Thesis Changes Log

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PhD Program: Physics

Title of Thesis: Single-Walled Carbon Nanotubes in Top Cell for Perovskite – Silicon Tandems

Supervisor: Prof. Albert Nasibulin

The thesis document includes the following changes in answer to the external review process.

Dear Jury Members,

I would like to express my gratitude for your comments and suggestions which helped to significantly improve my PhD thesis.

Sincerely

Aly

Prof. Maoshuai He:

Comments:

1. There are some typos in the thesis, the authors could pay more attention to the writing.

   Thank you very much for your comment I have reviewed the thesis and corrected all the mistakes addressed.

2. In the Chapter 2, review of articles should include a brief introduction of SWCNTs, like SWCNT structure and their previous applications in perovskite solar cells.

   Thank you very much for your comment. Surely, it is important to address this introduction to SWCNTs. We have included it in chapter 3 instead where in section 3.1 we investigate the synthesis and in 3.2 we address the previous application of SWCNTs in perovskite solar cell.

3. As the SWCNT properties are crucial for their applications, some basic characterization results of SWCNTs are suggested to present

   Thank you very much for your comment

The Transmittance spectra of the 80% transmittance SWCNTs used in this work was reported in Figure A2. We have also included SEM and TEM images of Carbon nanotubes were provided in the Appendix in Figure A20

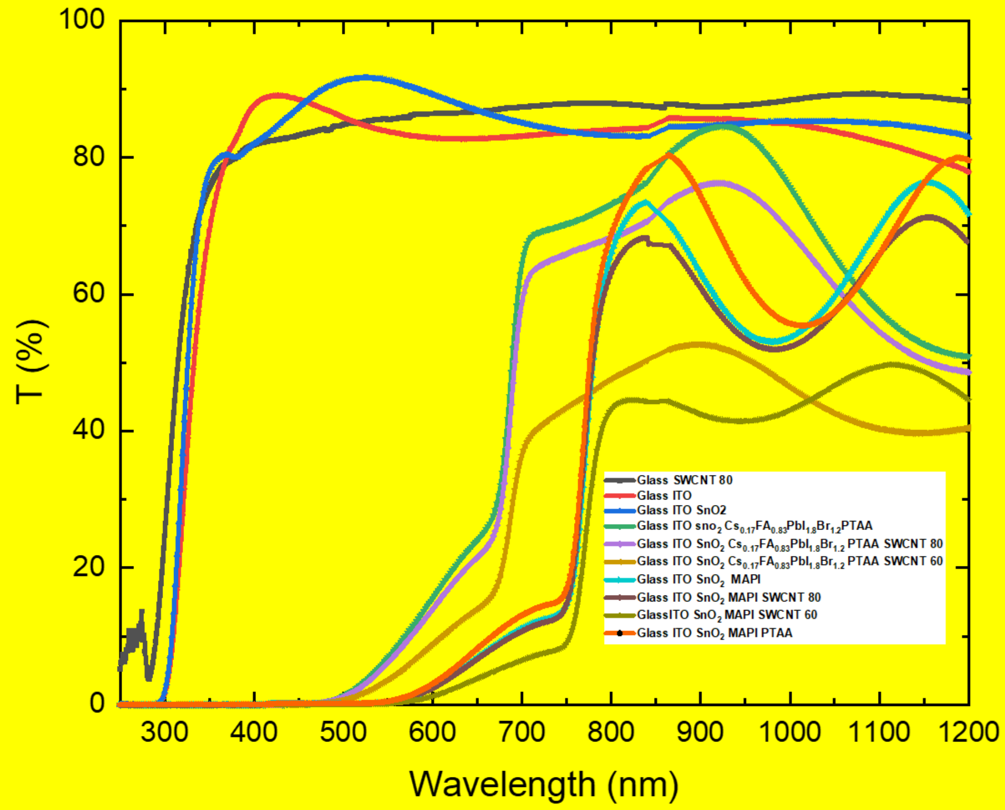

Figure A2: Transmittance spectra of various layers used to fabricate the solar cells.

