

Efficient Semi-Transparent Organic Solar Cells with High Color Rendering Index Enabled by Self-Assembled and Knitted AgNPs/MWCNTs Transparent Top Electrode via Solution Process

Yuniu Zhang, Xinjun He, Dickson Babu, Wenhui Li, Xiaoyu Gu, Chengwei Shan, Aung Ko Ko Kyaw,* and Wallace C. H. Choy*

Semi-transparent organic solar cells (STOSCs) have attracted tremendous attention in power-generating windows for buildings and automobiles. Although STOSCs based on vacuum-deposited thin metal films exhibited power conversion efficiency exceeding 10%, solution-processed top transparent electrode (TE) is desirable for large-area and low-cost fabrication of STOSCs. Here, we present a self-assembled and knitted Ag nanoparticles/multi-walled carbon nanotubes composite thin film by solution process as transparent top electrode for STOSC. The composite film exhibits an extremely low sheet resistance of $14.5 \Omega \text{ sq}^{-1}$, an average visible transmittance (AVT) of $\approx 67\%$, and a high color rendering index (CRI) of 97. The optimized device with solution-processed top TE achieves an AVT of 36% and a high CRI of 90. This work paves a simple and promising route towards low-cost fabrication of power-generating window.

conversion efficiency (PCE) has already exceeded 16% enabled by advanced photovoltaic materials.^[3–6] Although opaque OSCs exhibit high efficiency, their usage is limited because they demand dedicated space and additional installation work on the roof, like traditional silicon solar cells. Therefore, the transparent property of OSCs was exploited for semi-transparent photovoltaic modules to extend their application in power-generating windows for buildings and automobiles. To fabricate efficient semi-transparent OSCs (STOSCs) with high average visible transmittance (AVT),^[7] several approaches have been attempted for improving the visible light transparency of active layer, including

1. Introduction

On account of the shortage of global resources and development of sustainable energy technology, the way to combine renewable energy with daily life is increasingly desirable. Organic solar cells (OSCs) own attractive potential as a competitive renewable energy source due to the low-cost fabrication, light weight, flexibility, and semitransparency nature.^[1,2] In the past decade, OSCs have gained a lot of attention and the highest power

molecular energy level modulating in non-fullerene acceptors,^[8–12] usage of low-band gap organic semiconductors to shift absorption to near-infrared region,^[13] fabrication of active layer with fiber network structure^[14] and so on.

On the other hand, developing transparent electrodes (TEs) with high conductivity to reduce the absorption/reflection in visible light without degrading interfacial contact is also equally important to achieve high-performance STOSCs.^[2] Evaporated thin metal-based top electrodes were most reported to date due to their high conductivity and transparency.^[15–17] However, the high cost and strict conditions of vacuum-deposited TEs are not suitable for large-area device fabrication and contradict the aim of renewable energy.^[18] Furthermore, the transmittance of evaporated thin metal is not uniform throughout the visible region, resulting in low color-fidelity in STOSCs.^[19] Therefore, in the past decade, scientists have advocated to develop solution-processed TEs, such as conducting polymers,^[20–22] Ag nanowires (AgNWs),^[23–26] graphene,^[27–30] and carbon nanotubes (CNTs).^[31–34] Nonetheless, the sheet resistance of polymers-based and carbon-based TEs is relatively high and even the lowest reported values to date is larger than $50 \Omega \text{ sq}^{-1}$. Moreover, the acid treatment at high temperature for the conductivity enhancement of polymers adversely damages the underlying layers of OSC,^[35–37] and hence complicated transfer process is required to be used as top TEs.^[38,39] In addition, the unsatisfactory vertical conductivity of carbon materials and the stability issue of AgNWs and conducting polymers make them unappealing to be used in STOSCs.

Y. N. Zhang, Dr. D. Babu, Dr. W. Li, X. Gu, C. Shan, Prof. A. K. K. Kyaw
Guangdong University Key Laboratory for Advanced Quantum Dot Displays and Lighting
Department of Electrical & Electronic Engineering
Southern University of Science and Technology
Shenzhen 518055, China
E-mail: aung@sustech.edu.cn

Y. N. Zhang, X. J. He, Prof. W. C. H. Choy
Department of Electrical & Electronic Engineering
The University of Hong Kong
Pokfulam Road, Hong Kong 852, SAR, China
E-mail: chchoy@eee.hku.hk

Y. N. Zhang, Prof. W. C. H. Choy
Guangdong-Hong Kong-Macao Joint Laboratory for Photonic-Thermal-Electrical Energy Materials and Devices
Shenzhen 518055, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adom.202002108>.

DOI: 10.1002/adom.202002108

Thin film formed by self-assembly of metal nanoparticles shows great potential as electrode because of excellent mechanical flexibility and low-cost technique of fabrication.^[40–42] However, due to the poor conductivity between individual particles, they are usually required to deposit on the substrates with transparent grids/meshes via solution-based printing techniques for TE applications.^[43,44] Recent report on one-step sintered AgNPs thin film by chemical treatment indicate its potential as TEs.^[45] However, the sheet resistance of ultrathin connected Ag nanoparticles (AgNPs) film is large ($150 \Omega \text{ sq}^{-1}$) when AVT over 60% in visible region.

Herein, we present a simple solution route to knit self-assembled AgNPs thin film with multi-walled CNTs (MWCNTs) employing silver nitrate (AgNO_3) solution in ethanol at room temperature. AgNO_3 serves as chemical welder to knit the AgNP mesh and MWCNTs together. The resultant AgNPs/MWCNTs composite (AgCNTs) transparent film shows an exceptionally low sheet resistance of $14.5 \Omega \text{ sq}^{-1}$ with AVT over 65% in visible region, which is the lowest reported sheet resistance for room-temperature solution-processed top TE used in STOSC at similar AVT. STOSCs with inverted configuration have been demonstrated using solution-processed AgCNTs thin film with different AVTs as transparent top electrode. The optimized semi-transparent device with an active layer of Poly[[5,6-difluoro-2-(2-hexyldecyl)-2H-benzotriazole-4,7-diyl]-2,5-thiophenediyl][4,8-bis[5-(tripropylsilyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-2,5-thiophenediyl : 2,2'-(2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile : [6,6]-Phenyl-C71-butyric acid methyl ester (J71:Y6:PC₇₁BM) shows PCE over 7% with AVT of 36% while the opaque one is 11.3%. Moreover, due to a relatively uniform transparency of AgCNTs thin film in visible range, the STOSCs exhibit high color-fidelity with a high color rendering index (CRI) around 90. This work provides a promising route towards low-sheet-resistance, high-AVT, and high-CRI thin film by solution process at room temperature for the top electrodes of STOSCs and paves a feasible way for low-cost fabrication of power-generating window.

