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**Project full title:** New technological advances for the third generation of Solar cells

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**Deliverable D4.4 : Public Report on the structural, optical characterization of newly developed scaffold materials**

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1. Deliverable description

This deliverable calls for the development of new metal oxides for their application in perovskite solar cells to reach high Voc and power conversion efficiency. Herein, we report structural, and optical characterization of newly developed metal oxide scaffold materials.

2. Summary

The remarkable potential of metal trihalide perovskite light absorbers has recently been demonstrated in the production of efficient perovskite solar cells (PSCs). Because of the unique crystal and energy structure of ABX$_3$ perovskites, the charge carriers in these materials exhibit long lifetime and high mobility, and a large diffusion length. Recent investigations have shown that the performance of the PSCs can be further improved by identifying an inorganic semiconductor material that can effectively extract electrons. Here we investigated several new metal oxide materials as scaffolds for PSCs and studied their structural, morphological, and optical properties.

We also introduced an electron selective contact for PSCs featuring 40 nm sized mesopores TiO$_2$ beads. The bimodal pore distribution inherent to these films produces a very large contact area of 200 m$^2$/g. Modification of the TiO$_2$ surface by CsBr further strengthens its interaction with the perovskite layer. In addition to this study, we have synthesized and characterized various metal oxides, such as ZnO, Zn$_2$SnO$_4$, α-Fe$_2$O$_3$, BaSnO$_3$ and SrSnO$_3$ and studied their optical characteristics to apply them as electron transport layers.
3. Introduction

There have been numerous studies on perovskite solar cells (PSCs) and solid-state dye-sensitized solar cells focusing mainly on optimizing methods for film formation and compositional engineering to achieve high power conversion efficiency (PCE) as well as stability of perovskite solar cells (PSCs), culminating in a certified PCEs of 22.7%. \[1–8\]

Studies on electron-selective layers (ESLs) have improved the device performance. For example, Sargent et al. used chlorine-capped TiO$_2$ nanoparticles to enhance the device performance, realized primarily due to passivation of defect along the interface between perovskite layer and the charge selective contact.\[9\] Other studies of TiO$_2$ modification with metal halides also showed improvement in terms of stability and performance of planar PSCs.\[10–14\] Nevertheless, today’s most efficient devices employ still a mesoscopic TiO$_2$ scaffold as electron selective layer (ESL) despite significant progress on planar PSCs.\[2,9,15–17\]

Although the mesoporous TiO$_2$ scaffold is considered to be beneficial for PSCs as an electron transport material, there are only a few studies of the effect of its architecture and surface modification on the PSC performance. Indeed, mesoscopic perovskite solar cells so far used 30 nm sized TiO$_2$ nanoparticles that constitute the mesoscopic scaffold acting as ESL: However, they lack any porosity with their surfaces being composed of smooth facets with mainly (101) and 001 orientations. By contrast, there have been several encouraging reports about introducing mesopores in the TiO$_2$ particles in the area of dye-sensitized solar cells (DSSCs) where this resulted in improved device performance.\[18,19\] Another issue with TiO$_2$ is that electron trapping by coordinatively unsaturated Ti (IV) ions is likely to occur at its interface with the perovskite, which hampers charge transport and enhances radiationless charge carrier recombination as well as the appearance of a hysteresis in the J-V curves.\[20\] Theoretical calculations for TiO$_2$ suggest that electrons prefer to localize just below the surface being trapped by oxygen vacancies and Ti (IV) ions.\[21,22\] One of the most effective methods to reduce the trap states in the TiO$_2$ is surface or bulk doping, which has been widely investigated for mesoporous TiO$_2$ electrodes in dye-sensitized solar cells and more recently in PSCs.\[23–25\] Some dopants reduce the charge recombination and increase electron transport by passivating oxygen defects in the TiO$_2$ lattice and reducing trap states below the conduction band (CB) of TiO$_2$ in PSCs. Another effect of doping is the stabilization of power conversion efficiency and the suppression of hysteresis in PSCs.\[25–30\]