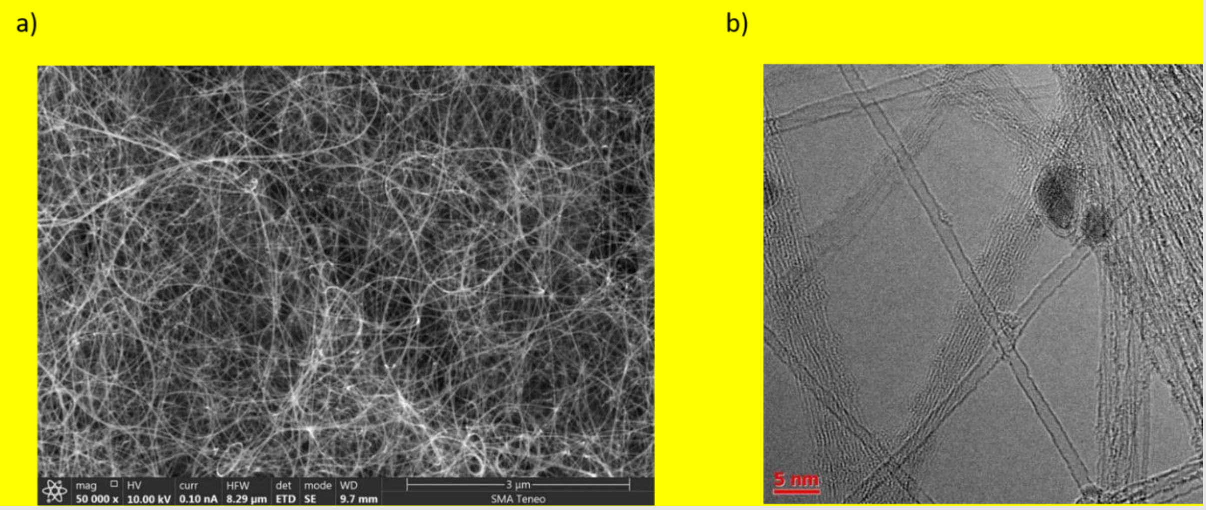

Figure A20: a) SEM image of SWCNTs network films, b) TEM image for SWCNTs.

Prof. Dmitry Lyubchenko

Comments:

- Fig.3.3 PL in (au) why is that? I would say it is dimensionless.
- Fig.4.1 Caption – correct misprints chemical eq.
- Fig.4.10 Absorbance more than 1, why is that?
- Fig.4.10 d) PL in (au) why is that?
- all plots are in different formats.

Thank you very much for your comment I have made the corrections considering the units on the figure and replotted the figure.

