UNIVERSITY
OF WOLLONGONG
AUSTRALIA

University of Wollongong
Research Online

Australian Institute for Innovative Materials - Papers

Australian Institute for Innovative Materials

2019

Cubic aggregates of Zn_2SnO_4 nanoparticles and their application in dye-sensitized solar cells

Kadhim Al-Attafi

University of Wollongong, kmkaa533@uowmail.edu.au

Fanar Hussein Jawdat

University of Wollongong, fahj806@uowmail.edu.au

Hamzeh Qutaish

University of Wollongong, hqmq581@uowmail.edu.au

Patricia Y. Hayes

University of Wollongong, phayes@uow.edu.au

Amar Al-Keisy

University of Wollongong, ahjak378@uowmail.edu.au

See next page for additional authors

Publication Details

Al-Attafi, K., Hussein Jawdat, F., Qutaish, H., Hayes, P., Al-Keisy, A., Shim, K., Yamauchi, Y., Dou, S. Xue., Nattestad, A. & Kim, J. (2019). Cubic aggregates of Zn_2SnO_4 nanoparticles and their application in dye-sensitized solar cells. *Nano Energy*, 57 202-213.

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Cubic aggregates of Zn_2SnO_4 nanoparticles and their application in dye-sensitized solar cells

Abstract

Zinc Tin Oxide (Zn_2SnO_4 or ZTO) has emerged as an alternate photoanode material for dye-sensitized solar cells (DSCs), as it offers some advantages as compared to Titania (TiO_2). In this work, crystalline ZTO nanoparticles, formed into cubic aggregate structures were synthesised by a solvothermal reaction and employed in photoanodes of DSCs, using either a high extinction coefficient organic (D149) or an organometallic (N719) dye. These were investigated in comparison with devices based on TiO_2 photoanodes, with DSCs based on ZTO|D149 showing a promising solar-to-electric conversion efficiency of 4.9%, close to that of TiO_2 |D149. In addition, experiments were performed using ZTO and TiO_2 in aqueous dispersions to degrade Rhodamine B, suggesting ZTO based DSCs should be more stable. Further to this, the low photocurrents seen in ZTO|N719 based devices were investigated, with the dye binding mechanism appearing to significantly impact charge injection efficiency. While the reported PCEs using this material are not as high as for the best TiO_2 based devices, the device engineering strategies outlined here provide guidelines for future development of DSCs based on this material.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Al-Attafi, K., Hussein Jawdat, F., Qutaish, H., Hayes, P., Al-Keisy, A., Shim, K., Yamauchi, Y., Dou, S. Xue., Nattestad, A. & Kim, J. (2019). Cubic aggregates of Zn_2SnO_4 nanoparticles and their application in dye-sensitized solar cells. *Nano Energy*, 57 202-213.

Authors

Kadhim Al-Attafi, Fanar Hussein Jawdat, Hamzeh Qutaish, Patricia Y. Hayes, Amar Al-Keisy, Kyubin Shim, Yusuke Yamauchi, Shi Xue Dou, Andrew Nattestad, and Jung Ho Kim

Cubic aggregates of Zn_2SnO_4 nanoparticles and their application in dye-sensitized solar cells

*Kadhim Al-Attafi^{a,b}, Fanar Hussein Jawdat^a, Hamzeh Qutaish^a, Patricia Hayes^c, Amar Al-Keisy^a
Kyubin Shim^a, Yusuke Yamauchi^{a,d}, Shi Xue Dou^a, Andrew Nattestad^{c,*} and Jung Ho Kim^{a,*}*

^a Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Wollongong, NSW 2525, Australia.

^b Department of Physics, College of Science, University of Karbala, Karbala 56001, Iraq.

^c Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, Australian Institute for Innovative Materials, University of Wollongong, Wollongong, NSW 2525, Australia.

^d World Premier International Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

* Corresponding authors

Andrew Nattestad anattest@uow.edu.au

Jung Ho Kim jhk@uow.edu.au

Keywords: Dye binding, N719, ZTO

Abstract

Zinc Tin Oxide (Zn_2SnO_4 or ZTO) has emerged as an alternate photoanode material for DSCs, as it offers some advantages as compared to Titania (TiO_2). In this work, crystalline ZTO nanoparticles, formed into cubic aggregate structures were synthesised by a solvothermal reaction and employed in photoanodes of dye-sensitized solar cells (DSCs), using either a high extinction coefficient organic (D149) or an organometallic (N719) dye. These were investigated in comparison with devices based on TiO_2 photoanodes, with DSCs based on ZTO|D149 showing promising solar-to-electric conversion efficiency of 4.9%, close to that of TiO_2 |D149. In addition, experiments were performed using ZTO and TiO_2 in aqueous dispersions to degrade Rhodamine B, suggesting ZTO based DSCs should be more stable. Further to this, the low photocurrents seen in ZTO|N719 based devices were investigated, with the dye binding mechanism appearing to significantly impact charge injection efficiency. While the reported PCEs using this material are not as high as for the best TiO_2 based devices, the device engineering strategies outlined here provide guidelines for future development of DSCs based on this material.

1. Introduction

Since 1991, binary semiconducting metal oxides such as ZnO, TiO₂, and SnO₂, have been utilised as photoanode materials for DSCs.[1-5] Meanwhile, ternary metal oxide semiconductors such as Zinc Tin Oxide (ZTO) have attracted a modest amount of attention more recently, as promising alternative photoanode material. [6-10] ZTO photoanode-based DSCs have achieved efficiencies over 6% to date, as reported by Hwang *et. el.* [11] ZTO has also recently been applied as an electron transparent layer (ETL) for high-efficiency perovskite solar cells. [12-14] The DSCs as the PSC can be integrated with other energy storage systems for efficient energy harvesting-storage systems.[15] DSCs based on metal oxide photoanodes are still the subject of interest by researchers as clean energy resource due to their promising performance in indoor and outdoor applications.[16, 17]

Among the properties making ZTO of interest are the high electron mobility (10-15 cm² V⁻¹ s⁻¹), compared to TiO₂ (0.1-1 cm² V⁻¹ s⁻¹) and low absorption in the visible light range. [7, 18] ZTO is also seen to be less response to UV irradiation than TiO₂ suggesting its use can extend DSC service life. [19-21] Furthermore, ZTO does not suffer the same chemical stability issues which ZnO or SnO₂ photoanodes do in acidic local environments, such as can result from attachment by dyes. [6, 10, 19, 22] Furthermore, ZTO has a significantly higher isoelectric point compared to TiO₂ which is expected to lead to better light-harvesting efficiency through higher dye loading. [23-25] ZTO photoanodes have been reported using nanoparticles [6, 9, 18], as well as hierarchical structures. [22, 26, 27]

In spite of record solar-to-electric conversion efficiencies being set recently using other dyes, [28-31] and the research is in a progress to synthesis other dyes [32], N719 is still a common benchmark dye, for DSC researchers. N719 has a high electrostatic binding on TiO₂ with low

electrostatic repulsion among the dye molecules leading to high dye loading, and good shielding against recombination. [33-35] TD-DFT modelling performed by De Angelis *et al.* of N719 bound to TiO₂ through different mechanism revealed significant differences in charge injection rates based on this binding. [36] These calculations showed electron density of the excited state frontier orbital (approximated by the LUMO) physically overlaps significantly with the TiO₂, when the dye is bound in its protonated state. This work also showed (from a theoretical approach) the impact that different binding mechanisms has upon the absorption properties of N719.

The role of N719 as a benchmark dye has largely continued with ZTO, where reports of comparatively low current densities (and subsequently efficiencies), are mainly attributed to high charge recombination and/or low light harvesting efficiencies (LHE).[6, 9, 18] Improvements in V_{oc} values, attributed to decreased recombination, were achieved by using core-shell structured (ZTO-ZnO) thin film photoanodes, resulting in a PCE of 6%.[37] Wang *et. al* employed a bi-layer structure with microporous ZTO as a scattering layer over ZTO nanoparticles to enhance the LHE through increasing the light scattering ability. This resulted in a higher efficiency of 6.1% compared to 4.7% for nanoparticle-only photoanode. [18]

As mentioned, the majority of the work in ZTO development has been done using N719; however, the low quantum efficiencies seen motivated some authors to investigate organic dyes, with more success. Recently the highest ZTO based DSCs efficiency has been achieved of 6.3% using hierarchically structured mesoporous ZTO microspheres assembled, from nanobeads with an organic dye and the iodide-triiodide redox mediator, [11] higher than any reported ZTO|N719 system. The high efficiency resulting from these ZTO aggregated nanobead microspheres was attributed to the high LHE, resulting from the high surface area, high light scattering resulting

from the microsize as scattering centres, efficient electrolyte penetration which was claimed to be an issue with I^-/I_3^- in an organic solvent. [11, 38] Meanwhile, Wang reported 4.28% for ZTO nanoparticles sensitized with organic dye [24], with it being observed that higher dye packing densities can be achieved on ZTO, due to its higher isoelectric point (IEP) compared to TiO_2 [24]. One of the advantages of organic dyes is the higher extinction coefficient, therefore near unity LHE can be achieved for films of either ZTO and TiO_2 with even modest surface areas.

