

Electron Blocking Behavior of Electrochemically deposited TiO₂ Compact layers for meso- and planar-perovskite Solar Cells

Swe Swe Than¹, Tin Htun Lwin², Su Htike Aung^{3,*}, Nyein Wint Lwin³, Than Zaw Oo⁴

¹Department of Physics, Yadanabon University, Mandalay, 05063 Myanmar

²Department of Physics, Hakha College, Hakha, 03011 Myanmar

³Materials Research Laboratory, Department of Physics, University of Mandalay, Mandalay, 100103 Myanmar

⁴Universities' Research Centre, Yangon University, Yangon, 11041 Myanmar

*Corresponding Author: suhtikeaung.2012@gmail.com

Received :10 July 2019; Revised: 15 October 2019; Accepted :22 October 2019; Available online : 1 January 2020

Abstract

The TiO₂ layers were electrochemically deposited under galvanostatic mode using three different deposition times. They were intended to be used as compact layers in perovskite solar cells. The structural and optical properties and surface morphology of electrochemically deposited TiO₂ compact layers (TiO₂ ED-CLs) were studied by X-ray diffraction, scanning electron microscopy and UV-vis absorption spectroscopy. The present work mainly examined the quality and electron blocking behavior of TiO₂ ED-CLs developed under different deposition times and modified electrolytes (TiCl₃/K₂CO₃ and TiCl₃/Na₂CO₃) by cyclic voltammetry. This electrochemical study indicated that the ED-CL deposited at 800s offered an optimum blocking behavior and the TiO₂-CLs formed from TiCl₃/K₂CO₃ is apparently less dense giving lower blocking effect compared to TiO₂-CLs deposited from TiCl₃/Na₂CO₃ system.

Keywords: Electrochemical Deposition; TiO₂ Compact layer; Chronopotentiometry; Titanium(III)chloride & Blocking behavior

©2020 Sakon Nakhon Rajabhat University reserved

1. Introduction

With rapid development of perovskite solar cells (PSCs) and photovoltaic technologies, a lot of efforts have been reported addressing new materials and application methods to be applied in the devices. Perovskite solar cells can be basically categorized into two architectures, mesoscopic- and planar structured devices. Usually, mesoscopic perovskite solar cells (meso-PSCs) consist of fluorine doped tin oxide (FTO) photoanode, meso-titanium oxide (meso-TiO₂) layer to request more amount of photosensitizer, perovskite light absorber and hole transporting material (usually, state of the art one, Spiro-OMeTAD) and metal Au contact while for planar devices, there is no meso-TiO₂ layer and other layers are the same as in a meso-perovskite solar cell. During charge collection process, recombination losses occur in between FTO and TiO₂ or hole transporting material after harvesting light by perovskite light absorber. By adding a compact layer FTO/meso-TiO₂ in meso-PSCs or FTO/ perovskite in planar devices, such recombination losses can be decreased properly, preventing direct contact between the FTO and hole transporting material (HTM) to further increase device performance [1 – 3]. It is critical to reduce such recombination losses since power conversion can be lost at least around 2% in perovskite cells without a compact layer or blocking layer. Utilizing a TiO₂ compact layer in PSCs should be pin-holes-free and as thin as possible so that they could have better contact in between FTO/meso-TiO₂ or to prevent direct contact with HTM.

Several preparation methods such as chemical vapor deposition (CVD), dip coating, spin-coating, spray pyrolysis, atomic-layer-deposition (ALD) and sputtering methods have been recognized to develop TiO₂ compact layer [4, 5]. Among them, spray pyrolysis, the method introduced in 1995 by Kavan and Graätzel, is one of the popular ones to prepare a compact TiO₂ layer by using titanium precursor in diluted titanium bis-(acetoacetonato)-di-(isopropanoxylate) ethanol solution [3]. Although atomic layer deposition (ALD) and sputtering could yield favorable results for planar devices, it is costly against spray pyrolysis method [6]. Recently, efficient TiO₂ compact layer were developed by electrochemically deposition method [7]. In the pioneer work, the TiO₂ layer was prepared and applied as TiO₂ scaffold to uptake dye in electrochemical cell [8]. In fact, several reports were published for preparing TiO₂ layers with different kinds of electrolyte and additives [5, 6]. Recently this method was applied in perovskite cell as blocking layer and the performance were compared with the spin coat one and power conversion efficiency about 17% [7, 9]. S.H. Aung and coworkers reported that extremely thin layer prepared by electrochemical deposition method is very comparable in performance to the sprayed TiO₂ compact layer yielding power conversion efficiency over 20% for meso-PSCs and 17.50% for planar devices in which acidic titanium (III) chloride (TiCl₃) is used main electrolyte and sodium carbonate were used to adjust pH values [10]. In that report, it is highlighted that the TiO₂ sintered at low-temperature is promising for flexible device and large-scale production.

