Spray deposited thin uniform NiO/Spiro-OMeTAD composite hole transport layer with top carbon nanotube electrode

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Abstract. Thin Spiro-OMeTAD and NiO nanoparticles layers, as well as their composite layer was formed by layer-by-layer spray deposition as hole-transport layer (HTL), with followed carbon nanotubes (CNT) deposition to form Ti/TiO$_2$/HTL/CNT structures. Layers’ uniformity was estimated by Raman intensity maps, AFM and current-voltage characteristics of the CNT layer and between CNT and Ti contacts. The possibility of formation of thin, less than 100 nm, pinhole-free uniform composite NiO/Spiro-OMeTAD layer by spray-deposition was shown, which manifests itself as continuous HTL even after top CNT layer deposition.

1. Introduction
Due to the insufficient time stability at work under ambient conditions of solar cells based on organic materials, especially in the case of perovskite solar cells [1], new materials and formation principles of the hole-transport layers (HTL) are developing, which characterized by dopant-free conception, using composites based on oxide nanoparticles and low molecular weight organic compounds or polymers [2]. Although it is possible to achieve relatively acceptable quantum efficiency even using the dopant-free thin Spiro-OMeTAD layer formed by vacuum deposition, the best values are achieved only with dopant, however, it significantly decreases time stability at ambient conditions [3]. Lifetime stability can be also increased by inorganic compounds adding to the HTL composition [4]. Thus, the development of thin composite HTL based on undoped Spiro-OMeTAD or other molecules with nanoparticles, formed by low temperature spray deposition is a relevant task, which is the subject of present work. Another important aspect of present work is the possibility of using carbon nanotubes (CNT) and their composites with polymers as the top conductive layer (and also, possibly, transparent), which allows improving the perovskite cells stability [5]. Moreover, the replacement of metal and/or ITO with CNTs provides a weak dependence of the electrode conductivity on the concentration of I$^-$ and CN$^-$ anions, which additionally increasing the stability of the structures [6].

2. Materials and methods
Cover glasses 24x24 mm with magnetron deposited thin layers: Ti (about 30 nm) and then TiO$_2$ (about 3-7 nm with roughness less than 1 nm), were used as substrates. TiO$_2$ sputtered by Ti target in argon-oxygen gas mixture at rate about 0.5 nm per minute. Substrates with TiO$_2$/Ti were used for spray-deposition and investigation HTL and top CNT layer (used functionalized single-wall CNT P3-SWNT, Carbon Solutions Inc., USA). Pure Spiro-OMeTAD (99 % (HPLC), Sigma Aldrich, USA), Spiro-OMeTAD using of nickel oxide nanoparticles (nNiO) sublayer (diameter < 80 nm, but with large conglomerates ~ 150 nm presence, 99.9 %, Simplex LLC, Russia), as well as simply nNiO layer
were investigated as a HTL. As a result, four types of structures were formed on the substrates with a TiO$_2$/Ti sublayer to analyse the possibility of uniform HTL and CNT layer forming: A) CNT, B) nNiO/Spiro-OMeTAD/CNT, C) nNiO/CNT and D) Spiro-OMeTAD/CNT. The deposition of both CNTs and Spiro-OMeTAD, as well as nNiO, was carried out by spray-deposition from various solvents: dimethylacetamide (DMA, > 99.5 % (HPLC), Applichem GmbH, Germany) for Spiro-OMeTAD, propyleneglycol with cyclohexanol (PG and CHL, > 99 %, Component-Reactive Ltd., Russia) for CNT, and PG with DMA for nNiO by a method that similar to described earlier [7]. The deposition was carried out on heated substrate (about 90 ºC) by own designed spray-coating system with use shadow mask on 2 mm diameter round area for HTL deposition, and then on rectangular area 4x1.5 mm for top CNT layer deposition (centred in HTL area). To estimate the mixing/dipping of CNT into the Spiro-OMeTAD, nNiO and nNiO/Spiro-OMeTAD sublayers atomic force microscope (AFM, Solver Pro, NT-MDT, Russia) was used. Also for this and to measure electrical characteristics of the formed CNT layers (with two Ag-paste contact pads at short sides of CNT rectangular area that not covers HTL area) and structures as a whole (between CNT and Ti layers as contacts) semiconductor parameters analyser IPPP 1/5 (OJSC “MNIPI”, Belarus) was used. The nonuniformity degree of Spiro-OMeTAD and CNT materials in appropriate layers were analysed by Raman mapping at 20x20 points (Centaur HR, Nano Scan Technology Ltd., Russia).