2. Results and Discussion

2.1. Preparation and Characterization of AgCNTs Film

A thermal reduction method with AgNO_3 was employed to synthesize AgNPs.^[46] To achieve high-quality solution-processed

AgCNTs thin film at room temperature, the synthesized AgNPs ink with specific concentration was firstly spin-coated to form self-assembled AgNPs film, then MWCNTs/ AgNO_3 mixed ethanol dispersion was dropwise added on the AgNPs film for 15 s to treat the AgNPs film while spinning. The whole process is illustrated in **Figure 1**. Under the natural light, the AgNPs thin film shows brownish color (Figure S1, Supporting Information), which is not very conducive for human eye to look through, and fluctuant transmittance spectra with almost no conductivity. The apparent brownish color of AgNPs film can be attributed to diffused reflection of film caused by random arrayed AgNPs, and the localized surface plasmon resonance occurs in AgNPs, in which some photons may be absorbed by valence electrons via small particle size ($\approx 10 \text{ nm}$).^[47–48] After the one-step treatment, the apparent color of the film was turned to gray color, which is more natural to human eye (**Figure 2a**), and an obvious morphology change was also observed in scanning electron microscopy (SEM) images (**Figure 2b**). The originally densely packed AgNPs are connected as network grid and formed a knitted mesh structure with uniformly spread CNTs. The formation of Ag network reduces the localized surface plasmon resonance caused by AgNPs, lowers the diffused reflection to transmit visible light,^[47,48] and forms the gaps in the mesh structure, which turn the gray color and enhance the transparency. This knitted mesh not only facilitates light transmission through the gap but also dramatically reduces sheet resistance due to the connected nanoparticle network by MWCNTs. **Figure S2**, Supporting Information, exhibits the sheet resistance change of AgNPs-based TE treated with/without MWCNTs, in which the AgCNTs films show much lower sheet resistance when AVT over 60%. The thickness of AgCNTs is around 25 nm as measured by profilometer (**Figure S3**, Supporting Information). The transmittance of AgCNTs film is strongly related to the concentration of AgNPs, as shown in **Figure 2c**. The AVT decreases from 85% to 35% when AgNPs concentration increases from 12 to 100 mg mL^{-1} . AgNO_3 has been reported as chemical solder to weld AgNWs,^[49–51] and therefore, it might connect AgNPs and MWCNTs together at the junctions. For AgNPs solution with high concentration, more AgNO_3 in MWCNTs dispersion increases the transmittance slightly. This is because AgNPs and MWCNTs knitted with extra solder cause more dense network, which will result in “cracks” in the film (**Figure S4**, Supporting Information) as there are not enough AgNPs to be sintered.^[45] However, extra solder may also lead to discontinuous film due to the over-treatment and excessive sinter, and increase the sheet resistance.

The relation between sheet resistance of AgCNTs film and concentration of AgNPs in the ink or concentration of AgNO_3

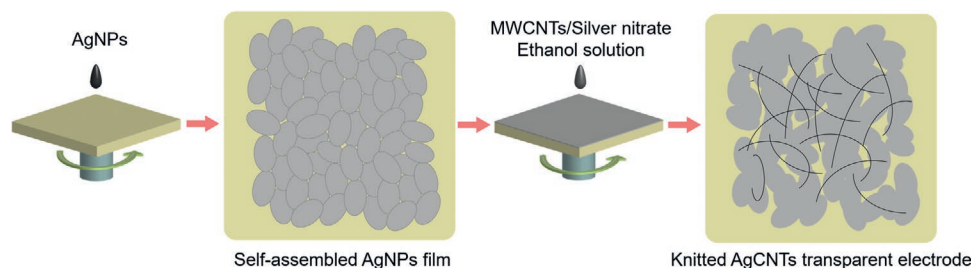


Figure 1. Process schematic of knitted AgCNTs transparent thin film by one-step treatment.

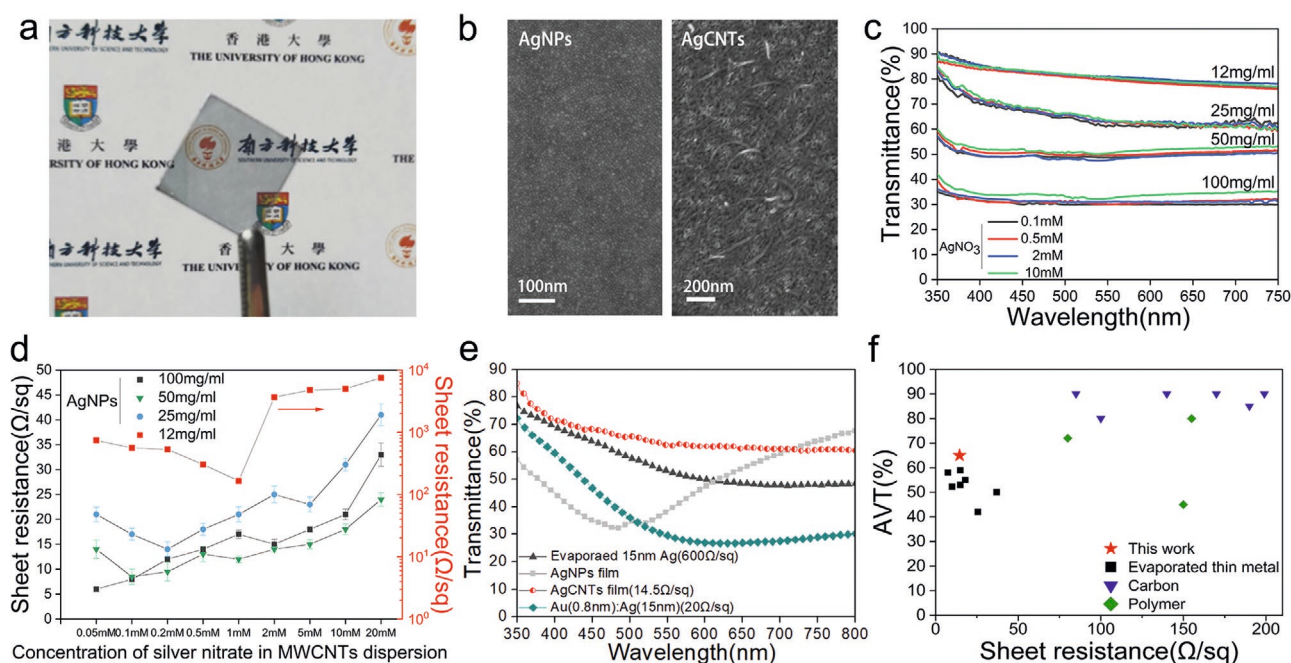


Figure 2. a) Image of AgCNTs electrode with transmittance over 65%. b) SEM images of AgNPs film (left) and AgCNTs film (right). c) Transmittance and d) sheet resistance of electrode with different concentrations AgNPs in the precursor ink and AgNO₃ in MWCNTs dispersion. e) Transmittance spectra of evaporated Ag (15 nm), AgNPs film, AgCNTs composite film, and evaporated Au (0.8 nm):Ag (15 nm) film. f) Comparison of AgCNTs with other top electrodes applied in semi-transparent solar cells.^[16,17,20–22,30,34,52–59]