In spite of excellent PCEs displayed by titanium dioxide nanoparticles structures, the transport rate of electrons is known to be slow due to low electron mobility. Thus, the alternative oxides, including SnO$_2$ and ZnO, which possess high electron mobility, are being investigated as potential candidates to support the novel pigments developed in WP2. In comparison to TiO$_2$ anatase, ZnO possesses a significantly higher electron mobility, which favours electron transport across its structures. Such a property acts as a double-edged sword as it promotes charge separation and recombination simultaneously. However, multiple studies demonstrated that the optical transparency, mobility, and interfacial properties of ZnO do not rely only on the processing conditions but also depend strongly on the applied synthetic methods. Correspondingly, the device performance of PV devices using various
ZnO materials as ETL are different. Therefore, development of new methods of the interface engineering of ZnO NCs materials is critical for achieving high efficiency and long-term stability in PSCs. In this context, polymer modification of ZnO nanomaterials has been shown to be an immensely effective route for increasing their stability, providing good solution processability as well improving charge extraction in resulting PV devices. The search for ZnO scaffold materials that can be solution processed into thin-film form at low temperature, while simultaneously providing quality device characteristics still remains a challenge. To meet this challenge, within GOTSolar project during the first year, we have developed a novel organometallic approach for the synthesis of readily processable ZnO NCs stabilized by a carboxylate oligoethylene glycol (OEG-carboxylate).
4. Materials and methods

All reagents were purchased from commercial vendors and used as received.

4.1 Preparation of CsX doped Mesoporous TiO$_2$ beads

Mesoporous titania gel, (washed CristalACTiV™ HPX-100™ prior to spray drying) was modified by treating with cesium iodide (HPX-100CsI) or cesium bromide (HPX-100CsBr) to obtain a 5% mole fraction of cesium halides on the titania, respectively. CristalACTiV™ HPX-100™ is available from Cristal Inc. and is a mesoporous titania nanoparticulate. The gel was then dried for 12 hours at 105°C. The dried powder was milled in a planetary mill in terpineol at a solids concentration of 20%. Untreated HPX-100™ was dried and milled using the same conditions.

4.2 ZnO-OEG preparation and characterization

Solution-processable ZnO NCs were prepared according to the developed organometallic synthetic approach.[1,2] For the synthesis we employed 2,5,8,11-tetraoxatetradecan-14-oic acid (denoted as OEG-H) as oligoethylene glycol proligand, which formed the carboxylate stabilizing shell of ZnO-OEG NCs. Precursor solution (S1) was prepared in –78 °C by mixing of Et$_2$Zn (1 mmol, 124 mg) in THF (5 mL) with 2 mL of 1 M water solution in THF. The S1 was then brought from -78 °C to -15 °C and stirred for 2 hours. The resulting mixture was then warmed up to 25 °C and stirred for further 12 hours. After this time 1 mL of OEG-H (0.15 M) was added. The resultant mixture was then stirred for further 7 days to produce well-dispersed ZnO-OEG NCs. After evaporation of THF, ZnO-OEG NCs were readily dispersed in proper solvent e.g. water, alcohols, DMSO or DMF.

Samples for HRTEM were prepared by drop casting of a solution of the material onto 300-mesh, holey-carbon coated copper grids (Quantifoil). The characterization of size, shape, and morphology was carried out on a high-resolution Scanning Transmission Electron Microscope (FEI TECNAI G2 F20 S-TWIN. Particle size distributions were calculated by counting the diameters of more than 100 particles. Powder XRD data was collected on Empyrean diffractometer (PANalytical). Measurements employed Ni-filtered Cu Kα radiation of a copper sealed tube charged with 40kV voltage and 40mA current and Bragg Brentano geometry with a beam divergence of 1 deg. in the scattering plane. The hydrodynamic diameter of NPs was determined by DLS measurements performed on Malvern Zetasizer Nano ZS.