3. Results and discussions

Spray deposition of undoped Spiro-OMeTAD on a substrate does not provide a thin (< 150 nm) uniform layer, which was revealed both by AFM and Raman 1615 cm$^{-1}$ region intensity map [3] (figure 1a, where shaded area is the Raman spectrometer background signal < 180 arb.units with Spiro-OMeTAD absence, according to AFM). The substrate was heated to 90 ºC during deposition, so Spiro-OMeTAD was crystallized, which was confirmed by Raman spectroscopy. The use of a uniformly deposited nNiO (uniform, but island-like sublayer), which have an energy levels similar to Spiro-OMeTAD [4, 6] and suitable for HTL formation, significantly improved the Spiro-OMeTAD uniformity in sequentially spray-deposited uniform nNiO/Spiro-OMeTAD composite layer when nNiO used as sublayer (figure 1b,c) especially when optimal nNiO substrate coverage was achieved. The value of layer nonuniformity was determined by ratio of standard deviation to median value of Raman intensity [8], that was 0.8 for Spiro-OMeTAD in composite layer, which, although higher than for spray deposited CNTs (ratio is 0.2-0.3), but much lower than for pure Spiro-OMeTAD layer, only partially covering the surface (ratio is 3.3). Spiro-OMeTAD uniformity significantly depends on the nNiO density on the substrate: low nanoparticles covering degree (< 20-30 %) still forms areas without Spiro-OMeTAD (compare figure 1a (corresponds to structure D) and 1b). Therefore significant percent of the surface was still not covered by Spiro-OMeTAD (value of layer nonuniformity is about 1.7, but still higher than 1.0), and that percent was significantly more than in the case of 60-70 % surface coverage of the substrate by nNiO formed sublayer. That percent coverage by nNiO (60-70 %) determined as optimal because acceptable substrate coverage by Spiro-OMeTAD as part of the composite layer was obtained (figure 1c). After obtaining a uniform Spiro-OMeTAD layer, CNTs were deposited on the structure of this type (structure B), as well as on structures of other types to compare uniformity and resistivity of CNT layer. The results of AFM control of the top CNT layer are shown in figure 2. To compare the AFM data in figure 2 with the initial nNiO layer the sublayers of nNiO were also investigated by AFM. Figure 3a,b demonstrated the cases of the substrate covered by nNiO formed island-like underlayer with different percent coverage that lower than 100 % even for figure 3b taking into account deconvolution parameters of AFM tip and true nNiO diameter that equal to height on AFM image. Non-full coverage by nNiO sublayer was used to obtain the composite structure of HTL as nNiO/Spiro-OMeTAD and to form the possibility of charge transport through Spiro-OMeTAD as well as nNiO material or both. Measured CNT layer resistance ($R_{CNT}$) was: A - 35.7 kΩ, B - 37.6 kΩ, C - 116.9 kΩ, D - 51.8 kΩ; while the CNT surface density differences were < 15 % (control by Raman spectroscopy). According to the AFM data there is a smoother and denser CNT layer on top of composite nNiO/Spiro-OMeTAD with less roughness and a smaller
amount of observed deepened areas in comparison to on nNiO sublayer. And finally CNTs weren't observed on top of pure Spiro-OMeTAD (complete CNTs dipping into or mixing with covered by pure Spiro-OMeTAD areas in sublayer is realized). But composite structure provides the absence of deeply dipped into the HTL sublayer CNTs (in contrast to structure D), with nonlinear current-voltage characteristics (CVC) between CNT and Ti (at positive voltage \( U_{CNT-Ti} \), that described below) and therefore the pinhole absence and no shunting of HTL (through formation of shunt CNT-TiO\(_2\)/Ti contacts), in contrast to the CVC for structures C and D, which indicates to better sublayer quality and continuous and uniform HTL structure realizing by nNiO/Spiro-OMeTAD composite sublayer.