Most of micro and nano size ZTO morphologies were synthesised either using a surfactant to control the morphology or using long synthesis procedures or obtained as a mixed crystalline phase (presence of other phases, mostly SnO_2).[39-41]

There are many advantages to use ZTO aggregated nanoparticles morphologies compared to other counterparts-nanoparticles, nanoplates, nanowires, nanoflower, etc. [6, 19, 22, 27, 42] Cubic ZTO aggregated nanoparticles can ensure high dye loading through maintaining high surface area, the packing density of cubic ZTO aggregated nanoparticles also can enhance the light scattering ability and also the planar contact among these aggregates particles can form a uniform connected porous structure which is important for better electron transportation and better electrolyte diffusion.[12, 43] The cubic ZTO aggregated nanoparticles was observed as an initial shape during some synthesis[8, 44], however, there are only two reports to date of cubic ZTO aggregated nanoparticles for DSCs, both with efficiencies of about 2% when sensitized with N719.[21, 45] Therefore, the appropriate particle size and the phase purity need to be obtained for efficient photoanode material based on DSCs (as shown in this work).

In ZTO synthesis, crystalline phases formed and their morphology are strongly affected by the Zn/Sn metal ion ratio and mineralizer concentration. [12, 39] Zinc Tin hydroxide $ZnSn(OH)_6$ is generally formed as an intermediate phase due to the reaction of $Zn(OH)_4$ and $Sn(OH)_6$, which

themselves result from the reaction of Zn^{2+} and Sn^{4+} ions respectively with OH^- , released from the mineralizer in the alkali solution.[12, 21, 39, 45, 46] At temperatures over 200 °C $\text{ZnSn}(\text{OH})_6$ can be thermally decomposed to Zn_2SnO_4 and either SnO_2 or ZnO depending on the Zn/Sn ratio in the precursor.[12, 39] High sintering temperatures, in the range of 600-800 °C, normally result in thermal decomposition of ZTO and forms ZTO composited with other phases such as SnO_2 or ZnO . [12, 13, 21, 25, 45, 47-50]

It is expected that the presence of other secondary crystalline phases, such as ZnO or SnO_2 among the cubic ZTO aggregates nanoparticles, could negatively impact DSC efficiencies, as previously reported by some authors.[21, 45] As such, and in the interest of completeness, the performances of mixed oxide ($\text{ZTO}+\text{SnO}_2$ and $\text{ZTO}+\text{ZnO}$) based DSCs were also investigated in this work. Typically either large particle sizes (low surface area) or excess SnO_2 result when synthesised using a Zn/Sn ratio of 1:1, and/or using mineralizers.[12, 39, 45, 48, 49] Although Zn_2SnO_4 stoichiometry assumes Zn:Sn=2:1, using this ratio of precursors has been shown to produce ZTO with a secondary ZnO phase [13, 25, 50]. Therefore, in order to synthesise a pure phase of ZTO cubes aggregated nanoparticles sintering temperature, Zn:Sn of 1:1 ratio and the amount of mineralizer should be carefully adjusted.

In spite of the number of reports on ZTO to date, the band gap value is still controversial, with values from 3.2-3.9 eV reported.[21, 39, 48, 51] The sintering temperature and presence of SnO_2 as a secondary phase are likely to be factors affecting the measurement of the optical band gap of ZTO, as well as multiple trap states, located near to the conduction band edge. [45, 48] One of the larger estimates of the band gap (around 3.8 eV) was reported using a photo-electrochemical method, indicating that trap states are localised close to the conduction band, resulting in smaller

optical band gap values.[39] Also, It has been reported that the presence of a secondary phase of SnO₂ in ZTO resulted in stronger UV absorption.[48]

In this work, cubic aggregates of ZTO nanoparticles, along with some non-aggregated particles, have been synthesised using a mixed solvent approach (ethanol: water) and control of the sintering temperature. Zinc acetate Zn(CH₃COO)₂·2H₂O and sodium stannate Na₂SnO₃·3H₂O were used as precursor materials (1:1 Zn:Sn atomic ratio) in a mixture of ethanol and water without any additional mineralizer. This procedure gave a phase pure, polycrystalline ZTO material, with morphology as mentioned above.

DSC performance was investigated using the synthesised ZTO, formed into porous films, deposited on top of a ZTO blocking layer and sensitized with either the organic dye D149 or N719. Previously there has only been one study using a ZTO blocking layer to limit charge recombination from the FTO. Shin *et al.* deposited ZTO using a pulsed laser deposition method.[37] While others have also tried to use TiO₂ blocking layers (from TiCl₄), the higher conduction band edge of TiO₂ (compared to ZTO) introduced a barrier and led to a decreased efficiency compared to the devices without a blocking layer.

In this work, DSCs using ZTO sensitized with D149 is shown to lead to a PCE of about 4.9%, higher than that of ZTO sensitized with N719 (4%). The value of 4.9% achieved here is among the highest reported for ZTO based DSCs. As mentioned above, N719 is commonly used in DSCs (as it has been a benchmark dye for many years now), however low quantum efficiencies have regularly been observed when using ZTO, especially compared to on TiO₂, while both semiconductors had similar responses with organic dyes. We examine this discrepancy, which may allow for even higher ZTO conversion efficiencies in the future.

2. Experimental

2.1 Synthesis of ZTO material

1 mmol of zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$, Sigma-Aldrich) and 1 mmol of sodium stannate trihydrate ($\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, 95%, Aldrich) were dissolved separately in mixtures of ethanol (100% Chem-Supply) and distilled water (1:1 v/v). After stirring for 20 minutes, the sodium stannate solution was added dropwise to the zinc acetate solution ($\text{Zn}:\text{Sn}=1$) and again stirred for 20 min. The solution was then transferred into a Teflon-lined stainless steel autoclave bomb, 45 mL (Parr Instrument Company) and heated up to 180 °C for 12 h (ramp rate 1 °C/min starting from RT). After cooling down to room temperature, the obtained white precipitate was thoroughly centrifuged (several times) with a mixed solution (again 1:1 distilled water: ethanol) to remove any unreacted material. After that, the powder was dried overnight at 90 °C and calcined at 400 °C for 6 h (ramp time 5 °C/min). Alternately, 2 mmol zinc acetate dihydrate and 1 mmol sodium stannate trihydrate ($\text{Zn}:\text{Sn}=2$) were used following the above protocol.

A ZTO precursor solution, prepared using a modified solvothermal method [52] was employed to deposit a ZTO blocking layer. Here, 0.66 g of zinc acetate dihydrate (0.150 M) and 0.53 g of (tin (IV) chloride pentahydrate, 98%, Sigma-Aldrich) (0.075 M) were dissolved in 20 ml of absolute ethanol and stirred for 2 h. (NaOH, $\geq 97\%$ Sigma) (0.5 M) was added dropwise stirred for more 1 h. The solution was solvothermal treated at 180 °C for 12 h (ramp time 1 °C/min). After cooling down to room temperature, the precursor was used to deposit a dense ZTO blocking layer by spray pyrolysis (details below).

2.2 Materials Characterizations

The crystalline diffraction peaks of ZTO were examined using X-ray diffractometer (Bruker Advance, 40 kV, 30 mA) ($\text{Cu K}\alpha$, $\lambda = 1.5406 \text{ \AA}$) in the range of ($2\theta = 20^\circ\text{-}80^\circ$) with scan rate

(1°/min). The morphology and internal structure of ZTO were examined by field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7500) and transmittance electron microscopy TEM (JEOL JEM-2010). Microtrac Belsorp-mini nitrogen adsorption-desorption equipment was used to obtain specific surface area, and pore size distributions using the Brauner-Emmett-Tell (BET) and Brauner-Joyner-Halenda (BJH) approaches. The amount of N719 and D149 dyes on the different films was calculated by measuring the absorbance of dyes desorbed from the films (thickness = $5 \pm 0.3 \mu\text{m}$, area = 1 cm^2) in (4 ml) of (0.1 M) NaOH solution (distilled water: ethanol 1:1 v/v) for N719 or in (4 ml) of (0.4 M) NaOH in methanol (100% Chem-Supply) for D149 using a Shimadzu UV-3600 spectrophotometer. The diffuse reflectance and optical band gap measurements were conducted using an integrating sphere (ISR-3100) and the above spectrophotometer. A Veeco Dektak 150 Surface Profiler was used for the film thickness measurements. Zetasizer Nano-ZS was used to measure zeta potentials of TiO_2 and ZTO in order to determine the isoelectric points. TiO_2 and ZTO aqueous solution with different pH values (2-12) were prepared using 0.25 M NaOH and 35-37 vol% HCl (Sigma-Aldrich) to increase and decrease the pH values respectively. VSP-300 potentiostat workstation (Biologic science instruments) was used to carry out Mott-Schottky measurements (conducted at 1 kHz) to determine the flat band potential of TiO_2 and ZTO films ($3 \mu\text{m}$) deposited on FTO glass. 0.1 M (Na_2SO_4 , $\geq 99\%$ Sigma-Aldrich) was used as an electrolyte, Saturated Calomel Electrode (SCE) as a reference electrode and platinum counter electrode. Simulated solar illumination (Oriel LCS-100, 100 mW/cm^2) was used to measure the photocatalytic activity of ZTO and TiO_2 materials dispersed in an aqueous solution of (Rhodamine B dye, 95% Sigma) (catalyst loading $\sim 20 \text{ mg}$ per 20 mL of $25 \mu\text{M}$ dye solution). Shimadzu IR prestige-21 was used to measure FTIR spectra of dyed/undyed TiO_2 and ZTO films ($3 \mu\text{m}$ thicknesses) and for N719

and D149 dyes powders. The transmittance spectra of materials in FTIR measurements were normalized to make a reasonable comparison. Keithley 2400 used to measure the J-V response for ZTO blocking layer test.