Water stability experiments of ZnO-OEG NCs were carried out by the addition of 50 μL of a water solution of ZnO-OEG NCs (20 mg/mL) to 2 mL of HCl or NaOH water solution with a pH range of 1–14. For the pH lower than 3.0 and higher than 9.0 gradual sedimentation of highly luminescent precipitate was observed. Therefore, further UV–vis and DLS measurements were conducted for the samples in the pH range of 3.0–9.0.
4.3 Zinc stannate (Zn₂SnO₄) preparation and characterization

Two methods were performed for the synthesis of zinc stannate: (a) inorganic; from two acetate salts of tin and zinc with the addition of ammonia and (b) organometallic; from diethylzinc solution and tetrakis(dimethylamino)tin(IV) (TMDAS) solution.

**Inorganic procedure:**

0.1 mmol of tin(IV) acetate and 0.2 mmol of zinc acetate were dissolved in 6 mL of deionized water and mixed on a magnetic stirrer. After complete dissolution, 2 mL of 25% ammonia was added to mixture causing precipitation of zinc and tin oxides. The white product was filtered, washed with 20 mL of deionized water, dried and sintered in 880°C in a tube furnace under air flow. The final product was measured with PXRD method.

**Organometallic method:**

0.1 mmol of TMDAS and 0.2 mmol of diethylzinc were mixed in Schlenk vessel using air-free technique. The white slurry product was obtained and sonicated for 10 minutes. After sonication the 2 mL of water dissolved in THF (concentration 1.5 M) was added to product. The excess solvents were evaporated and the final white product was sintered at 880°C in a tube furnace under flowing air.

4.4 Synthesis of SrTiO₃

1) Hydrothermal reaction with TiO₂ powder for 20h.

The conversion from TiO₂ powder to SrTiO₃ was carried out by hydrothermal reaction in an autoclave using Sr(OH)₂ aqueous solution (80.0 mg ml-1) heated and stirred on a hotplate at 150 °C for 20 h. After cooling down to room temperature, the production was centrifuged with a rate of 5000 rpm and then washed with deionized water for 5 times and ethanol for 2 times, finally dried in an oven at 60 °C for 5 h, the white powder was obtained.

2) The reaction time (20h) was found to be unnecessarily long hence we reduced it to 2h and monitored the reaction, indicating the TiO₂ was fully transformed to SrTiO₃.

3) When the concentration of Sr(OH)₂ is reduced and the autoclave time is reduced to 0.5h then the conversion of SrTiO₃ is incomplete indicating that the minimum required reaction time is 2h. 6.0 g TiO₂ powder was put into an autoclave containing 50 ml Sr(OH)₂ aqueous solution (17.7 mg ml-1) heated and stirred on a hotplate at 150 °C for 0.5 h. After cooling down to room temperature, the production was centrifuged with a rate of 5000 rpm and then washed with deionized water for 5 times and ethanol for 2 times, at last, dried in an oven at 60 °C for 5 h, 5.5 g white powder was obtained and made into a paste with the standard method.
5. Results and discussion

5.1 Characterization of CsBr, CsI doped Mesoporous TiO\(_2\) beads.

At first, we examine the effect of introducing nanopores in the TiO\(_2\) particles that constitute the electron transport layer. **Figure 1** compares scanning electron microscopy images (SEM) for the conventional films constituted by nonporous particles produced from a commercial paste, 30NR-D (Dyesol) and with the new HPX-100 material (Cristal). The particle size of the latter is larger than that of the standard and the particles are endowed with pores of a few nanometer diameter. These mesoporous beads exhibit a high BET value of 206.31 m\(^2\)/g offering a larger contact area to the perovskite than the standard formulation. To investigate the effect of surface porosity of TiO\(_2\) on device performance, we made PSCs with the same thickness of TiO\(_2\) scaffold layer using non-porous (**Figure 1a**) and the mesoporous beads (**Figure 1b**), respectively.