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**Figure 1.** Raman map of Spiro-OMeTAD peak for: a) pure Spiro-OMeTAD; b,c) composite layer nNiO/Spiro-OMeTAD: with ~30% surface coverage by nNiO sublayer (b), and with ~70% coverage (c). Scale bar is 10 µm.

**Figure 2.** AFM data of structures A-D: a) CNT, b) nNiO/Spiro-OMeTAD/CNT, c) nNiO/CNT, d) Spiro-OMeTAD/CNT. Scale bar is 1 µm.

**Figure 3.** AFM data of nNiO underlayer obtained with: a) 20-30% covering substrate, b) 60-70% covering. Scale bar is 2 µm.

That behavior also confirmed by similar \( R_{CNT} \) for structure B in comparison with A, having smooth substrate, in contrast to the increased \( R_{CNT} \) on nNiO sublayer of structure C, where some CNTs were dipped between nanoparticles (according to AFM there is lower CNTs density on the top of structure C than for A or B). Despite CNTs to Spiro-OMeTAD dipping for structure D, it weakly affects the uniformity of presumably thin and dense CNT layer (according to Raman map) but it couldn't be detected under Spiro-OMeTAD layer by AFM. So \( R_{CNT} \) for structure D insignificantly differs from structure A, despite alcohols used for CNTs deposition, partially dissolve Spiro-OMeTAD. Despite to partially dissolving of Spiro-OMeTAD lower influence of that to \( R_{CNT} \) for composite sublayer in comparison to structure A was obtained. But differences in \( R_{CNT} \) between structures A and B
significantly lower than between structures A and D. So Spiro-OMeTAD mixing with CNT in composite HTL layer of structure B was insignificant in comparison to structure D (compare figure 2b and 2d). So Spiro-OMeTAD uniformity insignificantly changed even after the top CNT layer deposition as for composite layer (structure B) as structure D (compare figure 4 and figure 1). The additionally obtained Raman maps of the ratio \( \frac{I_{\text{Spiro}}}{I_{\text{CNT}}} \) of the main peak of Spiro-OMeTAD (1615 cm\(^{-1}\)) to CNT G-band (1590 cm\(^{-1}\), figure 4a,b) and the CNT G-band (figure 4c,d) demonstrated that even after the CNT deposition on top of nNiO/Spiro-OMeTAD composite sublayer, the distribution of CNTs and the nonuniformity degree of CNT layer was insignificantly changed (value of layer nonuniformity is 0.25) relative to the case of CNTs on the initial TiO\(_2\)/Ti substrate (nonuniformity value is 0.24, compare figure 4c and 4d). In addition, in the case of the nNiO/Spiro-OMeTAD composite sublayer, the redistribution of Spiro-OMeTAD with the formation of not covered by Spiro-OMeTAD areas didn't observe, which was determined by comparing the \( \frac{I_{\text{Spiro}}}{I_{\text{CNT}}} \) intensity ratio for structure B in comparison with the values obtained for pure CNT layer (structure A). Estimation of layer nonuniformity value for Spiro-OMeTAD in composite HTL by this ratio was 0.58, which lower than for initial HTL.