Here in present report, the electrochemically deposited TiO₂ compact layers (ED-CLs) were developed under galvanostatic electrodeposition mode using different deposition times, 600 s, 800 s and 1000 s. Several characterization techniques, scanning electron microscopy (SEM), X-ray diffraction (XRD) method and UV-vis spectroscopy were used to examine the structure, morphology and quality of ED-CLs and explore the optimal condition for superior performance of ED-CL.

2. Materials and methods

Materials

The materials utilized in this project are all commercially available. The details were described specifically in related parts. Fluorine-doped tin oxide (FTO) glasses were purchased from Nippon (Japan). Titanium (III) Chloride Solution $\geq 12\%$ TiCl₃ Basis was purchased from Sigma Aldrich.

Preparation of TiCl₃ solution

The acidic titanium (III) chloride solution (Sigma Aldrich) were utilized for titanium oxide layer onto FTO. Potassium carbonate (K₂CO₃) was used to adjust pH values. The pH value in the range 2.0 – 2.5 was used for Ti^{IV} layer deposition. The required solutions were obtained by adding some amounts of K₂CO₃ into 100 ml TiCl₃ (3 mM) solution. Following this, the aqueous 3 mM TiCl₃ solution (pH = 2.0 – 2.5) was used for the electrochemical deposition on transparent FTO.

Electrochemical deposition of TiO₂ compact Layer (ED-CL)

The bare FTO 3.2×10 cm² were utilized for pre-treating photoanode by electrochemical deposition. Initially, the FTO (sheet resistance ~ 10 ohm sq⁻¹) were washed by detergent 30 minutes following ethanol, DI water and acetone for 15 minutes, respectively. Then the substrates were rinsed with water and dried under airflow and electrochemically deposition on pre-cleaned FTO were performed directly. The electrochemical deposition was monitored in a three-electrode cell configuration by means of an Corr-Test potentiostat, Electrochemical workstation CS 350. The Ag/AgCl/saturated KCl was utilized as reference electrode. A titanium sheet with surface area $\sim (4 \times 12)$ cm² was used as counter electrode. A cleaned bare FTO glass of (3.2×10) cm² area was used as working electrode and then the three electrodes were dipped into the pre-pH adjusted TiCl₃ electrodeposition bath for the desired electrochemical deposition. Then the electrochemical deposition was carried out by the constant current (galvanostatic) method in air surrounding under room temperature. As optimal (in our case) a constant

current density of $\sim 25 \mu\text{A cm}^{-2}$ was applied for 600 s, 800 s and 1,000 s respectively in order to obtain a homogeneous TiO_2 layers. Afterwards, the electrochemically deposited pre-photo-anodes were washed with water in order to remove residues that could decrease the quality of ED-CLs. Thereafter, the compact form of the electrochemically deposited pre-treated photoanodes were sintered at 450°C for half an hour, with programmed heating time of 30 min from room temperature to 450°C and cooling time of 1 and half hours from 450°C to room temperature.