![Figure 1. SEM images of the TiO\(_2\) nano-particles. (a) 30NR-D and (b) HPX-100, respectively. Scale bar is 100 nm.](image)

Cs ion doped mp-TiO\(_2\) films were prepared by sintering CsX premixed TiO\(_2\) paste for 30 minutes at 450° C as described in the Experimental Section. Transmission electron microscope (TEM) images of the mp-TiO\(_2\) nanoparticles (NPs) with (CsI, CsBr) and without doping (Control) are shown in **Figure 2**. The TiO\(_2\) nanocrystals with an average size of 40 nm are mesoporous, **Figure 2a**. After treatment with CsX, the morphology of the nanocrystals shows negligible difference compared to the untreated TiO\(_2\) scaffold, **Figure 2b**. The Cs ions are well dispersed in the TiO\(_2\) structure, as confirmed by scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDX) elemental mapping measurements (**Figure 2c** and **d**), indicating successful and homogenous doping. X-ray photoemission spectroscopy (XPS) was performed to further investigate the elemental composition of the Cs-doped and undoped TiO\(_2\).
Figure 2. TEM and EDX elemental mapping characterizations of the mesoporous TiO$_2$ particles. (a) High-resolution TEM image and elemental mapping of (b) Ti and O for control and (c-d) element mapping of Ti, O and Cs for a CsI and CsBr doped TiO$_2$ particles, respectively.

5.2 ZnO NCs scaffolds studies: structural and optical characterization of the hybrid organic-inorganic ZnO NCs stabilized by carboxylate oligoethylene glycol shell

During the first year of GOTSolar, novel alternative materials to TiO$_2$ scaffold that can act as efficient electron selective contacts were developed. IChF PAN partner prepared novel zinc oxide (ZnO) nanostructures including: (i) carboxylate oligoethylene glycol (OEG-carboxylate) coated ZnO nanocrystals, as well as (ii) mesoporous structures composed of ZnO nanoparticles. A detailed structural (i.e. crystallinity, porosity, pore size, pore morphology) as well as optical characterization of newly developed scaffold materials was carried out. Preliminary studies on the combination of the developed ZnO scaffolds with perovskite pigments and correlation of resulting parameters with photovoltaic device performance was also performed. Current work is focused on application of the newly developed alternative oxide materials as electron selective contacts with operating devices.

Morphology of ZnO-OEG NCs

HRTEM micrographs display wurtzite-type ZnO NCs and indicated that shape of the inorganic core of ZnO-OEG NCs is roughly spherical and crystalline with a mean diameter of 8.5 ± 1.2 nm (Figure 3 &4). The purity of crystal phase and the degree of crystallinity of ZnO-OEG NCs were further confirmed by PXRD.
Figure 3. The HRTEM (a) and STEM (b) images of ZnO-OEG NCs drop-casted from solution.

Figure 4. Statistical analysis of the size of ZnO-OEG NCs based on TEM imaging. Mean size: 8.5±1.2 nm.

The analysis of PXRD pattern revealed well-defined peaks, which were indexed to the wurtzite structure of ZnO (Figure 5). Based on the peak broadening, according to the Scherer equation, the crystallite size has been estimated to be 6.8 ± 0.6 nm.

Figure 5. Main graph: The PXRD diffractogram of ZnO-OEG NCs (black line) and the simulated ZnO pattern (red line). Inset: Williamson-Hall plot of ZnO-OEG NCs (β – FWHM of the reflections). The ZnO crystallite size was estimated at 6.8 ± 0.6 nm based on the y-intersection of the linear function fitted to the data points at the Williamson-Hall plot.
Organic shell composition of ZnO-OEG NCs

The spectrum of ZnO-OEG NCs is similar to the transmission spectrum of the neat OEG-COOH oligomer in the range 4000-1800 cm\(^{-1}\) (Figure 6). However, the carbonyl region of the OEG-functionalized ZnO NCs is distinct from that of the neat OEG-COOH oligomer. In the FT-IR spectrum of ZnO-OEG NCs, the intensive bands at 1434 and 1564 cm\(^{-1}\) characteristic for carboxylate (O–C–O) stretching modes are observed. This indicates that the carboxylic oligomers are anchored to the ZnO surface in the deprotonated form.