in MWCNTs dispersion was studied as shown in Figure 2d. Firstly we clearly found that the sheet resistance of AgCNTs film increases when reducing the concentration of AgNPs, but not linearly. Very low AgNPs concentration results in formation of unconnected island in the film (Figure S4, Supporting Information) and the lowest sheet resistance of 12 mg mL⁻¹-series AgCNTs film is over 150 Ω sq⁻¹. Regardless of AgNPs concentration, both incomplete treatment or over treatment leads to non-uniform “knot” which increases the sheet resistance. Generally, films with lower AgNPs concentration requires more AgNO₃ to complete treatment (soldering effect). After finding a good balance between the concentration of AgNPs and AgNO₃ in MWCNTs dispersion, a transparent AgCNTs film with AVT of ≈67% and low sheet resistance of ≈14.5 Ω sq⁻¹ is achieved. The sheet resistance and transmittance of AgCNTs film, compared with AgNPs film, evaporated thin Ag (15 nm) film and Au (0.8 nm): Ag (15 nm) film between wavelength range of 350–800 nm, are shown in Figure 2e. It can be clearly seen from the transmittance spectrum that AgCNTs film has a higher AVT than other films while the sheet resistance (14.5 Ω sq⁻¹) is the lowest among the various films, exhibiting a good characteristic of TE. The sheet resistance and AVT of our AgCNTs film are also benchmarked with various kinds of top electrode reported in literature by others,^[16,17,20–22,30,34,52–59] as shown in Figure 2f. The AVT of 67% is higher than reported evaporated metal-based TEs used in STOSC with similar sheet resistance. We also recorded the sheet resistance change of AgCNTs thin film in atmospheric environment for 60 days and compared with that of commonly used AgNWs. AgCNTs film shows a remarkable stability with very little increase in sheet resistance whereas AgNWs exhibit a significant increase in sheet resistance (Figure S5, Supporting

Information). The characterization with energy dispersive spectrometer (EDS) confirms the uniform distribution of AgNPs and CNTs in the entire film (Figure S6, Supporting Information). In the EDS image, both Ag and C elements are evenly distributed on the sample, implying that AgNPs and MWCNTs are knitted uniformly without excessive aggregation or formation of unconnected islands. It is also worth mentioning that this one-step treatment can be completed within a short period of time using the chemically compatible solvents with underlying layers of OSCs, ensuring the robustness of active layer of OSC as well as high-throughput fabrication of OSCs.

Next, we further investigated X-ray photoelectron spectroscopy (XPS) to study the binding energy evolution of AgNPs and AgCNTs thin films. The corresponding XPS survey spectra can be found in Figure S7, Supporting Information, and core level Ag 3d and C 1s XPS spectra of AgNPs and AgCNTs are shown in Figure 3. For the AgNPs film as shown in Figure 3a, the peaks at 374.5 and 368.5 eV are indexed to Ag(0) 3d_{3/2} and Ag(0) 3d_{5/2} of bulk silver.^[60,61] Due to the size effect, lower binding energy of AgCNTs film with larger silver particle size should be detected.^[60] However, a shift of 0.3 eV to high binding energy is observed in AgCNTs film compared to AgNPs film, which indicates the formation of Ag/carbon composite film because the binding energy of metal composite is higher than that of pure metal. The other four small peaks should be indexed to the Ag–N bond (375.6 and 369.6 eV) and Ag–C bond (374.2 and 368.2 eV).^[62,63] The decrease in amplitude of Ag–N bond in AgCNTs film confirms its broken bond during the solution process and formation of pure Ag in the composite film.^[45] As shown in Figure 3b, the core level C 1s spectra of AgCNTs is wider than that of AgNPs. The peaks at 284.8 and 286.5 eV can

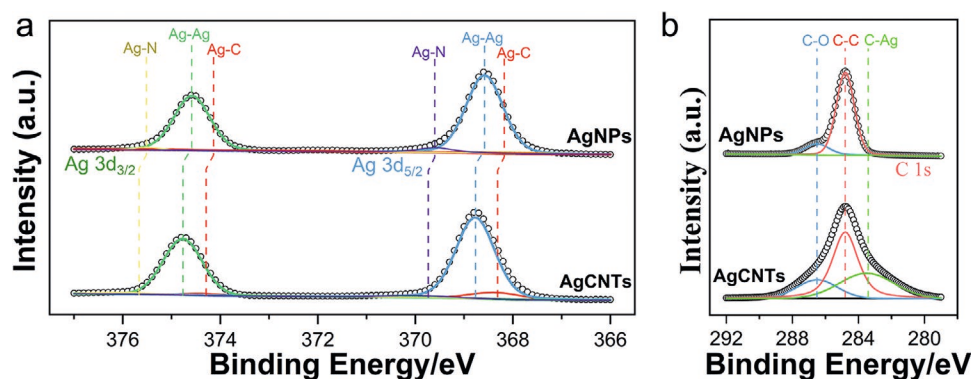


Figure 3. Core-level a) Ag 3d and b) C 1s XPS spectra of the AgNPs and AgCNTs film.

be indexed to C–C bond and C–O bond in both films while the peak located at 283.5 eV in AgCNTs film can be attributed to C–Ag bond,^[64] which proves the strong combination of Ag and MWCNTs. The atomic ratios of Ag and C of AgNPs thin film before and after treatment are shown in Figure S8, Supporting Information, which also proves the formation of Ag–C composite film. Ultraviolet Photoelectron Spectroscopy (UPS) was also carried out to measure the work function of AgCNTs electrode. The valence band maximum (VBM) of AgCNTs can be calculated by using Equation (1):

$$\text{VBM} = h\nu - (E_{\text{cutoff}} - E_{\text{onset}}) \quad (1)$$

The photon energy ($h\nu$) of light sources He1 α is 21.22 eV, and the high-binding energy secondary electron cut-off (E_{cutoff}), and the onset energy (E_{onset}) in the VB regions can be determined

from the UPS spectra, as shown in Figure S9, Supporting Information. The VBM of AgCNTs was estimated to be -4.34 eV, which is favorable for extraction of charge carrier to electrode from the hole transporting layer.