2.3 Software

- ChemDraw Professional V17.1 and Chem3D V17.1 were used to draw the dyes structure and calculate the spacing between the functional groups.
- Vesta software was utilized to draw the crystalline structure of TiO₂ and ZTO.

2.4 DSC device assembly

ZTO and TiO₂ photoanodes were prepared as follows: FTO glass (Hartford) was cleaned using soapy water, acetone (100% Chem-Supply) and then ethanol in three successive sonication steps. Following this, it was heated to 450 °C where a blocking layer was deposited by spray pyrolysis. The ZTO precursor is described above, while a 1:9 v/v in ethanol dilution of titanium diisopropoxy bis(acetylacetonate) solution (75 wt.% in IPA, Sigma) in ethanol was used for TiO₂. After cooling down to room temperature, porous layers were deposited using commercially available TiO₂ pastes (NR18-T, WER2-O, Dyesol, Australia) or a ZTO paste prepared by a method analogous to one reported previously.[53] While TiO₂ was screen printed, ZTO was cast by a doctor blade method.

After that, the printed photoanodes were sintered using a multi-step program (up to 500 °C). Finally, TiO₂ photoanodes were treated by soaking the photoanodes in (20 mM) aqueous solution of (TiCl₄, ≥99% Fluka) for 30 min at 70 °C, then washed and re-sintered at (500 °C for 30 min), the photoanodes were immersed in an 0.5 mM N719 (Solaronix) dye solution of a mixture of tert-butanol (≥99% Sigma-Aldrich) and acetonitrile (99.8% Sigma-Aldrich) [1:1 v/v], or 0.5 mM D149 (1-material, Canada) also in a 1:1 (v/v) mixture of acetonitrile and tert-butanol. The

photoanodes were taken out from the dye solution after 24 h and washed with acetonitrile and then dried.

Counter electrodes were prepared by first drilling holes in a separate piece of FTO glass, to be used as a filling port for the electrolyte solution. One drop of 10 mM ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\geq 37.5\%$ Sigma-Aldrich) solution (in ethanol) was smeared on the cleaned pre-FTO counter electrode and heated to 400 °C for 20 min. The counter electrodes are cooled before being sandwiched together with the photoanode, using a 25 μm Surlyn (Solaronix) spacer, by a hot press. The electrolyte solutions [acetonitrile/valeronitrile (99.5% Aldrich) (85:15 vol %), 0.03 M iodine (I_2) (99.999% Merck), 0.5M 4-tertbutyl pyridine (4-tBP) (96% Aldrich), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII) (99% Sigma-Aldrich), and 0.1 M guanidinium thiocyanate (GuSCN) ($\geq 99\%$ Sigma-Aldrich)] for N719 or [50 mM iodine (Sigma), 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (Solaronix), 0.1 M lithium iodide (99% Acros Organics) in 3-methoxypropionitrile ($\geq 98\%$ Sigma-Aldrich)] for D149 were introduced into the filling port by the vacuum back-filling technique, and the filling port was then closed with a piece of Surlyn laminated to aluminium foil.

2.5 Device characterizations

Photocurrent density-voltage (J-V) measurements were measured using a solar simulator with an AM1.5 filter; set to 1 sun ($100 \text{ mW} \cdot \text{cm}^{-2}$, PV Measurements, Colorado). A QEX10 system from (PV Measurements) was used for the incident to photocurrent conversion efficiency (IPCE) measurements in 5 nm steps. A Reference 600 Potentiostat (GAMRY instrument) was used for electrochemical impedance spectroscopy measurements (EIS) which were carried out for DSCs based on different photoanodes under 1 sun illumination at V_{oc} in a frequency range ($0.1\text{--}10^6$ Hz) and AC voltage of 10 mV.

3. Results & Discussion

3.1 Nanostructure analysis

X-ray diffraction patterns (Figure 1a), and Selected Area Electron Diffraction (SAED) (Figure 1b) confirmed that both individual (non-aggregated) particles and those in the secondary cubic aggregates are both cubic spinel-type ZTO (JCPDS no. 00-24-1470). From this trace, the crystal size was estimated by the Scherrer equation to be about 13 nm. The crystallinity of the ZTO phase was controlled by adjusting the precursor concentration and sintering temperature, with pure, ZTO obtained by using a 1:1 Zn:Sn ratio and 400 °C. Crystalline SnO₂ appeared when using higher calcination temperatures (600-800 °C) and leads to a distortion in the shape of the cubic aggregated structures. It is believed that SnO₂ is present the whole time, however, does not crystallise until higher temperatures are reached, which is investigated below with quantitative XRD analysis. Mixed-phase products, including either ZTO:ZnO or ZTO:SnO₂:ZnO, were obtained when using a precursor ratio of 2:1 Zn:Sn (atomic) with either 400 °C or 800 °C calcination temperatures respectively (Figure S1a-d).

Scanning Electron Microscopy (SEM), (Figure 1c) and Transmission Electron Microscopy (TEM), (Figure 1d) shows the morphology and particle size of the synthesised ZTO sample. A secondary cubic structure of aggregated nanoparticles, with average size 75 nm, along with some unbound nanoparticles, both with an average size (13 nm), were observed. The majority of the ZTO nanoparticles were assembled to form these aggregate cubes during the solvothermal reaction (Figure S2a).

High-resolution TEM images (HRTEM) (Figure 1e and f) show the interplanar distances and the corresponding miller indices that again confirm the crystalline structure of the primary ZTO nanoparticles which form the secondary cubic structures. It can be noted that some ZTO

nanoparticles and cubic aggregated nanoparticles showed no fringes, indicating partially crystallisation, which suggests the presence of amorphous ZTO or SnO₂.

Na₂SnO₃·3H₂O is used here as a source of Sn⁴⁺ ions and as a mineralizer at the same time, reducing the formation of an excess of Sn(OH)₆ which in turn, could be thermally decomposed or reacted with the initial phase of ZnSn(OH)₆ during the solvothermal reaction and eventually produce SnO₂ as a separate phase. [12, 39] A 1:1 Zn:Sn ratio was found to be the optimum ratio, to prevent formation an undesirable excess of Zn(OH)₄ which can be thermally decomposed to ZnO resulting in a mixed phase ZTO+ZnO.[25] As for the calcination process, 400 °C is the optimum calcination temperature to form a pure polycrystalline ZTO, while at 800 °C, SnO₂ is also seen in other phases (Figure S1). Of those trialled, 400 °C was the highest that did not lead to decomposition of ZTO into other materials, but was high enough to give good crystallinity.

Using Zn:Sn =1, the resultant intermediate phase was ZnSn(OH)₆ with residual (unreacted) Zn(OH)₆ and Sn(OH)₄, as seen in Figure S1a. Since the ZnSn (OH)₆ is a metastable phase which can easily react with Zn(OH)₆ at 400 °C to form Zn₂SnO₄, Sn(OH)₄ can also easily thermally decomposed at this temperature to SnO₂ and OH⁻, however, it is not high enough to crystallise SnO₂, leaving amorphous SnO₂. At calcination temperature between (600-800 °C), this amorphous SnO₂ phase was seen to crystallise.

When a 2:1 Zn:Sn ratio nominally giving the correct stoichiometry was used, both ZnSn(OH)₆ and ZnO were seen after synthesis. It is speculated that some Sn⁴⁺ remains in the supernatant in the reaction vessel. Calcination at 400 °C (see Figure S2b) produced a Zn₂SnO₄+ZnO composite, while higher temperature (800 °C) treatments resulted in Zn₂SnO₄+ZnO+SnO₂. After the solvothermal reaction, the resulting intermediate phase (Figure S1b) is also ZnSn(OH)₆ and Sn(OH)₄, however, with a higher amount of unreacted Zn(OH)₆, some Zn(OH)₆ will decompose

to $\text{ZnO} + \text{OH}^-$. $\text{ZnSn}(\text{OH})_6$ can react with $\text{Zn}(\text{OH})_6$ at 400 °C calcination temperature to form Zn_2SnO_4 while $\text{Sn}(\text{OH})_4$ and the excess of $\text{Zn}(\text{OH})_6$ can easily decompose to $\text{SnO}_2 + \text{OH}^-$ and $\text{ZnO} + \text{OH}^-$ respectively. This temperature is high enough to crystallise ZnO but not SnO_2 , resulting in an amorphous SnO_2 with crystallised ZnO and low crystalline degree of ZTO. At higher calcination temperatures between (600-800 °C), the amorphous SnO_2 converted to a crystalline phase in addition to well-crystallised ZnO and ZTO.

The proposed chemical reaction mechanism during the synthesis of ZTO is described by scheme 1,

Scheme 1: Proposed mechanism of synthesis polycrystalline cubic aggregates of ZTO nanoparticles from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{SnO}_4 \cdot 6\text{H}_2\text{O}$ as first materials by solvothermal reaction method.