Optical properties of colloidal dispersions of ZnO-OEG nanocrystals

Furthermore, the quality, stability as well as the remarkable physicochemical properties of the resulting quantum-sized ZnO nanostructures with well-passivated surface were investigated. The unusual character of ZnO QDs derived from the organometallic method was substantiated by their ultra-long photoluminescence lifetime (Figure 7). The photoluminescence life times measured for these novel QDs are a few orders of magnitude longer (ca. 2.2 μs) than that typically observed for ZnO nanocrystals derived from sol-gel process (10-30 ps). In the former case the unique inorganic core-organic shell interface likely works as a hole stabilizer, which dramatically slows down the charge recombination process.
It is our conviction that this material surpasses the commonly used n-type TiO$_2$ since electrons were found to survive in the semiconductor conduction band up to seconds, which is at least four to six orders of magnitude of what has been reported for classical metal oxides nanoparticles, making it a new dawn for solar fuel and LED devices using ZnO as light absorber and emitter material, respectively.

**Solution processability and stability experiments**

The resulting ZnO-OEG NCs remained stable in the solid state for months when stored under N$_2$ at 25°C. On the other hand, the ZnO-OEG NCs are highly soluble (100 mg·per ml) e.g. in water, DMSO, DMF; alcohols. Photophysical properties of ZnO-OEG NCs remained essentially unchanged within minimum 7 days in water in a wide pH range (3-9) at 25°C. We note, however, that the prolonged storage of ZnO-OEG NCs in water (over 3 days) led to a gradual self-assembly of the NCs and appearance of larger aggregates (as indicated by DLS measurements; Figure 8), which resulted in a decrease in the absorption band intensity (Figure 9).
Solution stability and processability of ZnO-OEG NCs makes them ideal semiconducting material for preparation of e.g. thin blocking layers by spin coating, spray deposition or even screen printing technique. The future work will focus on the application of developed alternative oxide materials as electron selective contacts.

Further studies indicated that due to appropriate oligoethylene coating the resulting powders are highly soluble (100 mg per ml) and stable in various organic solvents e.g. DMSO, DMF; THF, alcohols and can be directly spin-coated from solution onto active layers or an ITO electrode, which make them a good candidate for efficient ETLs in both conventional and inverted devices. Current work is focused on the application of developed alternative oxide materials as electron selective contacts in fully operating devices.

5.3 Zinc stannate as an electron transport layer: synthesis and characterization

Zinc stannate is a layered metal oxide material that is usually obtained directly from mixing corresponding metal oxides or from inorganic salts by NaOH treatment, followed by ion extraction and further sintering process (standard temperature is over 1200°C). In the following experiments, we developed two new synthetic routes. One of them is based on inorganic salts, in which instead of NaOH we used other oxide precipitation medium. The second one originates from the organometallic methodology using organozinc intermediate compounds developed in our group.

In both cases, a white precipitate was collected and sintered in a tube furnace in temperature ranging between 500°C to 1200°C in air flow. The minimal temperature at which Zn2SnO4 phase forms as a dominant phase was determined to be ~880°C. Inorganic procedure leads to the formation of pale-colour material indicating the presence of vacancies/defects in the crystal lattice. The luminescence is observed upon using 365 nm light excitation source, but is quenched after a short time of moisture exposure. On the other hand, the organometallic synthesis provides a material with the same PXRD
patterns, but the obtained powders were bright white in colour. For the corresponding PXRD patterns see Figure 10-13. The luminescence of this material was active for a longer time as compared to the material obtained from inorganic approach indicating its higher purity. In both cases, zinc stannate possessed small impurities of ZnO or SnO$_2$, depending on the exact synthetic procedure. The pure Zn$_2$SnO$_4$ phase was obtained by dissolving the impurities. For the representative SEM images of zinc stannate synthesized by using inorganic as well as organometallic approach see Figure 14 - 15.