Materials characterization

Cyclic voltammetry

The electrochemical behaviors of ED-ULs @ 450°C with respect to control substrate, bare FTO were investigated by cyclic voltammetry (CV). The CV measurements were performed on the same potentiostat used for electrodeposition in a three-electrode cell. The 1mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M aqueous KCl was used as salt bridge. The system was calibrated with a glassy carbon disk semi-microelectrode (GC) of 0.07 cm^2 serving as working electrode. In all measurements, the Ag/AgCl/saturated KCl was utilized as reference electrode and the graphite rod was as counter electrode. Initially, the background current in 1 M KCl electrolyte was measured on the GC electrode. Thereafter, the cyclic voltammogram of 1 mM K_3FeCN_6 was recorded in the same electrolyte. Then the cyclic voltammograms of a cleaned bare FTO working electrode were measured for comparison with ED-UL@ 450°C utilized in this project.

X-ray diffraction (XRD)

The formation of TiO_2 onto FTO and its crystallinity were characterized by X-ray diffractometer (RIGAKU Multiflex). CuK_α (0.1541 nm) was used as a radiation source and measurements were performed at operating voltage 40 kV and current 20 mA in order to distinguish crystal structure of electrochemically deposited titanium oxide layer onto FTO. The intensity of the diffracted X-rays was recorded as a function of diffraction angle 2θ and observed data were analyzed.

Scanning electron microscopy (SEM)

The morphology of electrochemical deposited TiO_2 compact layers onto FTO were recorded on scanning electron microscopy (JCM-6000 Neoscope™) under operating condition of applied voltage and current 15 kV and 50 mA.

UV-vis Spectroscopy

The optical absorption properties of ED-CLs were recorded by using UV-vis spectrophotometer (Thermo, Genesys 10S) in the visible region. The baseline scan was performed using bare FTO glass substrate.

Estimation of thickness of ED-CLs: Faradaic efficiency

The thickness of ED-CLs were estimated from Faraday's law, $d_{100\%} = JtM_w / F\rho (1 - \varepsilon_{pore})$ presuming that a Faradaic efficiency is 100% for the fabrication of the ED-CLs. Then, for the application of the one-electron oxidation of the crystallographic form produced after heating at 450°C according to Kavan et al. [8], and (ε_{pore}) is the porosity of the UL. For $J = 20 \mu\text{A /cm}^2$, $t = 800 \text{ s}$, and assuming $\varepsilon_{pore} = 0$, a thickness of $\sim 34.00 \text{ nm}$ is calculated.

3. Results and Discussion

Structure and Surface Morphology of ED-CLs

XRD patterns of ED-CLs onto FTO substrates were shown in Fig 1. The overall spectra showed that TiO_2 layer were well formed onto required substrates. The XRD patterns of ED-CLs produced from

$\text{TiCl}_3/\text{Na}_2\text{CO}_3$ and $\text{TiCl}_3/\text{K}_2\text{CO}_3$, namely A and B in Fig.1 exhibited strong diffraction peaks at 35° and 55° as well as peaks contribution at 63° and 68° designating TiO_2 in the anatase phase for generation of TiO_2 ED-CLs generated at 800s with applied current $20 \mu\text{A cm}^{-2}$ from acidic titanium (III) chloride at room temperature following sintering temperature 450°C .

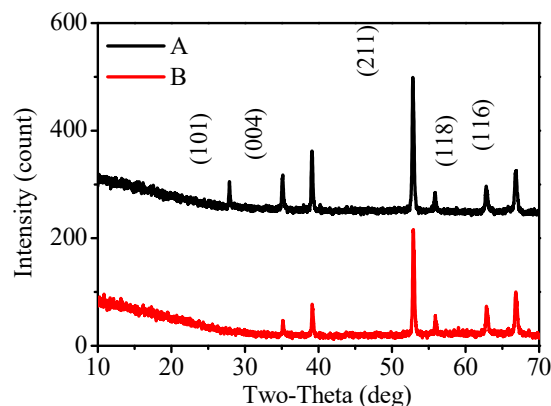


Fig. 1 XRD spectrum of ED-CLs formed from acidic titanium (III) chloride at room temperature following sintering temperature 450°C : (A-black line) TiO_2 -ED-CLs from $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ @800s) and (B-red line) ED-CL from $\text{TiCl}_3/\text{K}_2\text{CO}_3$ @800s.