As mentioned, the ZTO sample used for making devices (1:1 Zn:Sn) was suspected of containing amorphous SnO_2 , [48] accordingly, the reference intensity method (RIR) of XRD analysis for quantification analysis was used to assess the degree of crystallinity and quantify the amorphous content. [54] ZTO was mixed with about 10% silicon to act as an internal standard. In

spite of the XRD patterns in Figure 1a showing only a crystalline phase of ZTO (*i.e.* no other crystalline phases such as SnO₂ or ZnO), the lower peak intensity and the broadening hump observed in the diffraction patterns of ZTO compared to those of silicon confirmed the presence of some amorphous content after treatment at 400 °C which could be a non-crystallized SnO₂ (Figure S2b). This amount of amorphous content was only about 10% which may belong to SnO₂ or/and ZTO. This may affect the performance of DSCs,[55] however, a protocol for its removal has not yet been developed and is the subject of further investigation.

Figure 1: Structural characterizations of solvothermally synthesised (180 °C for 12 h) Zn_2SnO_4 (ZTO) (1:1 at. Zn:Sn), sintered at 400 °C for 6 h (a) X-ray diffraction patterns; (b) Selected Area Electron Diffraction (SEAD); (c) SEM, (d) TEM and (e,f) HRTEM of crystalline ZTO aggregated nanocubes and ZTO nanoparticles (from d).

Figure 2 a and b show the nitrogen adsorption/desorption isotherm, and the pore size distributions, calculated by the Barrett-Joyner-Halenda (BJH) technique of the phase pure ZTO sample, along with those of commercial TiO_2 nanoparticles (NR18-T) and TiO_2 scattering particles (WER2-O). The ZTO synthesised here, has a lower specific surface area ($58 \text{ m}^2 \cdot \text{g}^{-1}$) than that of NR18-T ($79 \text{ m}^2 \cdot \text{g}^{-1}$) but higher than that of WER2-O ($15 \text{ m}^2 \cdot \text{g}^{-1}$), as shown in Table 1. BJH analysis showed the mean pore diameter in the ZTO to be about 7.5 nm, which is smaller than both those of the transparent nanoparticles at 27 nm and the large scattering particles, which were 39-120 nm (not shown here due to equipment limitations). The small pores seen with ZTO are due to the high packing density. This tight packing of the nanoparticles in the aggregate also results in a lower porosity of 41% as compared to NR18-T at 66% (Table 1).

Figure 2: (a) N_2 adsorption/desorption isotherm; (b) the pore size distribution measurements of ZTO, NR18-T and WER2-O materials.

Table 1: Porosity, surface area of ZTO, 18NR-T, and WER2-O.

Samples	Porosity (%) ^a	Specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)
ZTO	41	58
NR18-T	66	79
WER2-O	35	15

^a the porosity calculated as $P = P_V / (\rho^{-1} + P_V)$, where P_V is the pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$), and ρ^{-1} is the inverse of the density of anatase TiO_2 or ZTO ($\rho^{-1} = 0.257$ and $0.155 \text{ cm}^3 \text{ g}^{-1}$) respectively.[23, 56]

In spite of having a slightly lower surface area than the TiO_2 nanoparticles, dye desorption measurements confirmed that ZTO could host a larger number of dyes per unit volume and higher dye packing density (dye molecules/ nm^2) for both N719 and D149 dyes as shown in Table 2 and Figure 3S. This may be attributed (at least in part) to the higher isoelectric point (IEP) of ZTO, as shown in Figure3a. The measured isoelectric point (IEP)s of ZTO and TiO_2 , were (pH = 8.3) (pH = 4.6) respectively, which can explain the higher dye loading on ZTO [23-25] (Table S1).

Table 2: Dye loadings of D149 and N719 on TiO_2 and ZTO films (thickness $5 \pm 0.3 \mu\text{m}$).

Dye	Photoanode	Dye loading ($\text{nmol} \cdot \text{cm}^{-2}$)	Dye loading ($\mu\text{mol} \cdot \text{cm}^{-3}$)	Dye packing ^a (nm^{-2})
D149	ZTO	69.7 ± 0.3	107.3 ± 0.5	2.6
	TiO_2 (NR18-T)	64.1 ± 0.6	98.6 ± 0.9	1.3
	TiO_2 (WER2-O)	20.2 ± 0.2	29.0 ± 0.3	1.5
N719	ZTO	80.4 ± 0.2	123.7 ± 0.3	2.3
	TiO_2 (NR18-T)	69.8 ± 0.6	107.4 ± 0.9	1.2
	TiO_2 (WER2-O)	23.3 ± 0.6	35.8 ± 0.9	1.3

^a dye packing density on ZTO and TiO_2 calculated using the porosity, surface area and dye loading per film area. [57]

Figure 3b shows the diffuse reflectance of films of 18NR-T, WER2-O and ZTO at the same thickness as used in the devices for each configuration. ZTO showed better scattering in the

whole wavelength range (>400 nm) compared to NR18-T but less than WER2-O. The scattering of ZTO could further contribute to enhancing the LHE.

3.2 Photovoltaic Tests (J-V & IPCE)

Device performances were investigated under simulated sunlight with either ZTO, or TiO₂ sensitized with either N719 or D149. As can be seen from Figure 3c and Table 3, TiO₂ and ZTO devices sensitized with D149 show similar J_{sc} values, however, the obtained V_{oc} using ZTO is ~80 mV lower. Similar deference in V_{oc} is seen with N719, however here the J_{sc} s are markedly different, with that of ZTO being about half that of N719|TiO₂. Interestingly, the ZTO|N719 devices have higher FF values than TiO₂|N719 ones, suggesting that recombination may not be as much of an issue, as other authors have previously claimed. [6, 9, 10, 21, 24, 45] This is investigated in depth later in this manuscript.

The peak quantum efficiencies of devices based on ZTO sensitized with D149 are comparable to those of TiO₂ sensitized with D149 and N719 while ZTO sensitized with N719 showed low quantum efficiency (Figure 3d); with these results matching well with the J_{sc} values of the devices measured under 1 sun.

Table 3: Key parameters from J-V measurements DSCs with photoanodes consisting of ZTO or TiO₂ sensitized with N719 or D149.

Device	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
ZTO D149	13.3 ± 0.4	0.56 ± 0.02	65 ± 1	4.9 ± 0.2
TiO ₂ D149	13.8 ± 0.2	0.64 ± 0.02	62 ± 1	5.5 ± 0.1
ZTO N719	8.2 ± 0.5	0.68 ± 0.01	73 ± 1	4.0 ± 0.2
TiO ₂ N719	14.3 ± 0.2	0.76 ± 0.01	68 ± 3	7.4 ± 0.3

The thickness of ZTO photoanodes sensitized with N719 and D149 dyes were optimized to give the highest PCE (see Table S2 and Table S3).

The effect of using spray pyrolysis deposited ZTO blocking layer on the performance of ZTO|D149 based devices was also investigated, with the sprayed ZTO layer shown to acts as a blocking layer, in Figure S4a and b. The performances of devices made using ZTO prepared either with 2:1 Zn:Sn ratio (i.e. resulting in the formation of a secondary phase of ZnO) or with 1:1 Zn:Sn ratio with high-temperature treatment (including SnO₂) were measured, using D149 and are shown in Figure S5 and Table S4. These devices showed substantially lower solar performance compared to devices based on a pure ZTO crystalline material.

Figure 3: (a) Isoelectric point measurements of TiO₂ and ZTO in aqueous solutions with different pH values; (b) Diffuse reflection measurements (film thickness 18 μ m, 12 μ m and 5 μ m for ZTO, NR18-T and WER2-O respectively); (c) J-V characterizations; (d) IPCE measurements, of devices based on TiO₂ and ZTO.

3.3 Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were carried out under open circuit conditions and simulated solar illumination (1 sun), to compare charge transfer rates and lifetimes under operational conditions, with Nyquist and Bode plots shown in Figure 4a and b respectively. This is particularly of interest in the context of literature claims about recombination issues in ZTO DSCs and concerns about trap states. Nyquist plots, which were fitted in Figure S6 using an equivalent circuit shown in the inset and Table 4, show that devices based on TiO_2 sensitized with either D149 or N719 have a slightly lower resistance to charge transport (R_{ct2}) compared to their ZTO counterparts. The R_{ct2} of devices based ZTO sensitized with D149 is also slightly lower than that of ZTO|N719. This is however not enough of a difference to explain the variation in J-V responses. Indeed, the differences in EIS responses here can themselves be explained by the lower J_{sc} seen in devices based on ZTO|N719 (lower charge injection leading to lower charge density in the films during testing).

As shown in Figure 4b, the frequencies of the local impedance maxima (f_{max} , low frequencies) in the devices based on TiO_2 and ZTO sensitized with D149 were 31 Hz and 50 Hz respectively. The electron lifetime was calculated using $\tau_n = 1/2\pi f_{max}$. In TiO_2 based devices these values are seen to be longer than in their ZTO counterparts, consistent with observed R_{ct2} values. While frequencies of the local impedance maxima in the devices based on TiO_2 and ZTO sensitized with N719 were 25 Hz and 79 Hz respectively, indicating there is the more substantial difference between their electron lifetimes. In addition, the electron transit diffusion time (the electron transit time) calculated using $\tau_d = 1/f'_{max}$, where f'_{max} is the maximum frequency of the second semicircle, which is 80 μs for ZTO|D149 devices 40 μs for TiO_2 |D149 60 μs for TiO_2 |N719 devices, and 100 μs for ZTO|N719. This final value indicates slower charge transfer, in line with

expectation for a device with low charge density. The shorter electron lifetimes (τ_n) and longer electron transit diffusion times (τ_d) along with lower charge density of devices based on ZTO|N719 and ZTO|D149 could affect the charge collection efficiency.