2.2. Performances of STOSCs

To demonstrate AgCNTs film as top electrode, we fabricated STOSCs with inverted configuration of ITO/ZnO/J71: Y6: PC₇₁BM/MoO₃/AgCNTs, as shown in Figure 4. The energy levels of individual materials used in the device are displayed in Figure 4c. For comparison, opaque device with evaporated Ag and STOSC with evaporated thin Au (0.8 nm): Ag (15 nm) were also fabricated. The opaque device with evaporated Ag exhibits a PCE of 11.6% while STOSC with AgCNTs electrode

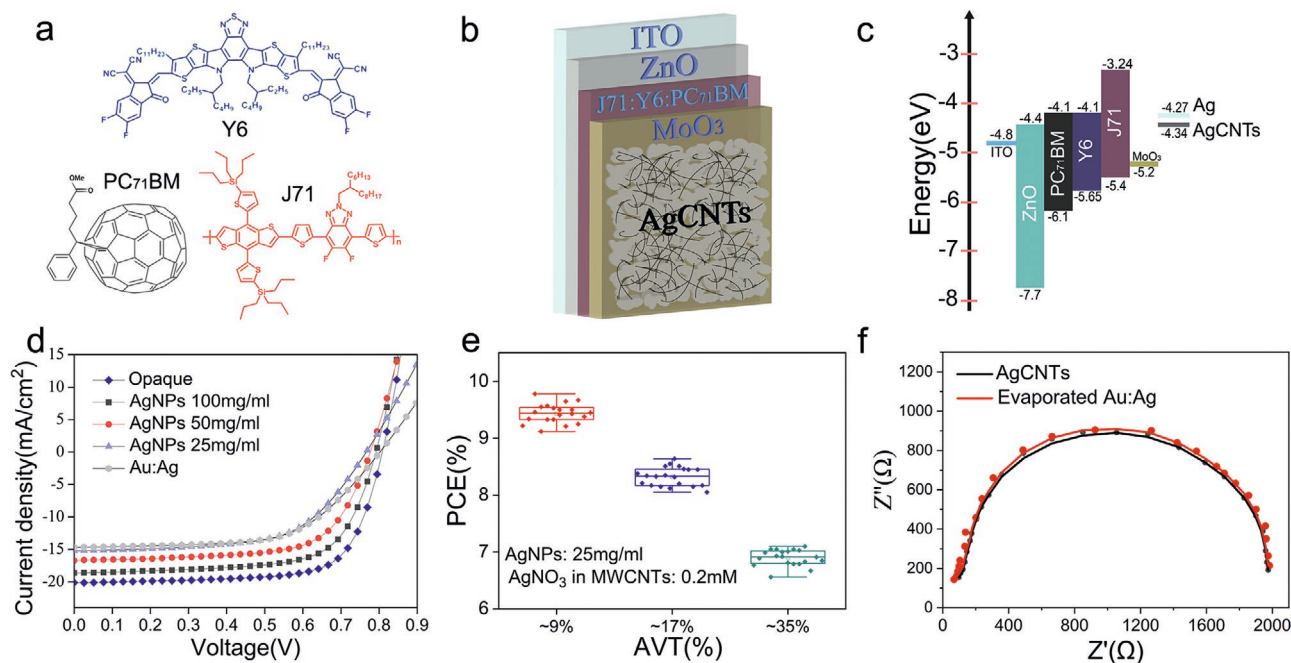


Figure 4. a) Chemical structures of J71, Y6, PC₇₁BM. b) Schematic illustration of inverted J71:Y6:PC₇₁BM semitransparent devices. c) Energy band diagram of individual layers in the device. d) The current density–voltage curve and e) PCE with distribution statistics of the devices with different AVT and f) impedance spectrum of STOSCs with AgCNTs electrode, compared with that of evaporated Au:Ag electrode.

(AgNPs concentration of 25 mg mL⁻¹) yields a short-circuit current density (J_{sc}) of 15.23 mA cm⁻², open-circuit voltage (V_{oc}) of 0.76 V, and fill factor (FF) of 60%, resulting in PCE of 7%, which is 60.3% of opaque devices (Figure 4d and Table 1). The PCE of STOSC with AgCNTs electrode is similar to that of STOSCs with evaporated Au: Ag thin metal (PCE = 7.08%) but the former has advantage in transparency. The AVT of STOSCs with AgCNTs achieves an AVT of 36%, which is higher than that of STOSC with evaporated Au:Ag thin metal (AVT 31% only). It is important to test the device transparency from both top and bottom sides. Hence, we measured the device transmittance from ITO and AgCNTs simultaneously as shown in Figure S10, Supporting Information. The transmittance spectra do not vary when the direction of illumination is changed. We also fabricated STOSCs with AgCNTs prepared by different AgNPs concentrations of 50 and 100 mg mL⁻¹. With the increase of AgNPs concentration, the AVT of STOSCs drops significantly to ≈17% and 9%, respectively, due to the denser meshes, which also results in higher PCE of 8.64% and 9.53%, respectively (Figure 4d and Table 1). We also measured the electrochemical impedance spectra (EIS) of devices with AgCNTs and evaporated Au: Ag as shown in Figure 4f, to examine the interfacial contact between electrodes and underlayer. The EIS spectra exhibit two semicircles which indicate a carrier transport resistance and a charge recombination resistance (R1 and R2).^[65] R_s and two constant phase elements (CPE1 and CPE2) were applied to present the series resistance, carrier transport capacitance, and charge recombination capacitance in OSCs. After fitting the spectrum by the equivalent circuit shown in Figure S11, Supporting Information, the device with AgCNTs electrode exhibited similar value of R1 and R2 to device with Au: Ag electrode, as shown in Table S1, Supporting Information, indicating that the interfacial contact between the AgCNTs electrode and underlayer is comparable to evaporated one despite a solution process.

Besides, we also fabricated STOSCs with inverted structure of ITO/ZnO/P3HT:PC₆₁BM/PEDOT:PSS/AgCNTs, where P3HT, PC₆₁BM and PEDOT:PSS are poly(3-hexylthiophene-2,5-diyl), [6,6]-phenyl-C61-butyric acid methyl ester and poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid) respectively, to evaluate the compatibility of the solution-processed AgCNTs electrode in all-solution-processed STOSC. The devices' performance is shown in Table S2 and Figure S12, Supporting Information. The all-solution-processed STOSCs show PCE of 2.38% with AVT of 29% while that of opaque devices is 3.33%,

Table 1. Photovoltaic performance parameters of opaque and semitransparent J71:Y6:PC₇₁BM devices.