The scanning electron microscopy SEM was utilized to examine morphology of ED-CLs. Fig. 2 shows the SEM images of TiO_2 ED-CLs prepared from $\text{TiCl}_3/\text{K}_2\text{CO}_3$ and $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ (deposition times of 600 s, 800 s and 1000 s). It is clearly seen that the TiO_2 were fully formed on FTO for all samples but it is tough to see the morphology difference since the ED-CLs were extremely thin. The UV-vis absorption data in Fig. 3 will later suggest that the TiO_2 -ED-CLs grown from $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ is likely nicer than those of ED-CLs from $\text{TiCl}_3/\text{K}_2\text{CO}_3$ to be applied in solar cell devices. Apparently there is porous or some pinhole in the ED-CLs of $\text{TiCl}_3/\text{K}_2\text{CO}_3$ which results in less absorption.

Electrochemical blocking Behaviors of TiO_2 ED-CLs

The cyclic voltammograms were recorded to investigate the electrochemical electron blocking behaviors of TiO_2 ED-CLs. The thickness of ED-CL estimated from Faraday's equation is $\sim 26.0 \text{ nm}$, $\sim 34.00 \text{ nm}$ and $\sim 43.00 \text{ nm}$ for the deposition time of 600 s, 800 s and 1,000 s respectively. From the CV curves in Fig. 4, it can be seen that the electrochemical properties of the compact-layer at 800 s get enhanced for TiO_2 -ED-CLs compared to ED-CLs deposited at 600 s and 1,000 s. In particular, the ED-CL deposited at 800 s shows an optimum blocking behavior. The thickest compact layer at longest time scale (1,000 s) gives the least blocking quality which was recently reported by S.H. Aung and co-workers in their devices employing ED-CLs [10]. In fact using two sorts of additives to adjust pH values of TiCl (III) electrolyte doesn't impact significantly to get good quality compact layer in this scope, nevertheless they show the similar blocking trends on differently deposition time scales. It is found that the quality of ED-CLs is considerably dependent on the input parameters of electrochemical deposition. Although electrochemical deposition were carried under air surrounding, we received efficient dense compact layers. The different electrochemical behaviors were received and optimized by applying different deposition time. The cyclic voltammogram of ED-CLs produced at 800 s for both additives are presented in Fig. 4. The TiO_2 -CLs formed from $\text{TiCl}_3/\text{K}_2\text{CO}_3$ mixture is apparently less dense giving lower blocking effect compared to TiO_2 -CLs deposited from $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ system. Nevertheless it is still leading favorable results than TiO_2 -CLs deposited at 1000s from $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ system to work efficiently in device application.

In the previous studies, although electrochemical deposition of required materials were performed under an argon or an nitrogen surrounding[8 – 12], electrochemical deposition in this present work were performed in air surrounding. However we have found that, deposition of CLs under air surrounding could not be unbeatable the performance of CLs. Contribution of pH values above 2 may be facile advantageous to get efficient compact layer. In similar reports by B. Z Endrodi and co-workers, amorphous layer were observed for using low pH values, pH 2.00 and below pH 2.00 values [13].