Furthermore, devices based on TiO_2 sensitized with either D149 or N719 showed higher chemical capacitance (C_μ) compared to ZTO, in line with higher carrier density.[58]

Figure 4: EIS measurements (a) Nyquist plots; (b) Bode plots of DSCs using TiO_2 or ZTO, sensitized with either D149 or N719 dyes.

Table 4: Electrochemical impedance spectroscopy measurements of TiO_2 and ZTO sensitized with D149 and N719 Dyes.

Device	R_s ($\Omega \cdot \text{cm}^{-2}$)	R_{ct1} ($\Omega \cdot \text{cm}^{-2}$)	R_{ct2} ($\Omega \cdot \text{cm}^{-2}$)	C_μ ($\mu\text{F} \cdot \text{m}^{-1}$)
ZTO D149	4.9 ± 0.1	4.6 ± 0.1	28.6 ± 0.4	370 ± 40
TiO_2 D149	4.9 ± 0.1	4.1 ± 0.1	24.8 ± 0.3	900 ± 60
ZTO N719	4.9 ± 0.1	5.0 ± 0.4	32.5 ± 0.5	200 ± 30
TiO_2 N719	4.9 ± 0.1	4.3 ± 0.3	20.0 ± 0.4	930 ± 140

Using the above lifetime values, a lower bound estimation of the collection efficiency can be calculated as $\Phi_{cc}=1-(\tau_d/\tau_n)$. [59, 60] Both TiO₂|N719 and TiO₂|D149 based devices show similar charge collection efficiencies of ~99%, while ZTO|D149 has 97.5% and ZTO|N719 ~95%. In other words, the charge collections efficiencies in all the devices here are close to 100%, and the lower J_{sc} observed in ZTO|N719 devices is shown to not originate from charge recombination losses. Based on these observations of high light harvesting and charge collection efficiencies, the poor performance of ZTO|N719 is concluded to be related to charge injection issues.

At present, the highest efficiency TiO₂|N719 based devices in the literature use a Li⁺ free electrolyte, in contrast to DSCs made with TiO₂ and most other dyes, where it (or similar small cations) are understood to be essential for good charge injection and electron transport. [61, 62] To probe whether the absence of Li⁺ is the leads to low charge injection efficiency (Φ_{inj}) in ZTO|N719, devices were prepared using the same Li⁺ containing electrolyte as for the D149 based devices (Figure S7 and Table S5). While there is an enhanced J_{sc} (~15%) compared to the standard Li⁺ free electrolyte, there is also a lower FF and V_{oc} . Even though the maximum IPCE values of ZTO|N719 devices with different electrolyte compositions were roughly the same (~40%), the Li⁺ containing one resulted in a broader shape, leading to higher J_{sc} , although still well below those of the ZTO|D149 devices.

Figure 5a shows Mott-Schottky measurements for undyed TiO₂ and ZTO films. The E_{fb} value can be determined from the extrapolation of $1/C^2$. [63] The E_{fb} of ZTO (-0.68 V vs. SCE) is lower than that of TiO₂ (-0.78 V vs. SCE) suggesting the conduction band edge of ZTO should also be slightly lower than that of TiO₂. Since the conduction band edges (E_{CB}) of n-type semiconductors are typically reported to be approximately 0.1 eV more negative than their flat band potential value (E_{fb}), depending on the electron effective mass and the carriers concentration [64], the

approximated conduction band edges of ZTO and TiO₂, in the vacuum level scale, are -4.1 eV and -4.0 eV respectively [E (eV) = -4.5+[-SCE +0.244]].^[64-66] This lower E_{fb} potential, measured for ZTO compared to TiO₂, is consistent with values reported previously [14, 37, 44, 60, 67] and should favour charge injection, ruling out lower chemical driving forces (ΔG_{inj}) as a reason for low Φ_{inj} . Furthermore, these differences in CB edge are similar to the ~80 mV differences seen in the device in V_{oc} values.

Mott-Schottky plots also show that ZTO has a lower charge density than TiO₂, which can be estimated from the slope in the fitted Mott-Schottky plots $N_d = (2/e_0\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1}$ where N_d the electron donor density, e_0 the electron charge, ϵ the dielectric constant, ϵ_0 the permittivity of vacuum, C the capacitance and V the applied voltage. [68] The lower charge density of ZTO is confirmed by Mott-Schottky and the electrochemical capacitance (C_μ). Thus the lower charge density of ZTO along with lower extinction coefficient of N719 may slightly affect Φ_{cc} .

Figure 5b shows the measured optical band gap of TiO₂ and ZTO and a complete energy level diagram is shown in Figure 5c, with oxidation potentials of the dyes (measured attached to these semiconductors respectively, see Figure S8a-c) [69], while the I/I_3^- potential was obtained from the literature [70]. The optical bandgaps of TiO₂ and ZTO are seen to be 3.2 eV and 3.1 eV respectively; a factor further explored later in this manuscript with respect to photoactivity under AM1.5 illumination.

Figure 5: (a) Mott-Schottky measurements of TiO₂ and ZTO; (b) Tauc plot measurements of TiO₂ (inset) and ZTO, and (c) the relevant energy levels of the different components of the four DSC configurations.

As dye aggregation has previously been seen to be an impediment to charge injection efficiency,[71] and N719 packing on ZTO was shown to be higher than on TiO_2 . Films were examined after short (15 min) and long (24 hours) dying times, with only a slight shift in the ZTO|N719 absorbance peak position observed suggesting aggregation not significant. This was followed by with devices produced using with thin film ZTO|N719 DSCs, either with or without chenodeoxycholic acid as a co-adsorbant,^[71] to prevent aggregate formation. The Absorbed Photon to Charge carrier Efficiencies (APCE) for these devices were quite similar, discounting dye aggregation as a major contributing factor to the low J_{sc} in ZTO|N719 devices (Figure S9). It was however noted during this that the dye absorption profiles of N719 on ZTO were markedly different to those on TiO_2 , while ZTO|D149 and TiO_2 |D149 films showed similar absorbance profiles (Figure 6, below). The causes for these observed differences are explored further below.

Figure 6: Dye aggregation measurements on TiO_2 and ZTO films (a) N719 dye and (b) D149 dye.

3.4 Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy was employed to examine the bindings of both D149 and N719 on the two semiconductors (Figure 7a and b). As shown in Figure 7a, little difference was observed comparing ZTO|D149 and TiO₂|D149, in line with expectations given that there is only one carboxylic acid binding group as shown in Scheme 2a, limiting the ways in which the dye can bind to the surface (also corresponding well with the absorption properties in Figure 6).

Meanwhile, the FTIR response of N719 is strongly dependant on the semiconductor. It has previously been reported that N719 can bind to TiO₂ through a number of different mechanisms[72], including through two COOH groups on different bipyridyl ligands (bpy) (Scheme 2b), or COOH and COO⁻ on the same one. This second configuration may explain the presence of some residual COOH in the FTIR spectra of (at $\sim 1700\text{ cm}^{-1}$). The presence of dyes bound through a combination of these mechanisms can also explain the split in the NCS vibration (2102 and 2079 cm^{-1}) for N719|TiO₂, as the different configurations of N719 will either result in the ligand being pointed away from the surface (where it will not interact). In the case of binding through -COOHs of the two bpy's it will be far from the surface, while it will point slightly towards the surface if bound through COOH and COO⁻ groups on the same bpy.

The differing FTIR results for N719 bound to surfaces can be explained by looking inter-atomic spacing of the metals in the two oxides. In TiO₂ Ti are $\sim 3.78\text{ \AA}$ apart, which corresponds reasonably well with both the $7.1\text{ \AA}$ separation of the COOH and COO⁻ (measured from the carbon) and the $8.46\text{ \AA}$ between COOH on neighbouring bpy's (two across one down, similar to the way a knight moves in chess) as shown in Figure S10 and Scheme 2c-e. This suggests that both binding mechanisms should be favourable, with minimal strain. Meanwhile, the spacing of neighbouring metals in ZTO is $\sim 8.65\text{ \AA}$, which can accommodate binding from two COOH

groups, albeit with more strain than the dye experiences on TiO_2 . The alternate is of course that the dye only binds through one COOH , however the absence of COOH group vibration in the FTIR for N719/ZTO suggests this may not be so common. The single, symmetric binding mechanism of N719 to ZTO would be more likely to lead to the sharp optical absorption peak, whereas the combination of mechanisms on TiO_2 gives rise to a broader, convoluted absorption peak. This symmetry would also explain the presence of only one NCS peak (at 2102 cm^{-1}). It has also been claimed recently that the interaction between the NCS ligand and TiO_2 plays a major role in the effectiveness of this dye.[73, 74]

Figure 7: FTIR spectroscopy measurements (a) D149 dye; and (b) N719 dye as films and on TiO_2 and ZTO films.

Scheme 2: The chemical structures of (a) D149 and (b) N719; The crystalline structure of (c) ZTO and (d and e) TiO₂.

The binding between D149 and ZTO is similar to TiO₂ resulting from similar interaction with D149. There are multiple modes of binding between N719 and TiO₂, but more simple for N719 on ZTO, which correlates with less broadening in the optical absorption, as well as lower charge injection yields.