![Figure 4. Raman map of: a,b) intensity ratio of Spiro-OMeTAD peak to CNT peak for: structure B with composite nNiO/Spiro-OMeTAD sublayer (a), structure D with pure Spiro-OMeTAD sublayer (b); c, d) CNT peak intensity for: structure B (c), structure A (d). Scale bar is 10 µm.](image)

By analysing Raman map of structure A, the median value of the \( \frac{I_{\text{Spiro}}}{I_{\text{CNT}}} \) ratio was obtained, which when adding standard deviation of this ratio (threshold value 0.23+0.02) characterized situation when Spiro-OMeTAD is absent (shaded areas on figure 4a,b). Therefore values above this limit pointed to some amount Spiro-OMeTAD on the measuring map point. Despite CNTs dipping into or mixing with Spiro-OMeTAD, structure D is characterized by a high uniform CNT distribution (value of layer nonuniformity is 0.23). Comparison of Raman map on figures 4a and 4b can be used for one more evidence of Spiro-OMeTAD presence at almost all areas of the multilayer structure B since for it \( \frac{I_{\text{Spiro}}}{I_{\text{CNT}}} \) intensity ratio isn't decreased lower than the characteristic threshold value for pure CNTs or for areas of structure D with CNTs presence and Spiro-OMeTAD absence. For structure D, this map of \( \frac{I_{\text{Spiro}}}{I_{\text{CNT}}} \) ratio minus the threshold value characteristic for the Spiro-OMeTAD absence gave an estimation of the value of Spiro-OMeTAD sublayer nonuniformity for this structure about 2.7, that also slightly lower than 3.3 for initial pure Spiro-OMeTAD layer, so some smoothing of Spiro-OMeTAD during CNT deposition was observed. Also, to compare the conductivity between CNT and Ti layers for structures B-D, I–V characteristics (CVC) were measured (figure 5). Significant differences between them were observed only for the region of positive values of the \( U_{\text{CNT-Ti}} \) for
structure B. Small hysteresis observed for all structures at CVC cyclic measuring is apparently due to some traps at the HTL-TiO₂ interface. And, taking into account the incomplete coverage of the substrate surface by the HTL layer in the case of pure Spiro-OMeTAD and also pure nNiO, a significant part of CNTs (20-40 %) was in direct contact with the TiO₂/Ti substrate even in the area where the HTL sublayer was deposited, which makes CVCs of these structures (C and D) are similar (especially at “+” U_{CNT-Ti}). And in the case of structure D, the thickness in the regions where CNTs are separated from the substrate by Spiro-OMeTAD can be more than 200-300 nm (see figure 2d and also based on the R_{CNT} in comparison with structure A, CNTs are predominantly concentrated near the top of Spiro-OMeTAD regions), which eventually forms a rather smaller contact area with the substrate (in the round HTL area), as a result of which a slightly lower conductivity is observed both at low “-” and at “+” U_{CNT-Ti} in comparison with structure C.

Figure 5. CVC between CNT and Ti contacts for: structure B (black squares), structure C (blue circles) and structure D (green triangles). Ti contact for all structures was grounded. The insets schematically show changes in energy levels in the case of zero and “-” U_{CNT-Ti} for all structures and “+” U_{CNT-Ti} for structure B.

