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# Nanostructured zinc titanate wide band gap semiconductor as a photoelectrode material for quantum dot sensitized solar cells

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ABSTRACT

We synthesized zinc titanate nanopowder in different crystal structures by varying calcination temperature and time and phase evolution is qualitatively investigated using reference intensity ratio (RIR) approach. The electronic properties showed 2.9 eV as indirect band transition, and 3.59 ± 0.02 eV as direct band transition for the highest temperature annealed rhombohedral $ZnTiO_3$ and cubic spinel $Zn_2TiO_4$ zinc titanate materials. The intermediate temperature annealed (~850 °C) material consists of $ZnTiO_3$, $Zn_2TiO_4$, and $Zn_2Ti_3O_8$ zinc titanate nanopowder, showing similar two electronic transitions. Zinc titanate with dominant rhombohedral phase $ZnTiO_3$ (900 °C annealed) and dominant $Zn_2Ti_3O_8$ phase (750 °C annealed) are used to synthesize mesoporous electrodes for integrating the ZnS passivated CdS quantum dots. Finally, $Cu_2S$ counter electrode is integrated with polysulfide electrolyte to realize 1 $cm^2$ area quantum dot sensitized solar cells (QDSSCs). QDSSCs with dominant $ZnTiO_3$ phase are showing lower photovoltaic performance (short circuit current 0.76 $mA/cm^2$, open circuit voltage 0.55 V) with respect to that of dominant $Zn_2Ti_3O_8$ phase with 2.2 $mA/cm^2$ short circuit current and 0.69 V open circuit voltage, respectively. The observed difference is attributed to differences in electronic and morphological properties of the synthesized zinc titanate powders.

## 1. Introduction

Quantum dots sensitized solar cells (QDSSCs) are considered important photovoltaic systems and are evolving rapidly with a better understanding of the underlying principles of carrier generation and collection across the device. There are significant developments in the field of QDSSCs, resulted in the energy conversion efficiencies more than 10% (Jiao et al., 2015). These photovoltaic cells consist of (i) quantum dots (QDs) as the absorber, generating electron-hole pairs after absorbing incident light, (ii) a wide band gap nanostructured mesoporous electrode to accept the photo generated electrons from QDs and their transport to the electrode, (iii) redox electrolyte to accept the holes from oxidized QDs, and (iv) a counter electrode, which work as a catalyst for the electrolyte regeneration (Carey et al., 2015). The detailed balance calculations showed that QDSSCs may beat the Shockley–Queisser efficiency limit for a single p-n junction based solar cells (Klimov, 2006). In addition, QDs provide band gap tunability by simply varying their sizes and thus, the integration of variable size QDs may lead to closed matching with the solar spectrum to achieve enhanced absorption and thus better photovoltaic response (Alivisatos, 1996). In conjunction with band gap engineering, high molar extinction coefficients (Yu et al., 2003), large intrinsic dipole moments and the possibility for efficient multiple exciton generation (Schaller and Klimov, 2004) make QDs suitable for solar cell applications. In spite of functional QDs, development of QDSSCs depends on the nanostructured mesoporous electrode, showing efficient carrier transport. The nanostructured binary oxides, such as ZnO and $TiO_2$, are widely used as mesoporous electrodes for such applications (Jose et al., 2009). For example, QDs deposited on the wide band gap mesoporous $TiO_2$ electrode is used in QDSSCs due to its favorable band alignments. The requirement to achieve (i) high electron mobility for carrier transport and (ii) higher band gap to decrease oxidative holes in valence band directed to explore the suitable wide band gap semiconductors as probable photoanode materials (Lin et al., 2015). ZnO (Gao et al., 2011; Oleiwi et al., 2016), $SnO_2$ (Hossain et al., 2011), $Nb_2O_5$ (Le Viet et al., 2010), $Zn_2SnO_4$ (Choi et al., 2013), $BaTiO_3$ (Meng et al., 2014), $SrTiO_3$ (Burnside et al., 1999) and $ZnTiO_3$ (Habibi et al., 2012) are investigated as the possible wide band gap semiconductors for this application. However, the power conversion efficiency of these wide band gap semiconductor based nanostructured mesoporous electrodes remains