As N719 remains a common benchmark dye, especially for new (non-TiO₂) metal oxide semiconductors (MOS), the understanding developed here may be useful to other researchers and motivation to revisit previous materials.

3.5 Photo-degradation measurements

One of the key arguments in favour of using materials such as ZTO is their decreased response to UV light, which is anticipated to translate to better photostability. It is expected that ZTO is more likely to show lower photodegradation toward organic D149 dye (less dye bleaching), in part due to a lower absorption coefficient (Figure S11). On the other hand, the thicknesses of optimal working electrodes in DSCs means the differences in extinction coefficient have limited effect on the total number of UV photons absorbed and the absorption onset of ZTO is slightly red shifted. In spite of this, the photodegradation of organic D149 dye on ZTO is expected to be less than that of TiO_2 , in line with expectation based on previous reports.[19-21]

In order to investigate the difference in the photodegradation of dye on ZTO and TiO_2 , experiments were performed using ZTO and TiO_2 in aqueous dispersion to degrade Rhodamine B, verifying the dramatic difference in photodegradation. Under the same conditions (same solid loading, initial dye concentration and irradiation), degradation rate constants of 0.05 h^{-1} and 1.4 h^{-1} were observed for ZTO and TiO_2 respectively. Absorption traces and rate constants can be seen in Figure S12.

4. Conclusion

Cubic aggregates of ZTO nanoparticles were synthesized using a simple solvothermal approach. The primary nanoparticles (13 nm) self-assembled to form cubic aggregated structures using 1:1 Zn: Sn precursor ratio, in spite of the product having 2:1 ratio. The optimum compositional ratio Zn: Sn 1:1 and optimum sintering temperature were used to control the crystallinity.

ZTO was applied and compared against a benchmark TiO₂ material as a photoanode for DSCs with film thicknesses of photoanodes optimized with either N719 or D149 dyes. The ZTO material led to 4.9% PCE devices when sensitized with D149, higher than ZTO|N719 (4%).

Although having a slightly lower surface area, ZTO afforded higher dye loading (both for D149 and N719) which was attributed to its higher isoelectric point. In spite of this ZTO|N719, however, showed a low J_{sc} . The FF of the devices and EIS investigation suggest that recombination issues are not to blame for this issue. Equally, chemical driving forces for charge injection were shown to be similar for ZTO|N719 as for TiO₂|N719, with the different performance revealed to be related to the binding configuration, seen with both dye absorption and FTIR spectroscopy. Whereas the FTIR indicates multiple modes of binding between N719 and TiO₂, only one is seen for N719 on ZTO. This also correlates with less broadening in the optical absorption, as well as lower charge injection yields.

Furthermore, ZTO|D149 showed higher photostability under exposure to broad-spectrum light (300-350 nm) indicated that D149 is less likely to degrade on ZTO than on TiO₂. One of the persisting challenges is to get well-crystalized ZTO without presence other phases due to the thermal decomposition. As such, we see that ZTO is a promising photoanode material for organic dye based DSCs. Even though the performance of ZTO based devices is still lower than TiO₂ based devices, ZTO is still a promising photoanode material.

5. ASSOCIATED CONTENT

Supporting information is available in the supplementary information file.

6. AUTHOR INFORMATION

6.1 Corresponding Author

* Andrew Nattestad anattest@uow.edu.au

* Jung Ho Kim jhk@uow.edu.au

6.2 Author Contributions

The manuscript was written through contributions of all authors. All authors have approved the final version of the manuscript. K. Al-attafi, A. Nattestad and J. Kim designed the study and research plan. K.Al-Attafi synthesized the materials, prepared devices and characterized, analyzed the results (J-V, EIS, SEM, TEM, XRD, BET, FTIR, Mott-Schottky, Zeta potential, optical measurements and photostability and photoactivity measurements). F. Jawdat and K. Al-Attafi measured and analyzed the photoactivity measurements. Amar Al-Kasay and K.Al-Attafi measured and analyzed Mott-Schottky measurements. H. Qutaish and K. Al-Attafi measured and analyzed the Zeta potential and FTIR measurements. P. Hayes and K. Al-Attafi performed and analysis FTIR measurements. K. Shim and K. Al-Attafi contacted and analyzed TEM images. Y. Yamauchi and K. Al-Attafi measured and analyzed BET measurements. K. Al-Attafi and A. Nattestad wrote and revised the manuscript. S. Dou, J. Kim and A. Nattestad supervised the study.

7. ACKNOWLEDGMENT

This work is supported by Australian Research Council Discovery Projects (ARC). The authors would like to thank the Australian National Fabrication Facility (ANFF) and Electron Microscope Center (EMC) for access to equipment. Dr Andrew Nattestad would like to acknowledge the ARC for funds (DE160100504). Kadhim AL-Attafi would like to acknowledge Prof Brian Jones and Dr. Klaudia Wagner for assistance. Kadhim Al-Attafi would like to acknowledge the Higher Committee for Education Development in Iraq (HCED) for financial support.

8. REFERENCES

- [1] B. O'Regan, M. Grätzel, *nature*, 353 (1991) 737-740.
- [2] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.*, 110 (2010) 6595-6663.
- [3] M. Ye, X. Wen, M. Wang, J. Iocozzia, N. Zhang, C. Lin, Z. Lin, *Mater.Today*, 18 (2015) 155-162.
- [4] T. Miyasaka, *Bull. Chem. Soc. Jpn.*, 91 (2018) 1058-1068.
- [5] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao, Y. Chen, *Science*, (2018).
- [6] B. Tan, E. Toman, Y. Li, Y. Wu, *J. Mater. Chem. A*, 129 (2007) 4162-4163.
- [7] B. Sunandan, D. Joydeep, *Sci. Technol. Adv. Mater*, 12 (2011) 013004.
- [8] S. Sun, S. Liang, *J. Mater. Chem. A*, 5 (2017) 20534-20560.
- [9] T. Lana-Villarreal, G. Boschloo, A. Hagfeldt, *J Phys Chem C*, 111 (2007) 5549-5556.
- [10] P.P. Das, A. Roy, P. Sujatha Devi, *Tran ICS*, 75 (2016) 147-154.
- [11] D. Hwang, J.-S. Jin, H. Lee, H.-J. Kim, H. Chung, D.Y. Kim, S.-Y. Jang, D. Kim, *Sci Rep.*, 4 (2014) 7353.
- [12] E.J. Yeom, S.S. Shin, W.S. Yang, S.J. Lee, W. Yin, D. Kim, J.H. Noh, T.K. Ahn, S.I. Seok, *J. Mater. Chem. A*, 5 (2017) 79-86.
- [13] W. Li, Q. Jiang, J. Yang, Y. Luo, X. Li, Y. Hou, S. Zhou, *Sol Energy Mater Sol Cells*, 159 (2017) 143-150.
- [14] X. Liu, C.-C. Chueh, Z. Zhu, S.B. Jo, Y. Sun, A.K.-Y. Jen, *J. Mater. Chem. A*, 4 (2016) 15294-15301.
- [15] S. Yun, Y. Qin, A.R. Uhl, N. Vlachopoulos, M. Yin, D. Li, X. Han, A. Hagfeldt, *Energy Environ Sci*, 11 (2018) 476-526.
- [16] S. Yoon, S. Tak, J. Kim, Y. Jun, K. Kang, J. Park, *Build Environ*, 46 (2011) 1899-1904.
- [17] K. Kawata, K. Tamaki, M. Kawaraya, *J PHOTOPOLYM SCI TEC*, 28 (2015) 415-417.
- [18] Y.-F. Wang, K.-N. Li, Y.-F. Xu, H.-S. Rao, C.-Y. Su, D.-B. Kuang, *Nanoscale*, 5 (2013) 5940-5948.
- [19] Z. Li, Y. Zhou, J. Zhang, W. Tu, Q. Liu, T. Yu, Z. Zou, *Cryst Growth Des*, 12 (2012) 1476-1481.
- [20] M. Muruganandham, M. Swaminathan, *Sol Energy Mater Sol Cells*, 81 (2004) 439-457.
- [21] B. Li, E. Guo, C. Wang, L. Yin, *J. Mater. Chem. A*, 4 (2016) 466-477.
- [22] J. Chen, L. Lu, W. Wang, *J Phys Chem C*, 116 (2012) 10841-10847.
- [23] A. Annamalai, Y.D. Eo, C. Im, M.-J. Lee, *MATER CHARACTER*, 62 (2011) 1007-1015.
- [24] K. Wang, Y. Shi, W. Guo, X. Yu, T. Ma, *Electrochim. Acta*, 135 (2014) 242-248.
- [25] M.N. Khan, J. Dutta, *Mater Sci Semicond Process*, 36 (2015) 124-133.
- [26] M. Miyauchi, Z. Liu, Z.-G. Zhao, S. Anandan, K. Hara, *Chem Commun*, 46 (2010) 1529-1531.
- [27] M.M. Jaculine, C.J. Raj, H.-J. Kim, A.J. Rajendran, S.J. Das, *Mater Sci Semicond Process*, 25 (2014) 52-58.
- [28] Y. Qin, Q. Peng, *Int. J. Photoenergy*, 2012 (2012).
- [29] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, T. Kyomen, M. Hanaya, *Chem Commun*, 51 (2015) 6315-6317.
- [30] K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J.-i. Fujisawa, M. Hanaya, *Chem Commun*, 51 (2015) 15894-15897.