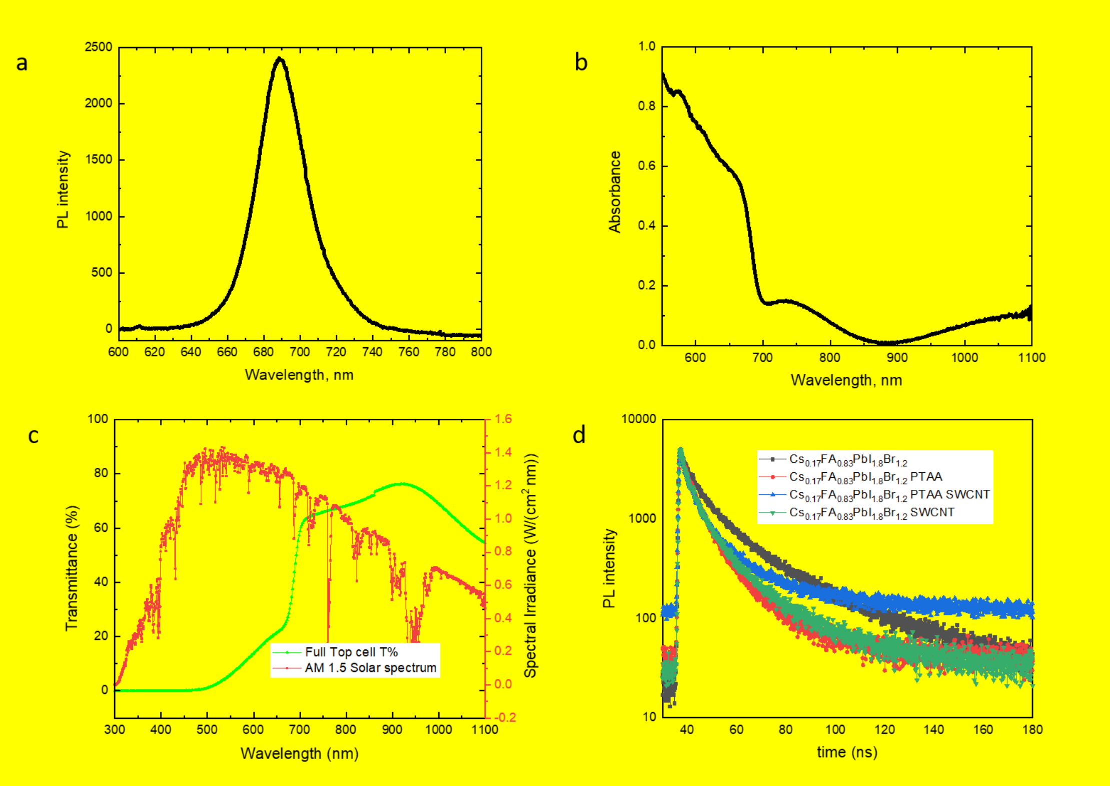

Figure 4.10. (a) Photoluminescence (PL) spectra of $Cs_{0.17}FA_{0.83}PbI_{1.8}Br_{1.2}$. (b) Absorption spectra of $Cs_{0.17}FA_{0.83}PbI_{1.8}Br_{1.2}$ (c) Transmittance spectra of ITO glass and coated with SnO_2 window layer (black and blue), respectively, perovskite top cell (green) compared to the AM1.5 spectra from NREL (red)[22]. (d) Time resolved photoluminescence spectra of wide bandgap perovskite $Cs_{0.17}FA_{0.83}PbI_{1.8}Br_{1.2}$ layer (black), covered with PTAA (red), covered with SWCNT (green), and ($Cs_{0.17}FA_{0.83}PbI_{1.8}Br_{1.2}$) covered with PTAA and SWCNT (blue).

Professor Nikolay A. Gippius:

Comments:

- Avoid abbreviations in the titles of chapters: e.g. 3.1.1 SWCNTs, 3.1.3 ETLs, 3.1.4 HTLs. The thesis is not at all too long and for the reader not from this field it is better to remind the abbreviations.

Thank you very much for your comment I have made the corrections corresponding to your comments in the titles.

"3.1.1 Single-Walled Carbon Nanotubes SWCNT, 3.1.3 Electron transport layer ETL, 3.1.4 Hole transport layer HTL"

Prof. Dmitry Gorin:

Comments:

1) page 13-15 Chapter 1 (Introduction) I recommend to formulate the goal and tasks in this part of PhD thesis. It would be inserted instead of brief results in the end of indroduction.

   Thank you very much for your comment I have rephrased the final paragraph in the introduction section to address the goal and tasks.

   "The goal of this work is to investigate the application of single-walled carbon nanotubes films as transparent back electrodes in perovskite solar cells. We aim to study the charge extraction capabilities using different electrical and optical methods. We also enhance the photovoltaic performance of the cells using passivation techniques. Then we apply SWCNT as back electrodes for wide band gap perovskite absorber, namely, $Cs_{0.17}FA_{0.83}PbI_{1.8}Br_{1.2}$. We investigate its electrical and optical properties from the perspective of the top subcell. And finally, we use them in perovskite silicon tandem in four terminal configurations."

2) Page 16 Chapter 2. Please add conclusions to the end of this chapter. Please formulate here the main challenge that you are going to overcome by your particular research.

   Thank you very much for your comment I have added the following paragraph at the end of chapter 2:

   " Therefore, in this work, we investigated the 4-Terminal Perovskite-Silicon tandem solar cell. In order to provide an alternative solution to the sputtered ITO in the back electrode in the top subcell, we incorporated SWCNT as transparent back electrode. We studied the electrical and optical characteristics of the top subcell and its influence on the overall performance of the full tandem cell."

3) Page 34, 3.3 Characterization Methods, please correct the equation 10, absorbance A is the
   logarithm of the ratio of incident light intensity (Io) to transmitted intensity trough the sample (I).

4) Page 34, 3.3 Characterization Methods, please correct equation 11, base of logarithm 10 shoud be written by the smaller letter as in equation 10.

Thank you very much for your comment, I have corrected equations 10 and 11 in the main text as requested.