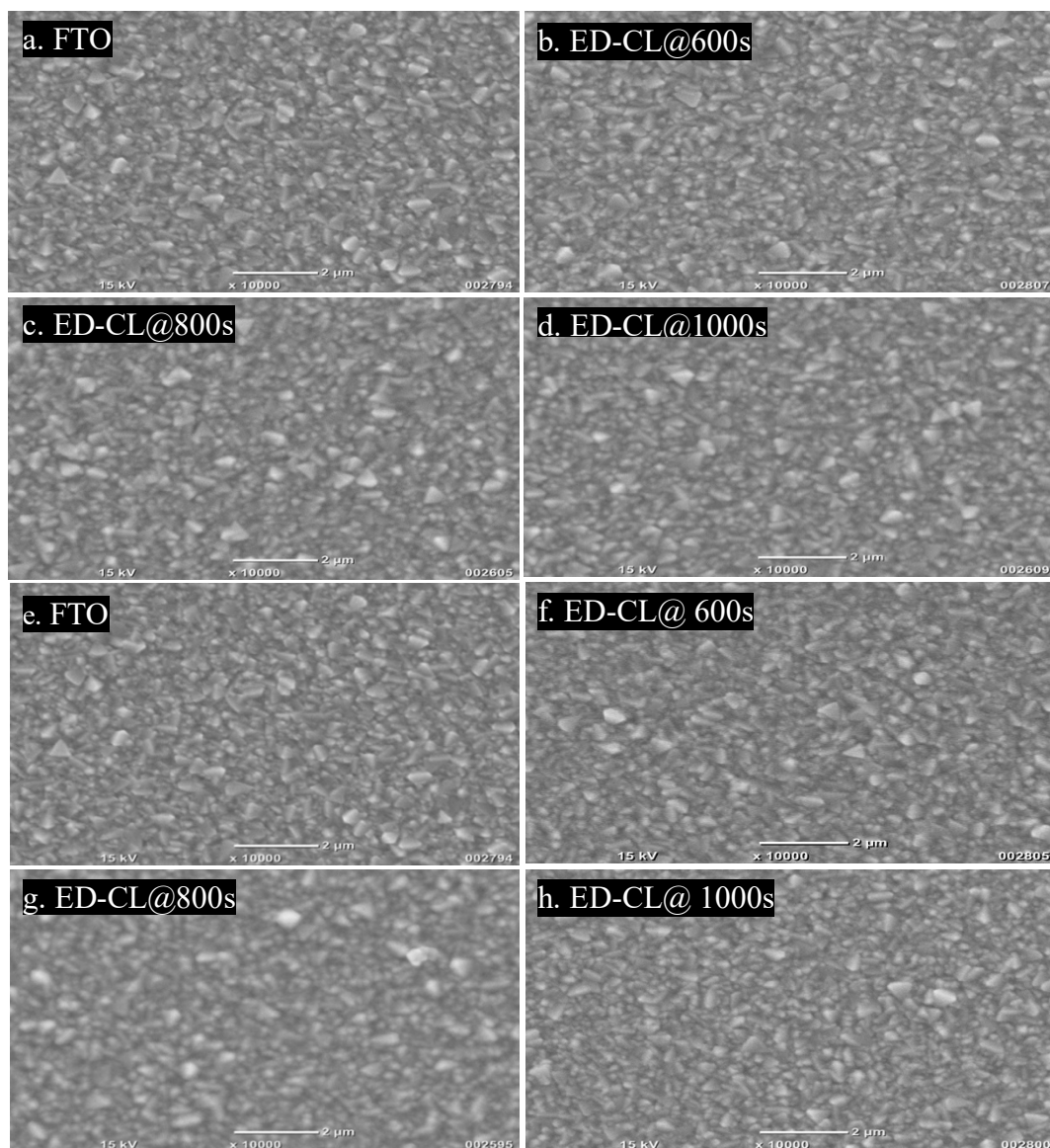


Fig. 2 SEM images (Front views) (a-d) bare FTO and ED-CLs from $\text{TiCl}_3/\text{K}_2\text{CO}_3$ at 600 s, 800 s and 1,000 s and (e-h) bare FTO and ED-CLs from $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ at 600 s, 800 s and 1000 s

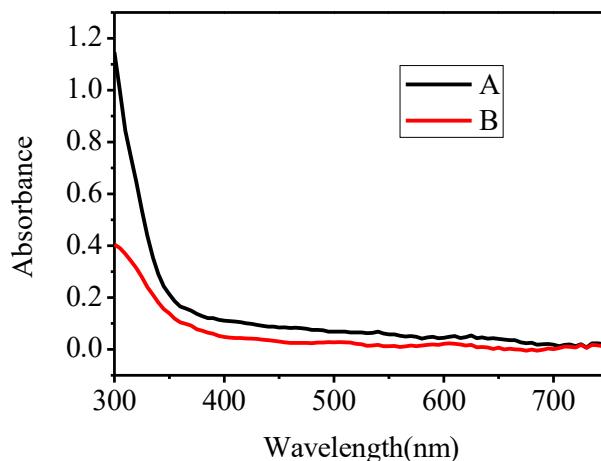


Fig. 3 UV-vis absorption spectra of (A-black line) TiO_2 -ED-CLs from $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ @800 s) and (B-red line) ED-CL from $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ @800 s.