Sample	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]	AVT
Opaque	20.13	0.808	71.32	11.60 (11.26 ± 0.34)	–
AgNPs 100 mg mL ⁻¹	18.14	0.788	66.68	9.54 (9.33 ± 0.21)	9%
AgNPs 50 mg mL ⁻¹	16.73	0.777	66.47	8.64 (8.16 ± 0.48)	17%
AgNPs 25 mg mL ⁻¹	15.23	0.766	60.03	7.00 (6.85 ± 0.15)	36%
Au 0.8 nm:Ag 15 nm	14.68	0.802	60.153	7.08 (6.96 ± 0.12)	31%

The average values with error range for 10 fabricated devices are shown in the brackets.

achieving over 71% of PCE of opaque device. This indicates the compatibility of AgCNTs electrode with multiple bulk-heterojunction systems and interfacial materials for universal applications, including all-solution-processed STOSCs.

The color rendering properties of the fabricated STOSCs were also investigated. The tristimulus value (X, Y, Z) and the color coordinates (x, y) from the transmission spectra of the semitransparent OSCs are calculated using Equations (2) to (6):

$$X = \int_{380\text{nm}}^{780\text{nm}} S(\lambda) \times \bar{x}(\lambda) \times T(\lambda) d\lambda \quad (2)$$

$$Y = \int_{380\text{nm}}^{780\text{nm}} S(\lambda) \times \bar{y}(\lambda) \times T(\lambda) d\lambda \quad (3)$$

$$Z = \int_{380\text{nm}}^{780\text{nm}} S(\lambda) \times \bar{z}(\lambda) \times T(\lambda) d\lambda \quad (4)$$

$$x = \frac{X}{X + Y + Z} \quad (5)$$

$$y = \frac{Y}{X + Y + Z} \quad (6)$$

In the above formulas, $S(\lambda)$ is the standard D65 illuminant spectrum, $\bar{x}$ $\bar{y}$ $\bar{z}$ are the color matching functions and $T(\lambda)$ is the experimental transmittance spectrum. These values are converted to x, y coordinates in the International Commission on Illumination (CIE) 1931 color space,^[66] which show how the light from an object changes when it passes the STOSCs as perceived by the observer's eyes. The CIE color space with coordinates of electrodes and devices is shown in Figure 5a. The color coordinates of AgCNTs film are located at (0.329, 0.343) and it is close to the achromatic point (0.33, 0.33), which indicates good achromatic or neutral color sensations when looking through the AgCNTs film under AM1.5G illumination. We also found that after changing evaporated Au:Ag to AgCNTs electrode, the color coordinates of semitransparent devices are closer to achromatic point, showing the high-quality light transmission of AgCNTs-based STOSCs. Due to a good achromatic ability, STOSC with AgCNTs electrode provides near-white sensation to the human eye and will not alter the original color of an object.

The CRI provides a description of the ability of devices to present an image accurately, as compared to a standard illuminant. The calculation method of CRI is according to the CIE 13.3 1995 protocol,^[67] and the details are shown in the ESI. To achieve high color-fidelity STOSCs, the light passing through STOSCs should maintain the original component with relative intensity, so the transmittance spectra with average, high-transparency in the visible region can enable neutral-color STOSCs.^[19] As listed in Figure 5a, our AgCNTs electrode renders relatively uniform transmittance (flat spectrum) in visual region and it shows a high CRI of 97. Also, compared to J71:Y6:PC₇₁BM based STOSCs with evaporated Au:Ag, the transmittance spectra of devices with AgCNTs are flatter (Figure 5c,d), which contributes to higher CRI of 90. Figure 5b shows the photograph of the complete J71: Y6: PC₇₁BM and AgCNTs based STOSC, demonstrating neutral color and semi-transparency. There is a noticeable enhancement in optical properties after replacing evaporated thin metal with

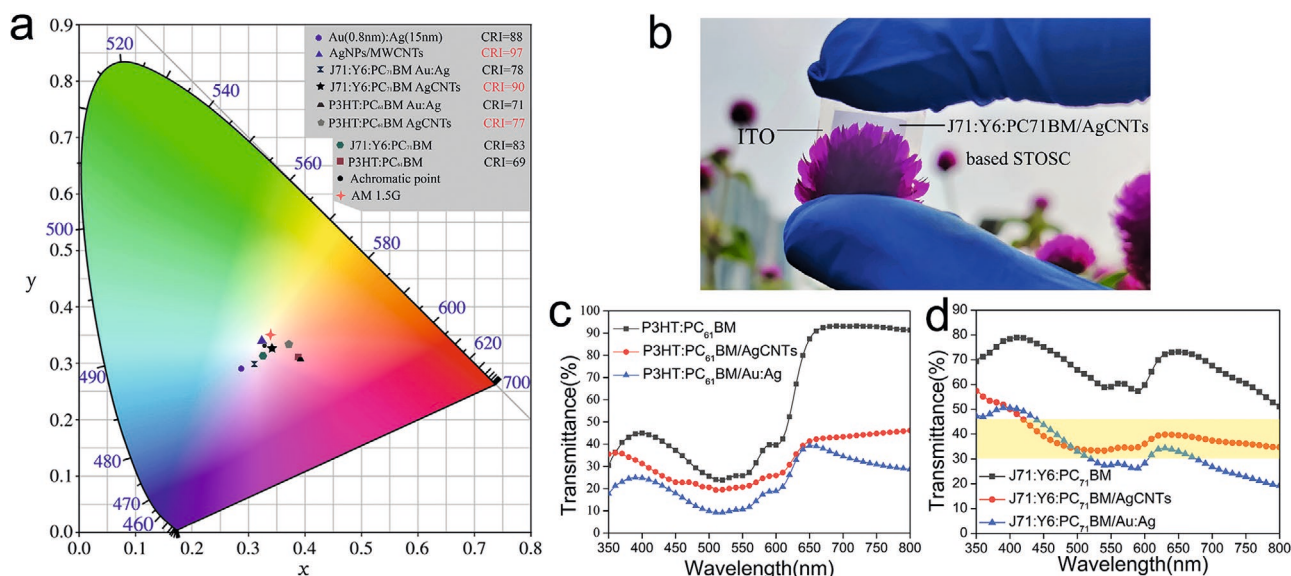


Figure 5. a) CIE 1931 coordinates of electrodes and devices. b) Image of J71:Y6:PC₇₁BM STOSCs under natural light. Transmittance of c) P3HT:PC₆₁BM and d) J71:Y6:PC₇₁BM-based devices using different electrodes (AgCNTs and Au:Ag) and without electrode.

solution-processed AgCNTs electrode, while maintaining almost unchanged device performance.