And in the case of structure C, which has lower conductivity over the CNT layer and, accordingly, a greater CNTs redistribution over the nNiO layer thickness, CNT contact area directly with the substrate can be some higher than for structure D due to the nNiO island layer. Even despite thin Spiro-OMeTAD layer separates CNTs from TiO₂ and reduces charge transport efficiency through TiO₂ in the case of composite HTL, however, due to fairly high effective area where CNTs locate still near TiO₂, the similarity of CVC in range -0.6 V to +0.2 V was observed, especially for structures B and C. As a result, for structure C (and also for B) the possibility of charge transport through TiO₂ (at high fields formed at “-” U_{CNT-Ti}, taking into account the small thickness of TiO₂) is higher than for structure D. This also can explain the increasing leakage currents through TiO₂ even at “+” U_{CNT-Ti}, when possibility of tunnelling or effective charge injection through TiO₂ cannot be achieved, and only TiO₂ breakdown becomes a possible mechanism of current flow at large positive U_{CNT-Ti} (except for structure B). The presence of regions in all structures of direct contact of CNTs with TiO₂/Ti outside deposited round region of HTL sublayer (2 mm in diameter) with a region's area of about half of the total CNT layer area (4x1.5 mm), determines the CVCs similarity and presence of current at “-” U_{CNT-Ti} by charge transport (possibly by tunnelling or field injection) through the triangular barrier of direct CNT-TiO₂/Ti contacts. That marked in the left inset of figure 5 as a dotted line inside the NiO or Spiro-OMeTAD material. Although, directly in the region where HTL forms a continuous layer, it doesn't realize (structure B). Additionally, the shunting of the small HTL islands by CNT, as well as
the large HTL thickness in regions where there is no direct CNT-TiO$_2$/Ti contact, explains the lack of involvement of such HTL layer in charge transport in CNT-Ti contacts in structures C and D. However, in the case of structure B with continuous composite nNiO/Spiro-OMeTAD layer formation, both a relatively small effective thickness of the HTL layer and its sufficient continuity were apparently achieved, which makes possible certain mechanism of current flow at "$+$" $U_{\text{CNT-Ti}}$, also with a pronounced nonlinear CVC in contrast to the structures C and D. Such a mechanism may be the charges injection (when a sufficient "$+$" $U_{\text{CNT-Ti}}$ voltage is applied) through narrowed barriers of the TiO$_2$ layer (it plays the role of an electron transport layer, ETL) and HTL: electrons through ETL and holes through HTL to the ETL-HTL interface with their subsequent recombination (figure 5, right inset). This mechanism forms the possibility of effective current flow through the ETL-HTL interface with a nonlinear CVC at "$+$" $U_{\text{CNT-Ti}}$, and also apparently indicates the formation of a thin continuous HTL in structure B with a significant effective area of the HTL (in contrast to structures C and D). In view of significant difference in LUMO and HOMO levels between ETL and HTL respectively (more than 1 eV), as well as some difference in the CNT work function and the nNiO/Spiro-OMeTAD HOMO level, recombination does not occur quite efficiently at low "$+$" $U_{\text{CNT-Ti}}$, that was revealed in noticeable CVC nonlinearity in this region and high threshold voltage for type B structures.

4. Conclusion
Spray deposition of only pure Spiro-OMeTAD doesn't provide thin continuous layer formation; however, the use of a sublayer of nNiO with an average size of less than 80 nm and with their filling of the substrate surface already from 70 % allows one to form a thin (less than 100 nm by Spiro-OMeTAD data from AFM, Raman) continuous composite nNiO/Spiro-OMeTAD layer acting as HTL. This manifests itself both on the AFM as a larger number of observed CNTs on top of that HTL and a smoother surface of the structure, as well as on the resistance of the top CNT layer, which only slightly different from the pure CNT layer on a flat TiO$_2$/Ti substrate, but which significantly higher in the case of island sublayers of nNiO or Spiro-OMeTAD. By obtaining Raman maps, the acceptable continuity and uniformity degree of both the CNT layer deposited on top and the Spiro-OMeTAD itself, and the small Spiro-OMeTAD redistribution with improving uniformity degree in the nNiO/Spiro-OMeTAD composite layer were confirmed, despite on subsequent CNTs deposition from the dispersion of CHL, which partially dissolving Spiro-OMeTAD. Also, this manifests itself when comparing the CVC of the CNT-Ti contacts for a structure with composite HTL, that demonstrates nonlinear CVC at a positive $U_{\text{CNT-Ti}}$ voltage, that associated with the possibility of recombination at the TiO$_2$-HTL interface, in contrast with the CVC of structures where the HTL is formed by an island layer of only nNiO or pure Spiro-OMeTAD, which both don't manifest itself as continuous HTL.

Acknowledgments
This work was supported by the President of the Russian Federation for young Russian scientists support (grant No. MK-1024.2020.8, agreement No. 075-15-2020-439 of 16.03.2020).

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