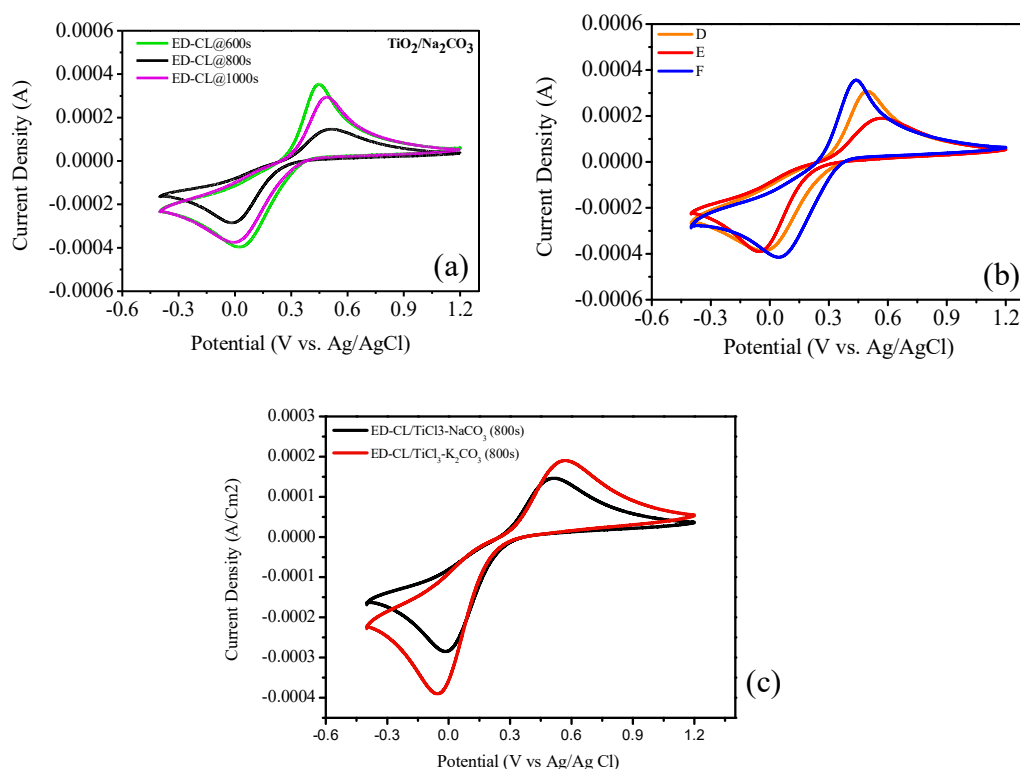


Fig. 4 Cyclic voltammograms of ED-CLs deposited from (a) $\text{TiCl}_3/\text{K}_2\text{CO}_3$, (b) $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ at different deposition times (600 s, 800 s and 1,000 s) and (c) $\text{TiCl}_3/\text{K}_2\text{CO}_3$, and $\text{TiCl}_3/\text{Na}_2\text{CO}_3$ at deposition time of 800 s. Scan rate (20 mV-s).

Furthermore, it was observed that on preparation of required electrolyte, adjusting a pH 2.50 values with Na_2CO_3 get much precipitation (TiO_2 particles) than that of using K_2CO_3 for adjusting pH values. For electrochemical deposition, differently with other studies [13], applying longer time scale and current few micron-amperes and it may lead better performance of CLs in agreement with S.H. Aung and co-workers [10]. The time scale we use may long however utilizing low applied current density may get covered for producing efficient compact layers and it kept stabilizing electrolyte solution. Alternatively, it would be interesting using other organic solvent instead of water for preparing denser

TiO₂CLs. Providing the thickness of ~ 34.0 nm, electrochemically deposited TiO₂ CLs at 800 s met the optimal performance for both Na₂CO₃ and KCO₃ compared to TiO₂ CLs at 1,000 s and 600 s respectively. Therefore further optimizing should be carried out for future solar cells application.