"According to the equations below absorbance can be described as:

$$A = \log_{10}(\frac{I_0}{I}) \quad , \tag{10}$$

where the transmittance T% is, by definition, the ratio between transmitted and incident photons neglecting the reflection factor.

$$A = \log_{10}(\mathrm{T}) = \log_{10}(\frac{T\%}{100\%} \quad , \tag{11}$$"

Assistant Professor: Sakellaris Mailis:

Comments:

There are several issues that I have identified, which are marked as comments in the submitted manuscript. One particular issue is the last section that discusses the tandem cell, which is extremely thin. I am sure that more characterization data could be presented there as well as comparison with the literature.
It is not clear to me what is the purpose of the figures in the appendix. They are not referred to in the manuscript

Thank you very much for your comments I followed your comments on the manuscript and made all the necessary corrections. Regarding the ambiguity of the Tandem characteristics in the last section and results in the Appendix, I have added the following Paragraph for explanation of tandem results and connection with the appendix:

"The four terminal tandem overall power conversion efficiency is calculated by summing the power conversion efficiency of the top subcell to the power conversion efficiency of the bottom subcell with top subcell's shadow. Here there has to be a tradeoff to make in order to achieve the highest efficiency of the over all tandem. The top subcell has to be as efficient as possible and at the same time it has to be as transparent as possible in order to pass sufficient light to the bottom subcell.
In order to accomplish this goal parasitic absorption from non-photoactive layers must be minimized. For example, the use of 80% transmittance SWCNT is optimum. When we use 60% SWCNTs the efficiency of the bottom subcell reduces dramatically as in Figure A5 in the Appendix"

Assistant Professor: Anatoly Pushkarev:

Comment:
"i) A complete expression for J-V curve of solar cells contains series and shunt resistance. How large these values in the fabricated top cells are? What is their impact on photoelectric conversion efficiency?"

Thank you very much for your comment. Indeed, the electrical properties of the cells are crucial for the overall performance assessment, especially the series resistance. For metal electrodes series resistance is quite low but we have to make a trade-off in order to use transparent electrodes for tandem applications. We explained in detail in figure 4.11. especially 4.11 b

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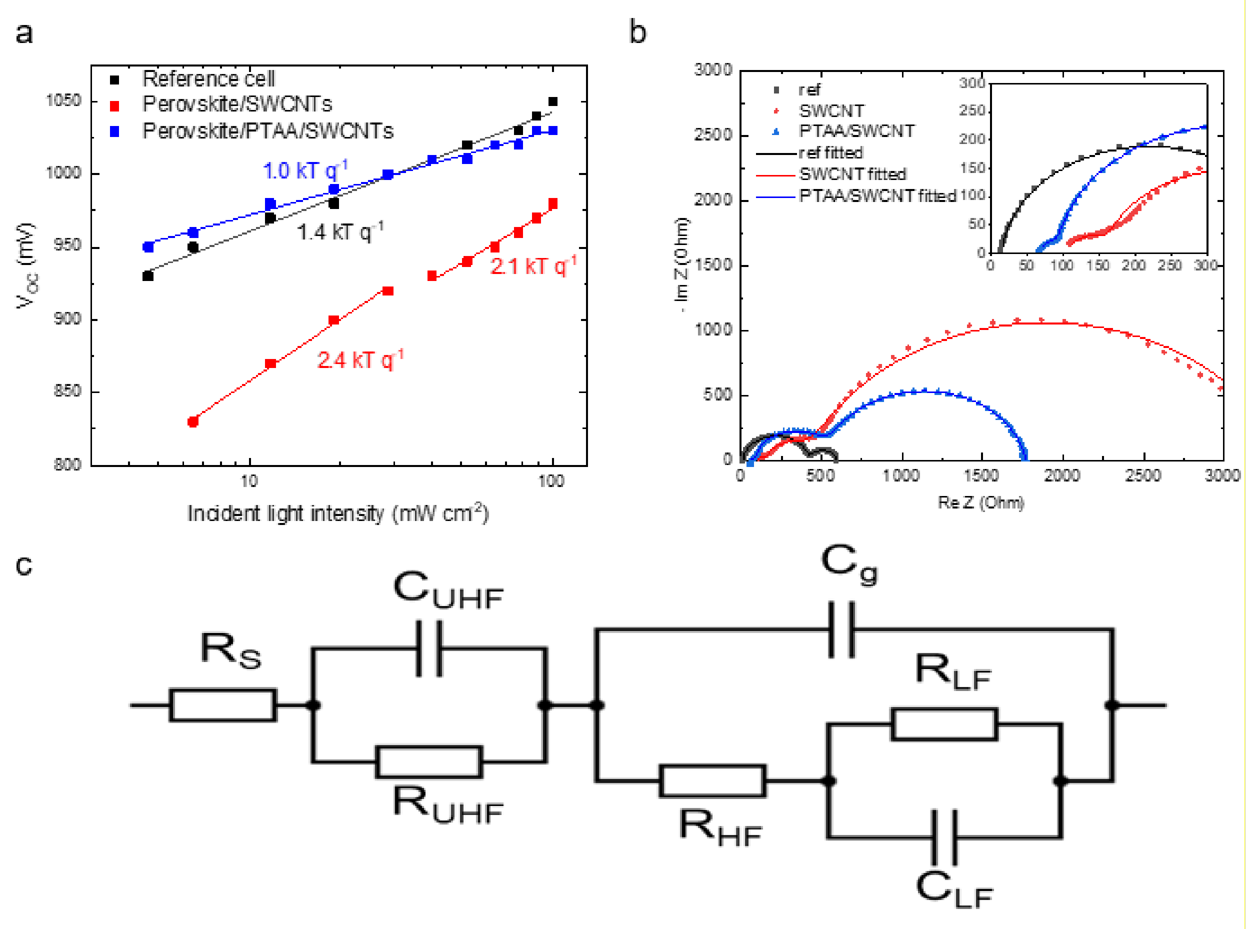