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lower than that of $TiO_2$ (Gong et al., 2012). Zhang et al. used flower shaped $SnO_2$ nanoparticles as wide band semiconductor for cadmium sulfide (CdS) QDs based QDSSCs, showing the maximum power efficiency ~3% (Gong et al., 2012). Highly crystalline $Nb_2O_7F$ nanoparticles based mesoporous electrodes with CdS QDs on fluorine doped tin oxide (FTO) glass substrate showed ~1.68% photovoltaic efficiency (Zhang et al., 2013). $Zn_2SnO_4$ nanowire with CdSe QDs showed ~0.3% power conversion efficiency (Dai et al., 2012). $BaTiO_3$ nanoparticles, synthesized using the hydrothermal method, with CdS QDs showed the maximum power conversion efficiency ~1.26% (Meng et al., 2014), whereas $SrTiO_3$ nanoparticles with CdS QDs showed ~0.78% efficiency (Chen et al., 2015).

Recently, zinc and titanium based ternary oxide nanomaterials are attracting attention as a photoanode material for the quantum dots (QDs) sensitized solar cells (QDSSCs), with a possibility of the better corrosion resistance with enhanced optical and electrical properties such as larger carrier mobility as compared to that of the binary oxide systems. These ternary oxides may provide reduced recombination losses and efficient electron transport, resulting in enhanced photovoltaic performance (Hod and Zaban, 2014). The wide band gap systems may also serve as (i) the window layer for QDSSCs, (ii) as a supporting matrix for QDs deposition, and (iii) responsible for the photo generated electron transport to the selective contact, normally fluorine doped tin oxide (FTO) substrate. Thus, the band gap and relative positioning of the conduction band minimum (CBM) of the wide band gap semiconductor with respect to Fermi energy of FTO and the lowest unoccupied molecular orbital (LUMO) of the QDs is important in conjunction with carrier mobility. A suitable band gap allows the incident light to be absorbed by QDs without any considerable absorption in the mesoporous electron conducting medium. Moreover, the proper CBM positioning is essential for the efficient injection of photo generated electrons from QDs to the photoanode material. The high carrier electron mobility can increase the electron transport rate and reduce the recombination probabilities (Hod and Zaban, 2014). Zinc titanate is a ternary oxide material, which is also explored as a photoanode material recently (Yu et al., 2016; Habibi et al., 2012). In these reports, zinc titanate ($ZnTiO_3$) is reported to perform better than $TiO_2$ mesoporous electrodes (Burnside et al., 1999; Hod and Zaban, 2014). The electron mobility in hexagonal $ZnTiO_3$ material is reported to be much larger than that of the $TiO_2$ system, suggesting one of the probable reasons of enhanced photovoltaic response (Hod and Zaban, 2014). However, the structural stability of cubic/hexagonal $ZnTiO_3$ is not well understood and the crystallographic phases are not identified in the reported literature (Li et al., 2000). Zinc titanate ($Zn_XTi_YO_Z$, with different X, Y and Z) can be considered as a highly doped anatase $TiO_2$ phase because of their structural similarity. This contains six fold octahedral coordination, similar to that of titanium arrangement in anatase $TiO_2$ phase (Conesa, 2013). The previous work suggests three different crystallographic phases with minor impurities for solid state synthesized zinc titanate material and detailed crystallographic phases as the function of annealing temperature are reported (Denosb, 1996). These are (i) zinc metatiatnate ($ZnTiO_3$) in rhombohedral ilmenite structure, (ii) zinc orthotitanate ($Zn_2TiO_4$) in a cubic spinel structure, and (iii) $Zn_2Ti_3O_8$ in a cubic defect spinel structure (Conesa, 2013). $Zn_2Ti_3O_8$ is considered as a metastable form of $ZnTiO_3$ and can be realized at 800 °C or lower annealing temperatures. In contrast, $ZnTiO_3$ is suggested to decompose into $Zn_2TiO_4$ and rutile $TiO_2$ at temperatures above 945 °C (Denosb, 1996). There are also reports on cubic $ZnTiO_3$ (Kong et al., 2009; Li et al., 2000) but the detailed crystallographic information is not presented. These ambiguities motivated to investigate the crystallographic phase of zinc titanate with annealing temperature and the effect of different zinc titanate phases in mesoporous electrodes on photovoltaic performance.