4. Conclusion

Conclusions and outlook

The TiO₂ layers were electrochemically deposited for compact layers in perovskite solar cells. SEM study showed that no significant morphology alteration was observed upon varying deposition time and electrolyte additive since the layers are too thin to see the difference. This electrochemical study indicated that the ED-CL deposited at 800 s offers an optimum blocking behavior and the TiO₂-CLs formed from TiCl₃/K₂CO₃ is apparently less dense giving lower blocking effect compared to TiO₂-CLs deposited from TiCl₃/Na₂CO₃ system. The deposition method for TiO₂ layer is straightforward and the resulting films are promising as electron blocking compact layer in perovskite solar cells. This study opens up the further investigation of ED-CLs using proper additives and/or changing applied current density under galvanostatic mode to realize an outperform ED-CLs for perovskite photovoltaics.

5. Acknowledgement

The authors acknowledge the research grant from the project (MYA:01 - 2017 – 19) supported by International Science Program (ISP), Uppsala University, Sweden.

6. References

- [1] M.M. Lee, J. Teuscher, T. Miyasaka, T.N. Murakami, H.J. Snaith, Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites, *Science*. 338 (2012) 643 – 647.
- [2] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitised solar cells, *J. Chem. Rev.* 110 (2010) 6595 – 6663.
- [3] L. Yang, Hole Transport Materials for Solid-State Mesoscopic Solar Cells, PhD, Uppsala University, Uppsala, 2014.
- [4] X. Chen, S.S. Mao., Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications, *J. Chem. Rev.* 107 (2012), 2891 – 2951.
- [5] L. Kavan, N. Tetreault, T. Moehl, M. Grätzel, Electrochemical Characterization of TiO₂ Blocking Layers for Dye- Sensitized Solar Cells, *J. Phys. Chem.* 118 (2014) 6408 – 1641.
- [6] L. Kavan, M. Grätzel, Highly efficient semiconducting TiO₂ photoelectrodes prepared by aerosol pyrolysis, *Electrochim. Acta*. 40 (1995) 643 – 652.
- [7] T.S. Su, T.Y. Hsieh, C.Y. Hong, T.C. Wei, Electrodeposited Ultrathin TiO₂ Blocking Layers for Efficient Perovskite Solar Cells, *Scientific Report*. (2015)16098.
- [8] L. Kavan, B.O'Regan, M. Grätzel, Preparation of TiO₂ (anatase) films on electrodes by anodic oxidative hydrolysis of TiCl₃, *J. Electroanal. Chem.* 346 (1993) 291 – 307.
- [9] T.S. Su, T.Y. Hsieh, C.Y. Hong, T.C. Wei, Electrodeposited TiO₂ Film with Mossy Nanostructure for Efficient Compact Layer in Scaffold-Type Perovskite Solar Cell, *Adv. Sci. News*. (2018) 1700120.
- [10] S.H. Aung, L. Zhao, K. Nonomura, T.Z. Oo, S.M. Zakeeruddin, N. Vlachopoulos, T. Sloboda, S. Svanström, U.B. Cappel, A. Hagfeldt, M. Grätzel, Toward an Alternative Approach for Preparation of Low-Temperature Titanium Dioxide Blocking Underlayer for Perovskite Solar Cells, *J. Mater. Chem. A*. 7 (2019) 10729 – 10738.
- [11] A. Manivannan, N. Spataru, K. Arihara, A. Fujishima. Electrochemical Deposition of Titanium Oxide on Boron-Doped Diamond Electrodes, *Electrochem. Solid-State Lett.* (2005)138 – 140.

- [12] S.Y. Lin, T.Z. Su, T.Y. Hsieh, P.C. Lo, T.C. Wei, Efficient Plastic Perovskite Solar Cell with a Low-Temperature Processable Electrodeposited TiO₂ Compact Layer and Brookite TiO₂ Scaffold, *Adv. Energy Mater.* 7 (2017) 1700169.
- [13] B. Endrődi, E. Kecskenovity, K. Rajeshwar, C. Janáky, One-step Electrodeposition of Nanocrystalline TiO₂ Films with Enhanced Photoelectrochemical Performance and Charge Storage, *ACS Appl. Energy Mater.* (2018) 851 – 858.