3. Conclusion

In summary, we have demonstrated a solution-processed transparent top electrode employing self-assembled and knitted AgNPs and MWCNTs composite film and applied it in STOSCs to achieve high efficiency and high transmittance simultaneously. By varying the concentration of AgNPs in precursor ink and AgNO₃ in MWCNTs dispersions, the as-prepared electrode achieved AVT of ≈67% with a low sheet resistance of 14.5 Ω sq⁻¹. By employing J71:Y6:PC₇₁BM bulk-heterojunction system as photo absorbing layer, PCE of 7% (opaque:11.6%) with a high AVT of 36% was obtained in STOSCs. In addition, the color rendering properties of electrode and STOSCs were analyzed by their color coordinates in CIE 1931 color space and CRI values. Besides similar PCE and higher AVT, the color coordinates and CRI values of the devices with AgCNTs electrode improves significantly compared to evaporated Au:Ag electrode. This work firstly applied solution-processed AgNPs composite film as transparent top electrode via a simple one-step treatment at room temperature. The AgCNTs based inverted STOSCs can provide sufficient transparency and good color rendering property, which extends a promising route for low-cost and large area power-generating window applications.

4. Experimental Methods

Materials: Silver nitrate (AgNO₃, 99%), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, 99.9%) ethanolamine (99.9%), 2-methoxyethanol (CH₃OCH₂CH₂OH, 99.8%), ethanol (99.9%), dichlorobenzene (DCB, 99.8%), 1-Chloronaphthalene (CN, >95.0%), oleylamine (98%), n-octane (99%), and n-hexane (GR) were purchased from Sigma-Aldrich. MWCNTs (inner diam: 2–5 nm, outer diam: 5–15 nm, length: 0.5–2 μm) and Molybdenum trioxide (MoO₃, 99%) were purchased from J&K.

CNT dispersant was purchased from XFNANO. P3HT, PC₆₁BM, PC₇₁BM were purchased from p-OLED. J71 was purchased from 1-material Co., Ltd. Y6 was purchased from Derthon Optoelectronic Material Science Technology Co., Ltd. PEDOT:PSS (HTL Solar) was purchased from Heraeus, Germany. AgNPs were synthesized with AgNO₃ and oleylamine. Briefly, 5 mL oleylamine was preheated for 10 min at 185 °C, then add 0.25 g AgNO₃ and react for 10 min. After the reaction, the AgNPs were cleaned with ethanol four times and dissolved in a mixed solution of n-octane and n-hexane. As for MWCNTs/AgNO₃ mixed ethanol solution, 10 mg MWCNTs and 3.4 mg AgNO₃ were added to 10 mL ethanol and intermittently dispersed for 2 h by ultrasonication. After centrifugation at 10 000 rpm, the supernatant was stored for later use. ZnO sol-gel solution (0.1 M) was prepared by dissolving zinc acetate dihydrate and ethanolamine in 2-methoxyethanol under vigorous stirring for at least 24 h then stored at least 48 h for later use.

Devices Fabrication: The ITO-coated glasses were cleaned by sonication in deionized water, acetone, and ethanol for 20 min. Then the substrates were treated with UV-O₃ cleaning for 20 min. Sol-gel processed ZnO electron transport layer was spin-coated on substrate with 3000 rpm for 45 s and baking at 170 °C for 60 min in air. Then the samples were transferred into glove box. For P3HT:PC₆₁BM (40 mg mL⁻¹, 1:1 weight ratio) as active layer, the solution was spin-coated with 800 rpm for 40 s then samples were immediately covered for slow growth. After 60 min, samples were taken out and baked at 130 °C for 10 min. Then, PEDOT: PSS was spin-coated with 3000 rpm for 40 s and baked at 100 °C for 10 min. For J71:Y6:PC₇₁BM (16 mg mL⁻¹, 1:1.2:0.2 weight ratio) as active layer, the solution was spin-coated with 2000 rpm for 40 s then baked at 110 °C for 10 min. MoO₃ (15 nm) was deposited by thermal evaporation. As for top electrode, 100 nm Ag or Au (0.8 nm):Ag(15 nm) were deposited via evaporation. For AgCNTs based STOSCs, the synthesized AgNPs were firstly spin-coated on PEDOT:PSS or MoO₃ with 2000rpm then AgNO₃/MWCNTs mix ethanol solution was dropped on and spin-coated with 2000 rpm after 15 s then baking at 80 °C for 5 min.

Materials and Devices Characterization: The film thickness was measured by a D500 stylus profilometer. The morphology and compositions of the electrodes were analyzed using SEM (Zeiss Merlin scanning electron microscope) and XPS (XIESCALAB 250Xi electron spectrometer from VG Scientific with a monochromatic Al K radiation). The sheet resistivity of electrode was measured by using a four-point probe system (MCP-T700, MITSUBISHI). The current density–voltage (J–V) measurements were performed using an I–V testing system from PV Measurements, Inc. under an illumination power of 100 mW cm⁻² by

an AM 1.5G solar simulator with a Keithley 2400 source meter, the active area of the all device was 0.11 cm² for *J*–*V* curve measurement. The EIS was measured by an electrochemical station (Zahner, Zennium Pro) with a frequency range from 100 Hz to 1 MHz and an AC amplitude of 10 mV under light illumination. For optical characterization of the electrodes, a UV–vis–NIR spectrometer (PerkinElmer–Lambda 950) was used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.K.K.K. thanks for general support by Shenzhen Science, Technology and Innovation Commission (No. JCYJ20180305180645221), Guangdong University Key Laboratory for Advanced Quantum Dot Displays and Lighting (No. 2017KSYS007), and High-level University Fund (G02236004). W.C.H.C. acknowledges the support from the University Grant Council (RGC) of the University of Hong Kong (Grants 201811159147, 2019157209, and Platform Technology Funding 2016/17, and UGC Equipment Grant 20/7/18), ECF Project 64/2018, as well as the General Research Fund (Grants 17204117, 17200518, and 17201819) and collaboration research fund (C5037-18G and C7035-20G) from the Research Grants Council of Hong Kong Special Administrative Region, China and Guangdong-Hong Kong-Macao Joint Laboratory for Photonic-Thermal-Electrical Energy Materials and Devices (2019B121205001). Y.N.Z. thanks Southern University of Science and Technology for SUSTech-HKU Joint-PhD Program Scholarship.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

organic solar cells, semi-transparent, silver nanoparticles/carbon nanotubes, solution process, transparent electrodes

Received: December 8, 2020

Revised: January 31, 2021

Published online: February 18, 2021

- [1] A. Polman, M. Knight, E. C. Garnett, B. Ehrler, W. C. Sinke, *Science* **2016**, 352, aad4424.
- [2] V. V. Brus, J. Lee, B. R. Luginbuhl, S.-J. Ko, G. C. Bazan, T.-Q. Nguyen, *Adv. Mater.* **2019**, 31, 1900904.
- [3] Q. Liao, Q. Kang, Y. Yang, C. An, B. Xu, J. Hou, *Adv. Mater.* **2020**, 32, 1906557.
- [4] L. X. Meng, Y. M. Zhang, X. J. Wan, C. X. Li, X. Zhang, Y. B. Wang, X. Ke, Z. Xiao, L. M. Ding, R. X. Xia, H. L. Yip, Y. Cao, Y. S. Chen, *Science* **2018**, 361, 1094.
- [5] J. Yuan, Y. Q. Zhang, L. Y. Zhou, G. C. Zhang, H. L. Yip, T. K. Lau, X. H. Lu, C. Zhu, H. J. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. F. Li, Y. P. Zou, *Joule* **2019**, 3, 1140.