In this work, zinc titanate nanoparticles are synthesized using the sol-gel method. The evolution of different crystallographic phases is investigated by varying the calcination temperature and time. The observed crystallographic phases are summarized in the crystallographic phase diagram. Further, the prepared zinc titanate nanopowder is utilized to fabricate the mesoporous photo-electrodes using drag blade (Dr. blade) coating process on FTO substrates. The photoelectrodes are sensitized with cadmium sulfide (CdS) QDs using a **s**uccessive **i**onic **l**ayer **a**dsorption and **r**eaction (SIALR) method, followed by zinc sulfide (ZnS) passivation using the same approach. The electrical response of the prepared QDSSCs using $Cu_2S$ counter electrode is investigated using current – voltage and impedance measurements. The studies suggest that the low temperature calcinated zinc titanate powder based QDSSCs are superior to that of high-temperature zinc titanate powder based QDSSCs. These results demonstrate that sol-gel derived, low temperature calcinated zinc titanate can be a promising photoelectrode material for QDSSCs.

## 2. Experimental details

### 2.1. Material required

Titanium (IV) isopropoxide $C_{12}H_{28}O_4Ti$ (Sigma-Aldrich), zinc acetate dihydrate $Zn(CH_3COO)_2{\cdot}2(H_2O)$ (Alfa-Aesar), mono ethanolamine $C_2H_7NO$ (Sigma-Aldrich), 2-Propanol $C_3H_8O$ (Sigma-Aldrich), nitric acid $HNO_3$ (Sigma-Aldrich), ethyl cellulose (20,000 MW, Sigma-Aldrich), terpene oil $C_{10}H_{18}O$ (Sigma-Aldrich), cadmium chloride $CdCl_2$ (Sigma-Aldrich), titanium (IV) chloride (99%, Alfa Aesar), sodium sulfide hydrate (assay > 60%, Sigma-Aldrich), sulphur powder (Merck) and potassium chloride (99.5%, Vetec) are purchased and used without any additional purification. FTO (with 7–10 ohm/sq resistivity) is purchased from Global Nanotech and 60 μm thick thermoplastic (Meltonix) is purchased from Solaronix.

### 2.2. Synthesis of zinc titanate nanoparticles

Zinc acetate dihydrate (14 mM) is added in 2-propanol (15 ml) and stirred continuously at 60 °C for complete dissolution of zinc precursor. Further, a 14 mmol mono ethanolamine (MEA) is added under continuous stirring at 60 °C for 20 min to get a transparent precursor solution. Titanium isopropoxide (14 mmol) is added drop wise under continuous stirring at 60 °C for one hour in prepared zinc precursor solution. Additionally, few ~4–5 drop of nitric acid is added in 40 ml deionized water, which is added drop wise in the metallic precursor solution. Thus, the prepared sol is stirred continuously at room temperature till gel formation. This gel is preheated at 110 °C (with 5 °C/min heating rate) for four hours and the collected powder samples are calcinated at different temperatures ranging from 750 °C to 900 °C (at 3 °C/min heating rate).

### 2.3. Photo-electrode fabrication

Initially, 1 g ethyl cellulose is mixed in 20 ml ethanol to prepare the ethyl cellulose solution. Further ethyl cellulose, terpene oil and synthesized zinc titanate nanopowder are mixed in 0.5 ml: 2.5 ml: 0.5 g ratio and stirred at ~70 ± 5 °C temperature to evaporate ethanol and terpene oil up to a certain extent to achieve the desired viscosity for depositing mesoporous electrode using drag blade method. FTO substrate is cleaned thoroughly using organic solvents and deionized water to remove the surface impurities before any surface treatment. The cleaned electrode is immersed in 30 mM $TiCl_4$ solution for 30 min at 70 °C to deposit amorphous $TiO_2$ blocking layer on FTO substrate, and is sintered at 450 °C. The prepared zinc titanate paste is applied on $TiCl_4$ treated FTO using scotch tape as a spacer and drag blade method to get the desired mesoporous zinc titanate electrodes. The synthesized electrodes are dried at 80 °C, followed by final sintering at 550 °C for 1 h. CdS QDs sensitization is carried out using SILAR, where one SILAR cycle comprises of dipping the mesoporous electrode in cation solution first for one minute, followed by deionized water rinsing and finally