Figure 4.11. a) Suns-V_{OC} curves of PSCs with different top electrodes; b) Spectra recorded from PSCs with different top electrodes under 20 mW cm^{-2} illumination and open circuit conditions. Inset shows a magnified high-frequency region; c) General equivalent circuit used to fit IS data.

First, series resistance R_S, which can be determined as the high-frequency intercept with the X-axis, differs significantly between the samples. For metal electrode reference it is about 14 Ohm which is consistent with most values reported in the literature. However, it drastically increases to 67 Ohm for the PTAA/SWCNT sample and even more so for the pure SWCNT sample (101 Ohm). This is most likely due to the higher sheet resistance of SWCNT electrodes compared to aluminum. We assume that the difference in R_S values between PTAA/SWCNT and SWCNT samples might come from the better SWCNT adhesion to PTAA compared to uncovered perovskite which improves mechanical and electrical contact between the active layer and electrode."

"ii) The Author uses Tauc plot approximation of the optical absorption spectrum edge to derive a band gap energy value (Eg). This approximation is applicable to square root relation between absorption and photon energy since optical transitions in a direct semiconductor are supposed to occur between two parabolic potentials in the conduction and valence bands, respectively. In the case of halide perovskites, the absorption spectrum edge has a complex lineshape. It consists of band-to-band and excitonic absorption. The latter one could be represented as a sum of Lorentzian peaks corresponding to optical transitions from the ground state to discreet excitonic levels and cannot be approximated by Tauc plot. Therefore, I think there is a small error in the derived value Eg. Could the Author comment about the accurate estimation of Eg and evaluate the error?"

Thank you very much for your comment, This absolutely true therefore, the bandgap was calculated from the Tauc plot and confirmed from the PL spectra.

"iii) Looking at equation for charge carrier dynamics one can see ABC model reported by Shen et al. [Appl. Phys. Lett., 2007, 91, 141101] is adopted in the thesis. In this model charge carriers do not reside in trap states and undergo rapid nonradiative relaxation. As a result, the concentration of excited electrons (n) and holes (p) is the same and can be described by n solely. However, the Author introduces p, n, and their lifetime τp and τn, that seems to be important when Shockley-Read-Hall model [Phys. Rev., 1952, 87, 835; Phys. Rev., 1952, 87, 387–387] is considered for the description of charge carrier dynamics. I was wondering if there is a particular reason for the mixing two different formalisms?"

Thank you very much for your comment I totally agree and use the same assumption for equal charge carrier concentrations.
P, n was only addressed for the literature review.

"iv) I noticed bi-exponential approximation of PL decay in Figure 3.3. If the Author employs ABC model and neglects third order member k3n3 associated with Auger nonradiative recombination, the solution of the equation (18) cannot be bi-exponential function. The Author should explain his approach to calculation of lifetime values for bi-molecular and monomolecular decay."

Thank you very much for your comment the biexponential decay is to fit the measured PL decay from the TRPL data. We do not neglect auger recombination in our calculations. In our investigation the TRPL decay lifetime is taken for the photoactive material regardless of its components. Our interest is to compare the lifetime of the same photoactive material in contact with different conductive layers such as SWCNTs and PTAA as shown in Figure 4.10.d. --