- [6] L. Feng, J. Yuan, Z. Zhang, H. Peng, Z.-G. Zhang, S. Xu, Y. Liu, Y. Li, Y. Zou, *ACS Appl. Mater. Interfaces* **2017**, 9, 31985.
- [7] C. J. Traverse, R. Pandey, M. C. Barr, R. R. Lunt, *Nat. Energy* **2017**, 2, 849.
- [8] W. Wang, C. Yan, T.-K. Lau, J. Wang, K. Liu, Y. Fan, X. Lu, X. Zhan, *Adv. Mater.* **2017**, 29, 1701308.
- [9] F. Liu, Z. Zhou, C. Zhang, J. Zhang, Q. Hu, T. Vergote, T. P. Russell, X. Zhu, *Adv. Mater.* **2017**, 29, 1606574.
- [10] Y. Cui, C. Yang, H. Yao, J. Zhu, Y. Wang, G. Jia, F. Gao, J. Hou, *Adv. Mater.* **2017**, 29, 1703080.
- [11] Y. Li, J.-D. Lin, X. Che, Y. Qu, F. Liu, L.-S. Liao, S. R. Forrest, *J. Am. Chem. Soc.* **2017**, 139, 17114.
- [12] S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, J. Hou, *Adv. Mater.* **2016**, 28, 9423.
- [13] Q. Xue, R. Xia, C. J. Brabec, H.-L. Yip, *Energy Environ. Sci.* **2018**, 11, 1688.
- [14] Y. Xie, Y. Cai, L. Zhu, R. Xia, L. Ye, X. Feng, H.-L. Yip, F. Liu, G. Lu, S. Tan, Y. Sun, *Adv. Funct. Mater.* **2020**, 30, 2002181.
- [15] G. Y. Xu, L. Shen, C. H. Cui, S. P. Wen, R. M. Xue, W. J. Chen, H. Y. Chen, J. W. Zhang, H. K. Li, Y. W. Li, Y. F. Li, *Adv. Funct. Mater.* **2017**, 27, 1605908.
- [16] C. C. Chueh, S. C. Chien, H. L. Yip, J. F. Salinas, C. Z. Li, K. S. Chen, F. C. Chen, W. C. Chen, A. K. Y. Jen, *Adv. Energy Mater.* **2013**, 3, 417.
- [17] M. B. Upama, M. Wright, N. K. Elumalai, M. A. Mahmud, D. Wang, C. Xu, A. Uddin, *ACS Photonics* **2017**, 4, 2327.
- [18] N. Espinosa, R. Garcia-Valverde, A. Urbina, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2011**, 95, 1293.
- [19] J. W. Zhang, G. Y. Xu, F. Tao, G. Zeng, M. Y. Zhang, Y. Yang, Y. W. Li, Y. F. Li, *Adv. Mater.* **2019**, 31, 1807159.
- [20] Y. Wang, B. Jia, F. Qin, Y. Wu, W. Meng, S. Dai, Y. Zhou, X. Zhan, *Polymer* **2016**, 107, 108.
- [21] L. Bu, Z. Liu, M. Zhang, W. Li, A. Zhu, F. Cai, Z. Zhao, Y. Zhou, *ACS Appl. Mater. Interfaces* **2015**, 7, 17776.
- [22] J. Czolk, A. Puetz, D. Kutsarov, M. Reinhard, U. Lemmer, A. Colmann, *Adv. Energy Mater.* **2013**, 3, 386.
- [23] F. Guo, X. D. Zhu, K. Forberich, J. Krantz, T. Stubhan, M. Salinas, M. Halik, S. Spallek, B. Butz, E. Spiecker, T. Ameri, N. Li, P. Kubis, D. M. Guldi, G. J. Matt, C. J. Brabec, *Adv. Energy Mater.* **2013**, 3, 1062.
- [24] G. Q. Ji, Y. L. Wang, Q. Luo, K. Han, M. L. Xie, L. P. Zhang, N. Wu, J. Lin, S. G. Xiao, Y. Q. Li, L. Q. Luo, C. Q. Ma, *ACS Appl. Mater. Interfaces* **2018**, 10, 943.
- [25] Y. S. Fang, Z. C. Wu, J. Li, F. Y. Jiang, K. Zhang, Y. L. Zhang, Y. H. Zhou, J. Zhou, B. Hu, *Adv. Funct. Mater.* **2018**, 28, 1705409.
- [26] M. L. Xie, H. Lu, L. P. Zhang, J. Wang, Q. Luo, J. Lin, L. X. Ba, H. Liu, W. Z. Shen, L. Y. Shi, C. Q. Ma, *Sol. RRL* **2018**, 2, 1700184.
- [27] J. H. Heo, D. H. Shin, D. H. Song, D. H. Kim, S. J. Lee, S. H. Im, *J. Mater. Chem. A* **2018**, 6, 8251.
- [28] D. H. Shin, C. W. Jang, H. S. Lee, S. W. Seo, S.-H. Choi, *ACS Appl. Mater. Interfaces* **2018**, 10, 3596.
- [29] Y. Song, S. Chang, S. Gradecak, J. Kong, *Adv. Energy Mater.* **2016**, 6, 1600847.
- [30] P. You, Z. Liu, Q. Tai, S. Liu, F. Yan, *Adv. Mater.* **2015**, 27, 3632.
- [31] Y. Zhou, X. Yin, Q. Luo, X. Zhao, D. Zhou, J. Han, F. Hao, M. Tai, J. Li, P. Liu, K. Jiang, H. Lin, *ACS Appl. Mater. Interfaces* **2018**, 10, 31384.
- [32] F. R. Li, Y. Xu, W. Chen, S. H. Xie, J. Y. Li, *J. Mater. Chem. A* **2017**, 5, 10374.
- [33] I. Jeon, J. Yoon, U. Kim, C. Lee, R. Xiang, A. Shawky, J. Xi, J. Byeon, H. M. Lee, M. Choi, S. Maruyama, Y. Matsuo, *Adv. Energy Mater.* **2019**, 9, 1901204.
- [34] I. Jeon, C. Delacou, A. Kaskela, E. I. Kauppinen, S. Maruyama, Y. Matsuo, *Sci. Rep.* **2016**, 6, 1.
- [35] A. K. K. Kyaw, T. A. Yemata, X. Wang, S. L. Lim, W. S. Chin, K. Hippalgaonkar, J. Xu, *Macromol. Mater. Eng.* **2018**, 303, 1700429.