- [31] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diao, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, *Science*, 334 (2011) 629.
- [32] H. Shimogawa, M. Endo, T. Taniguchi, Y. Nakaike, M. Kawayara, H. Segawa, Y. Murata, A. Wakamiya, *Bulletin of the Chemical Society of Japan*, 90 (2017) 441-450.
- [33] B.E. Hardin, H.J. Snaith, M.D. McGehee, *Nat Photon*, 6 (2012) 162-169.
- [34] M.K. Nazeeruddin, E. Baranoff, M. Grätzel, *Solar energy*, 85 (2011) 1172-1178.
- [35] A. Burke, S. Ito, H. Snaith, U. Bach, J. Kwiattkowski, M. Grätzel, *Nano Lett* 8(2008) 977-981.
- [36] F. De Angelis, S. Fantacci, A. Selloni, M.K. Nazeeruddin, M. Grätzel, *J. Am. Chem. Soc*, 129 (2007) 14156-14157.
- [37] S.S. Shin, D.W. Kim, D. Hwang, J.H. Suk, L.S. Oh, B.S. Han, D.H. Kim, J.S. Kim, D. Kim, J.Y. Kim, *ChemSusChem*, 7 (2014) 501-509.
- [38] S.M. Zakeeruddin, M. Grätzel, *Adv Funct Mater*, 19 (2009) 2187-2202.
- [39] Y. Zhao, L. Hu, H. Liu, M. Liao, X. Fang, L. Wu, *Sci Rep.*, 4 (2014).
- [40] N. Feng, S. Peng, X. Sun, L. Qiao, X. Li, P. Wang, D. Hu, D. He, *Mater Lett*, 76 (2012) 66-68.
- [41] Z. Lu, Y. Tang, *Mater Chem Phys*, 92 (2005) 5-9.
- [42] D. Hwang, J.-S. Jin, H. Lee, H.-J. Kim, H. Chung, D.Y. Kim, S.-Y. Jang, D. Kim, *Scientific Reports*, 4 (2014) 7353.
- [43] H.-S. Chen, H.-C. Lin, C. Su, M.-T. Shen, W.-R. Li, *J Nanopart Res*, 15 (2013) 1836.
- [44] S. Baruah, J. Dutta, *Sci Technol Adv Mater*, 12 (2011) 013004.
- [45] B. Li, L. Luo, T. Xiao, X. Hu, L. Lu, J. Wang, Y. Tang, *J Alloys Compd*, 509 (2011) 2186-2191.
- [46] Z. Wang, J. Liu, F. Wang, S. Chen, H. Luo, X. Yu, *The Journal of Physical Chemistry C*, 114 (2010) 13577-13582.
- [47] Z. Lu, Y. Tang, *Two-Step Synthesis and Ethanol Sensing Properties of Zn₂SnO₄-SnO₂ Nanocomposites*, 2005.
- [48] C. Liu, A. Piyadasa, M. Piech, S. Dardona, Z. Ren, P.-X. Gao, *J. Mater. Chem. C*, 4 (2016) 6176-6184.
- [49] R. Liu, W. Du, Q. Chen, F. Gao, C. Wei, J. Sun, Q. Lu, *Rsc Advances*, 3 (2013) 2893-2896.
- [50] M.N. Khan, M. Al-Hinai, A. Al-Hinai, J. Dutta, *Ceram Int*, 40 (2014) 8743-8752.
- [51] M.A. Alpuche-Aviles, Y. Wu, *J. Am. Chem. Soc.*, 131 (2009) 3216-3224.
- [52] G. Sun, S. Zhang, Y. Li, *Int. J. Photoenergy*, 2014 (2014) 580615.
- [53] J. Li, F. Kong, G. Wu, W. Chen, F. Guo, B. Zhang, J. Yao, S. Yang, S. Dai, X. Pan, *Synthetic Metals*, 197 (2014) 188-193.
- [54] A. Kern, I.C. Madsen, N.V.Y. Scarlett, in, *Springer Netherlands, Dordrecht*, 2012, pp. 219-231.
- [55] K. Al-Attafi, A. Nattestad, Q. Wu, Y. Ide, Y. Yamauchi, S.X. Dou, J.H. Kim, *Chem Commun*, 54 (2018) 381-384.
- [56] J. Lin, A. Nattestad, H. Yu, Y. Bai, L. Wang, S.X. Dou, J.H. Kim, *Journal of Materials Chemistry A*, 2 (2014) 8902-8909.
- [57] M. Pazoki, P.W. Lohse, N. Taghavinia, A. Hagfeldt, G. Boschloo, *Phys Chem Chem Phys*, 16 (2014) 8503-8508.
- [58] J. Bisquert, *Phys Chem Chem Phys*, 5 (2003) 5360-5364.
- [59] P.-T. Hsiao, Y.-L. Tung, H. Teng, *J Phys Chem C*, 114 (2010) 6762-6769.
- [60] C. Chen, Y. Li, X. Sun, F. Xie, M. Wei, *New J. Chem.*, 38 (2014) 4465-4470.

- [61] J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan, G. Luo, *Chemical Reviews*, 115 (2015) 2136-2173.
- [62] Z. Yu, N. Vlachopoulos, M. Gorlov, L. Kloo, *Dalton Transactions*, 40 (2011) 10289-10303.
- [63] K. Gelderman, L. Lee, S.W. Donne, *J Chem Educ*, 84 (2007) 685.
- [64] L. Yu, X. Zhang, G. Li, Y. Cao, Y. Shao, D. Li, *Appl. Catal., B*, 187 (2016) 301-309.
- [65] M. Sharon, *An Introduction to the Physics and Electrochemistry of Semiconductors: Fundamentals and Applications*, John Wiley & Sons, 2016.
- [66] A. Al-Keisy, L. Ren, D. Cui, Z. Xu, X. Xu, X. Su, W. Hao, S.X. Dou, Y. Du, *J. Mater. Chem. A*, 4 (2016) 10992-10999.
- [67] X.-Y. Liu, H.-W. Zheng, Z.-L. Zhang, X.-S. Liu, R.-Q. Wan, W.-F. Zhang, *J. Mater. Chem.*, 21 (2011) 4108-4116.
- [68] Y. Ling, J.K. Cooper, Y. Yang, G. Wang, L. Munoz, H. Wang, J.Z. Zhang, Y. Li, *Nano Energy*, 2 (2013) 1373-1382.
- [69] J.H. Yune, I. Karatchevtseva, P.J. Evans, K. Wagner, M.J. Griffith, D. Officer, G. Triani, *RSC Adv.*, 5 (2015) 29513-29523.
- [70] M. Wang, C. Gratzel, S.M. Zakeeruddin, M. Gratzel, *Energy Environ Sci*, 5 (2012) 9394-9405.
- [71] L. Zhang, J.M. Cole, *J. Mater. Chem. A*, 5 (2017) 19541-19559.
- [72] J. Singh, A. Gusain, V. Saxena, A.K. Chauhan, P. Veerender, S.P. Koiry, P. Jha, A. Jain, D.K. Aswal, S.K. Gupta, *J. Chem. Phys C*, 117 (2013) 21096-21104.
- [73] J.M. Cole, M.A. Blood-Forsythe, T.-C. Lin, P. Pattison, Y. Gong, Á. Vázquez-Mayagoitia, P.G. Waddell, L. Zhang, N. Koumura, S. Mori, *ACS Appl Mater Interfaces*, 9 (2017) 25952-25961.
- [74] C.-Y. Cai, S.-K. Tseng, M. Kuo, K.-Y. Andrew Lin, H. Yang, R.-H. Lee, *RSC Adv.*, 5 (2015) 102803-102810.

Cubic aggregates of Zn_2SnO_4 nanoparticles and their application in dye-sensitized solar cells

Kadhim Al-Attafi^{a,b}, Fanar Hussein Jawdat^a, Hamzeh Qutaish^a, Patricia Hayes^c, Amar Al-Keisy^a, Kyubin Shim^a, Yusuke Yamauchi^{a,d}, Shi Xue Dou^a, Andrew Nattestad^{c,*} and Jung Ho Kim^{a,*}

^a Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Wollongong, NSW 2525, Australia.

^b Department of Physics, College of Science, University of Karbala, Karbala 56001, Iraq.

^c Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, Australian Institute for Innovative Materials, University of Wollongong, Wollongong, NSW 2525, Australia.

^d World Premier International Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

*Corresponding authors

Andrew Nattestad anattest@uow.edu.au

Jung Ho Kim jhk@uow.edu.au

Figure S1: ZTO crystalline phases for materials prepared with different precursor ratios and or calcination temperature (a) XRD of as-synthesised precursor $[\text{Zn}_2\text{Sn}(\text{OH})_4]$ using Zn:Sn=1, Zn_2SnO_4 (ZTO) at 400 °C and $\text{Zn}_2\text{SnO}_4+\text{SnO}_2$ at 800 °C; (b) XRD of as-synthesised precursor $[\text{Zn}_2\text{Sn}(\text{OH})_4]$ precursor using Zn:Sn=2, $\text{Zn}_2\text{SnO}_4+\text{ZnO}$ at 400 °C and $\text{Zn}_2\text{SnO}_4+\text{SnO}_2+\text{ZnO}$ at 800 °C; (c and d) SEM images of Zn_2SnO_4 and $\text{Zn}_2\text{SnO}_4+\text{SnO}_2$ synthesised using Zn:Sn=1 ratio at 400 °C and 800 °C respectively; (◻) refers to $\text{Zn}(\text{OH})_4$ in the precursor before calcination; (*) refers to presence of SnO_2 ; (+) refers to ZnO phase; (◦) refers to $\text{Zn}_2\text{Sn}(\text{OH})_6$; (•) refers to Zn_2SnO_4 (ZTO); and (◊) refers to $\text{Sn}(\text{OH})_6$.