Figure 10. PXRD diffraction pattern of zinc stannate, from organometallic synthesis, with zinc oxide impurities obtained after sintering at 900°C for 4 hours.

Figure 11. PXRD diffraction pattern of zinc stannate, from organometallic synthesis, with zinc oxide impurities obtained after sintering at 1200°C for 4 hours.
Figure 12. PXRD diffraction pattern of zinc stannate, from organometallic synthesis, with zinc oxide impurities obtained after sintering at 900°C for 4 hours. Before sintering, there was a mechanochemical activation of zinc and tin oxides in a ball mill (30 Hz, 30 min), which decreased the content of impurities.

Figure 13. PXRD diffraction pattern of zinc stannate, from inorganic synthesis, with zinc oxide impurities obtained after sintering at 900°C for 4 hours.
5.4 In-situ transformation of mesoporous TiO2 to SrTiO3

Inorganic perovskite oxides such as SrTiO3 is promising electron transport materials for metal halide perovskite solar cells. Their conduction band levels are slightly higher than conventional TiO2 electron transport material, which can potentially result in higher photovoltage. Furthermore, they share the same crystal structure as metal halide perovskites, offering a better interface for charge transport. Here we tried to transform TiO2 mesoporous films into SrTiO3 perovskites using in-situ hydrothermal processes.

The transformation of TiO2 mesoporous films into SrTiO3 was carried out by hydrothermal reaction in an autoclave using Sr(OH)2 aqueous solutions with different concentrations at 150 °C for 20 h. After the reaction, the XRD patterns (Figure 16) showed the peaks of SrTiO3, indicating that the transformation reaction was successful. Future efforts will focus on perovskite device fabrication using these scaffolds.
When the hydrothermal reaction temperature is reduced to 0.5h the TiO$_2$ is partially converted to SrTiO$_3$ as shown in Figure 16 blue line.

Figure 16. The powder XRD spectra for the powder obtained after transforming TiO$_2$ powder

Figure 17. Transmission electron microscopy (TEM) images of (a, b) TiO$_2$ powder and (d-e) SrTiO$_3$ powder converted from TiO$_2$ powder. EDX elemental mapping of O, Ti, Sr elements in (c) TiO$_2$ powder and (f) SrTiO$_3$ powder obtained after transforming TiO$_2$ powder.
As shown in Figure 17, after the 20-h hydrothermal reaction, the morphology of the powder has changed dramatically. The TiO$_2$ particle is a porous sphere, and the SrTiO$_3$ particle is cuboidal in shape. EDX elemental mapping further confirmed the existence of Sr and Ti in the powder, both distributed uniformly.
6. Conclusion and future work

In summary, we introduced new and modified electron selective layers which hold a big potential for their application in mesoscopic architecture based PSCs. The bimodal pore distribution in 40 nm sized TiO$_2$ beads endowed with mesopores produces a very large contact area of 200 m$^2$/g thus facilitating the interaction between the absorber layer and the electron selective layer. Furthermore, the modification of the TiO$_2$ surface by CsBr strengthens its interaction with the perovskite, which therefore, provides a new strategy to enhance the quality of mesoporous (mp)-TiO$_2$ as an electron transfer layer (ETL) in the perovskite solar cell. In addition, we developed new electron transport materials like Zn$_2$SnO$_4$, ZnO, and SrTiO$_3$ to apply in perovskite solar cells.
7. References


8. Disclaimer excluding Agency responsibility

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