210-25221.
- Wang, X., He, G., Fong, H., & Zhu, Z. (2013). Electron transport and recombination in photoanode of electrospun tio2 nanotubes for dye-sensitized solar cells. *The Journal of Physical Chemistry C*, 117(4), 1641-1646.
- Wang, X., Kulkarni, S.A., Ito, B.I., Batabyal, S.K., Nonomura, K., Wong, C.C., Grätzel, M., Mhaisalkar, S.G., & Uchida, S. (2012). Nanoclay gelation approach toward improved dye-sensitized solar cell efficiencies: An investigation of charge transport and shift in the TiO₂ conduction band. *ACS applied materials & interfaces*, 5(2), 444-450.
- Wang, Z.-S., Kawauchi, H., Kashima, T., & Arakawa, H. (2004). Significant influence of TiO₂ photoelectrode morphology on the energy conversion efficiency of n719 dye-sensitized solar cell. *Coordination Chemistry Reviews*, 248(13–14), 1381-1389. doi: <http://dx.doi.org/10.1016/j.ccr.2004.03.006>
- Wei, D. (2010). Dye sensitized solar cells. *International journal of molecular sciences*, 11(3), 1103-1113.
- Wu, J.-J., & Yu, C.-C. (2004). Aligned TiO₂ nanorods and nanowalls. *The Journal of Physical Chemistry B*, 108(11), 3377-3379. doi: 10.1021/jp0361935

- Wu, J., Lan, Z., Lin, J., Huang, M., Huang, Y., Fan, L., & Luo, G. (2015). Electrolytes in dye-sensitized solar cells. *Chemical Reviews*, 115(5), 2136-2173.
- Xie, P., & Guo, F. (2007). Molecular engineering of ruthenium sensitizers in dye-sensitized solar cells. *Current Organic Chemistry*, 11(14), 1272-1286.
- Xing, G., Mathews, N., Sun, S., Lim, S.S., Lam, Y.M., Grätzel, M., Mhaisalkar, S., & Sum, T.C. (2013). Long-range balanced electron-and hole-transport lengths in organic-inorganic $\text{CH}_3\text{NH}_3\text{PbI}_3$. *Science*, 342(6156), 344-347.
- Yang, W.S., Noh, J.H., Jeon, N.J., Kim, Y.C., Ryu, S., Seo, J., & Seok, S.I. (2015). High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science*, 348(6240), 1234-1237.
- Yang, X., Yanagida, M., & Han, L. (2013). Reliable evaluation of dye-sensitized solar cells. *Energy & Environmental Science*, 6(1), 54-66. doi: 10.1039/C2EE22998F
- Ye, M., Chen, C., Lv, M., Zheng, D., Guo, W., & Lin, C. (2013). Facile and effective synthesis of hierarchical TiO_2 spheres for efficient dye-sensitized solar cells. *Nanoscale*, 5(14), 6577-6583.
- Ye, M., Wen, X., Wang, M., Iocozzia, J., Zhang, N., Lin, C., & Lin, Z. (2015). Recent advances in dye-sensitized solar cells: From photoanodes, sensitizers and electrolytes to counter electrodes. *Materials Today*, 18(3), 155-162.
- Ye, M., Zheng, D., Lv, M., Chen, C., Lin, C., & Lin, Z. (2013). Hierarchically structured nanotubes for highly efficient dye-sensitized solar cells. *Advanced Materials*, 25(22), 3039-3044.
- Yella, A., Heiniger, L.-P., Gao, P., Nazeeruddin, M.K., & Grätzel, M. (2014). Nanocrystalline rutile electron extraction layer enables low-temperature solution processed perovskite photovoltaics with 13.7% efficiency. *Nano letters*, 14(5), 2591-2596.
- Yella, A., Lee, H.-W., Tsao, H.N., Yi, C., Chandiran, A.K., Nazeeruddin, M.K., Diau, E.W.-G., Yeh, C.-Y., Zakeeruddin, S.M., & Grätzel, M. (2011). Porphyrin-sensitized solar cells with cobalt (ii/iii)-based redox electrolyte exceed 12 percent efficiency. *science*, 334(6056), 629-634.
- Yu, Y., Li, J., Geng, D., Wang, J., Zhang, L., Andrew, T.L., Arnold, M.S., & Wang, X. (2015). Development of lead iodide perovskite solar cells using three-dimensional titanium dioxide nanowire architectures. *ACS nano*, 9(1), 564-572.
- Zhang, Q., & Cao, G. (2011). Nanostructured photoelectrodes for dye-sensitized solar cells. *Nano Today*, 6(1), 91-109.