Figure S2: (a) TEM images of crystalline ZTO aggregated nanocubes/ZTO nanoparticles synthesised using Zn: Sn=1 molar ratio and calcined at 400 °C; (b) Quantifying of crystallinity degree in XRD traces of synthesised ZTO using the reference intensity method (RIR) using silicon as an internal reference. (this experiment was run by Prof. Brian Jones)

ZTO was mixed with about 10% silicon to act as an internal standard to assess the degree of crystallinity. The measured ratio of ZTO and Silicon was from this trace was 91:9 (wt %). However, the calculated weight ratios obtained from the integrated intensities (after subtracting the background) of ZTO and Silicon are 90% and 10% respectively (Figure S2b). The lower than expected amount of ZTO is due to the amorphous content, (i.e. the reduced intensity of ZTO phase will change the relative phase fractions in a spiked sample) which can be calculated as:

$$\begin{aligned}
 &\text{Amorphous ZTO (Wt\%)} \\
 &= 100 \text{ (Wt\%)} - \left[\text{Si}_{\text{mass}} \text{ (Wt\%)} + \frac{\text{Si}_{\text{mass}} \text{ (Wt\%)}}{\text{Si}_{\text{XRD}} \text{ (Wt\%)}} \right. \\
 &\quad \left. * \text{crystalline ZTO}_{\text{XRD}} \text{ (Wt\%)} \right]
 \end{aligned}$$

The amorphous content in ZTO is approximately 10% which may be partially attributed to a non-crystalline SnO₂.

Figure S3: absorption spectra of solutions of (a) D149 and (b) N719 after desorption from films of TiO₂ nanoparticles (NR18-T), TiO₂ scattering particles (WER2-O) or ZTO.

Table S1: Zeta potential measurements of TiO₂ and ZTO with different pH values.

Zeta Potential (mV)				
pH-ZTO	RUN1	RUN2	RUN3	Average
2	22	23	22	22
4	18	17	18	18
6	18	17	18	18
8	7	8	7	7
10	-39	-39	-39	-39
11.5	-41	-43	-44	-42
12	-41	-38	-41	-41
pH-TiO ₂	RUN1	RUN2	RUN3	Average
2	37	38	39	38
4	13	16	17	15
6	-31	-33	-33	-32
8	-43	-44	-44	-43
10	-45	-45	-45	-45
11.5	-42	-45	-46	-44
12	-41	-46	-50	-45

Table S2: Photoanode thickness optimisation for ZTO|D149 based DSCs

ZTO D149 Thickness (μm)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{oc} (V)	FF (%)	PCE (%)
14	12.6 ± 0.8	0.51 ± 0.01	58 ± 2	3.7 ± 0.3
16	12.6 ± 0.8	0.59 ± 0.02	59 ± 2	4.4 ± 0.3
18	13.3 ± 0.4	0.56 ± 0.02	65 ± 2	4.9 ± 0.2
20	13.4 ± 0.3	0.56 ± 0.02	61 ± 1	4.6 ± 0.3
22	13.7 ± 1.0	0.57 ± 0.01	60 ± 2	4.4 ± 0.2

Table S3: Photoanode thickness optimisation for ZTO|N719 based DSCs

ZTO N719 Thickness (μm)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{oc} (V)	FF (%)	PCE (%)
4	4.4 ± 0.1	0.65 ± 0.02	67 ± 5	2.0 ± 0.2
8	6.4 ± 0.5	0.68 ± 0.01	72 ± 1	3.1 ± 0.2
12	8.2 ± 0.6	0.68 ± 0.01	73 ± 1	4.0 ± 0.2
16	7.8 ± 0.3	0.67 ± 0.01	71 ± 1	3.7 ± 0.1
20	6.5 ± 0.6	0.63 ± 0.01	67 ± 1	2.7 ± 0.2

Figure S4: ZTO blocking layer investigation (a) J-V response for sandwich devices with either two FTO electrodes or two FTO|ZTO electrodes filled with 0.1 M Ferrocene electrolyte, showing much lower dark current across the operating voltage range (b) ZTO|D149 device performance with and without ZTO blocking layer (dark curves in inset).

Figure S5: Photovoltaic performance of devices based on ZTO composited with other secondary phases sensitized with D149 dye. ZTO:SnO₂ synthesised using Zn:Sn= 1:1 and a 800 °C calcination temperature; ZTO:ZnO synthesised using Zn:Sn=2:1 and a 400 °C calcination temperature, with the pure phase material for comparison. (a) J-V responses and (b) IPCE.

Table S4: Photovoltaic parameters of ZTO+SnO₂ and ZTO+ZnO devices sensitized with D149 dye.

Devices	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
ZTO+SnO ₂ -1	7.4	0.62	63	2.9
ZTO+SnO ₂ -2	7.7	0.60	64	3.0
ZTO+SnO ₂ -3	7.3	0.59	65	2.8
Average	7.5 ± 0.2	0.61 ± 0.02	64 ± 1	2.9 ± 0.1
ZTO+ZnO-1	5.7	0.49	62	1.8
ZTO+ZnO-2	5.5	0.48	60	1.6
ZTO+ZnO-3	5.6	0.49	62	1.6
Average	5.6 ± 0.1	0.49 ± 0.01	61 ± 1	1.6 ± 0.1

Figure S6: Nyquist plots fitting of TiO₂ and ZTO sensitized with D149 and N719 based DSCs.

Figure S7: Investigation of the electrolyte effect on the performance of ZTO|N719 devices

Table S5: Photovoltaic parameters of ZTO|N719 devices using different electrolytes.

Devices	J_{sc} (mA · cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
ZTO N719 (D149 electrolyte)	9.4 ± 0.4	0.66 ± 0.01	59 ± 1	3.7 ± 0.1
ZTO N719 (N719 electrolyte)	8.2 ± 0.5	0.68 ± 0.01	73 ± 1	4.0 ± 0.2

Figure S8: (a) Square wave voltammograms showing the oxidation potentials of N719 and D149 dyes bound to ZTO or TiO₂ (b) and (c) the absorption onsets of N719 and D149, bound to ZTO or TiO₂.

Figure S9: Dye aggregation investigations for ZTO sensitized with N719 or N719:Chenodeoxycholic acid (1:10 molar ratio). (a) Absorbance of ZTO|N719 and ZTO (N719:CDCA) films (b) Incident photon conversion efficiency (IPCE); (c) absorbed photon conversion efficiency (APCE) and (d) J-V responses of devices.

Figure S10: The spacing between the two carboxylic groups or between the carbonyl group and carboxylic group of N719 using Chem3D V17.1.

Figure S11: Absorption coefficients of ZTO and TiO₂ (films thickness 18 μm and 12 μm respectively).

Photo-degradation test

Dye bleaching or dye photodegradation is one factor that affects DSC operation lifetime. The response of wide bandgap semiconductors (photoanode material) to UV light can cause the dye degradation including due to generating reactive species (O_2^- , H^+ and OH^-) as a result of electron-hole charge separation or directly through oxidative strength of holes in the valence band.[1]

TiO_2 or ZTO can response to UV light because their band gaps are located within UV region. Therefore, the photocatalytic activities of TiO_2 and ZTO were investigated as shown in (Figure S12 a and b). ZTO exhibited very low photo-dye degradation rate compared to TiO_2 indicating that ZTO is inactive photocatalytically material compared to TiO_2 . This means ZTO is less likely to cause dye bleaching. Figure S12 b is a pseudo-first order reaction representing the reaction rate constants of TiO_2 and ZTO, obtained from the slope values, which are $1.4\ h^{-1}$ and $0.05\ h^{-1}$ respectively suggesting the poor photocatalytic efficiency of ZTO.

The differences in morphologies (reactivity of sites on the surface), surface area, porosity, crystal structure, band edge potentials (driving forces) and light harvesting between the TiO_2 and ZTO are also, responsible for the high variations in their photocatalytic activates.[1] Moreover, the lower dark charge carriers' density in ZTO may affect the electron-hole charge separation resulting in producing fewer radical species and hence reducing the photocatalytic activity.

As mentioned in the optical band gap measurements part, the optical band gap was smaller than nominally expected. This is probably attributed to the expected higher trap states localized close to ZTO conduction band resulting in narrowing the band gap value due to affecting the absorption properties.[2]

Figure S12: Photocatalytic activity measurements for ZTO and TiO₂ materials using Rhodamine B dye under simulator AM1.5 illumination.

References

- [1] R. Thiruvengatachari, S. Vigneswaran, I.S. Moon, Korean J Chem Eng, 25 (2008) 64-72.
- [2] Y. Zhao, L. Hu, H. Liu, M. Liao, X. Fang, L. Wu, Sci Rep., 4 (2014).