- [36] Y. Xia, K. Sun, J. Ouyang, *Adv. Mater.* **2012**, 24, 2436.
- [37] M. T. Z. Myint, M. Hada, H. Inoue, T. Marui, T. Nishikawa, Y. Nishina, S. Ichimura, M. Umeno, A. K. K. Kyaw, Y. Hayashi, *RSC Adv.* **2018**, 8, 36563.
- [38] Y. Zhou, T. M. Khan, J.-C. Liu, C. Fuentes-Hernandez, J. W. Shim, E. Najafabadi, J. P. Youngblood, R. J. Moon, B. Kippelen, *Org. Electron.* **2014**, 15, 661.
- [39] L. Yin, Z. Zhao, F. Jiang, Z. Li, S. Xiong, Y. Zhou, *Org. Electron.* **2014**, 15, 2593.
- [40] Y. Zhang, S.-W. Ng, X. Lu, Z. Zheng, *Chem. Rev.* **2020**, 120, 2049.
- [41] X. Ren, X. Li, W. C. H. Choy, *Nano Energy* **2015**, 17, 187.
- [42] H. Lu, X. Ren, D. Ouyang, W. C. H. Choy, *Small* **2018**, 14, 1703140.
- [43] J. H. Park, D. Y. Lee, W. Seung, Q. Sun, S.-W. Kim, J. H. Cho, *J. Phys. Chem. C* **2015**, 119, 7802.
- [44] J. Kang, C.-G. Park, S.-H. Lee, C. Cho, D.-G. Choi, J.-Y. Lee, *Nanoscale* **2016**, 8, 11217.
- [45] X. He, Y. Wang, H. Lu, D. Ouyang, Z. Huang, W. C. H. Choy, *J. Mater. Chem. A* **2020**, 8, 6083.
- [46] D. Wang, T. Xie, Q. Peng, Y. Li, *J. Am. Chem. Soc.* **2008**, 130, 4016.
- [47] D. D. Evanoff, G. J. C. Chumanov, *ChemPhysChem* **2005**, 6, 1221.
- [48] C. Dahmen, A. N. Sprafke, H. Dieker, M. Wuttig, G. von Plessen, *Appl. Phys. Lett.* **2006**, 88, 011923.
- [49] H. Lu, D. Zhang, J. Cheng, J. Liu, J. Mao, W. C. H. Choy, *Adv. Funct. Mater.* **2015**, 25, 4211.
- [50] J. Kim, D. Ouyang, H. F. Lu, F. Ye, Y. W. Guo, N. Zhao, W. C. H. Choy, *Adv. Energy Mater.* **2020**, 10, 1903919.
- [51] H. Lu, D. Zhang, X. Ren, J. Liu, W. C. H. Choy, *ACS Nano* **2014**, 8, 10980.
- [52] C. Roldan-Carmona, O. Malinkiewicz, R. Betancur, G. Longo, C. Momblona, F. Jaramillo, L. Camacho, H. J. Bolink, *Energy Environ. Sci.* **2014**, 7, 2968.
- [53] E. Della Gaspera, Y. Peng, Q. C. Hou, L. Spiccia, U. Bach, J. J. Jasieniak, Y. B. Cheng, *Nano Energy* **2015**, 13, 249.
- [54] S. Z. Pang, X. Y. Li, H. Dong, D. Z. Chen, W. D. Zhu, J. J. Chang, Z. H. Lin, H. Xi, J. C. Zhang, C. F. Zhang, Y. Hao, *ACS Appl. Mater. Interfaces* **2018**, 10, 12731.
- [55] Y.-Y. Lee, K.-H. Tu, C.-C. Yu, S.-S. Li, J.-Y. Hwang, C.-C. Lin, K.-H. Chen, L.-C. Chen, H.-L. Chen, C.-W. Chen, *ACS Nano* **2011**, 5, 6564.
- [56] Z. K. Liu, P. You, S. H. Liu, F. Yan, *ACS Nano* **2015**, 9, 12026.
- [57] F. Fu, T. Feurer, T. Jaeger, E. Avancini, B. Bissig, S. Yoon, S. Buecheler, A. N. Tiwari, *Nat. Commun.* **2015**, 6, 8932.
- [58] H. Kim, H. S. Kim, J. Ha, N. G. Park, S. Yoo, *Adv. Energy Mater.* **2016**, 6, 1502466.
- [59] Z. Liu, J. Li, Z.-H. Sun, G. Tai, S.-P. Lau, F. Yan, *ACS Nano* **2012**, 6, 810.
- [60] I. Lopez-Salido, D. C. Lim, Y. D. Kim, *Surf. Sci.* **2005**, 588, 6.
- [61] S. W. Han, Y. Kim, K. Kim, *J. Colloid Interface Sci.* **1998**, 208, 272.
- [62] M. Y. Bashouti, S. Resch, J. Ristein, M. Mackovic, E. Spiecker, S. R. Waldvogel, S. H. Christiansen, *ACS Appl. Mater. Interfaces* **2015**, 7, 21657.
- [63] G. Xue, Q. P. Dai, S. G. Jiang, *J. Am. Chem. Soc.* **1988**, 110, 2393.
- [64] Y.-Q. Zhang, M. Paszkiewicz, P. Du, L. Zhang, T. Lin, Z. Chen, S. Klyatskaya, M. Ruben, A. P. Seitsonen, J. V. Barth, F. Klappenberger, *Nat. Chem.* **2018**, 10, 296.
- [65] A. Guerrero, S. Loser, G. Garcia-Belmonte, C. J. Bruns, J. Smith, H. Miyauchi, S. I. Stupp, J. Bisquert, T. J. Marks, *Phys. Chem. Chem. Phys.* **2013**, 15, 16456.
- [66] X. Tian, Y. Zhang, Y. Hao, Y. Cui, W. Wang, F. Shi, H. Wang, B. Wei, W. Huang, *J. Nanophotonics* **2015**, 9, 093043.
- [67] A. Colmann, A. Puetz, A. Bauer, J. Hanisch, E. Ahlsweide, U. Lemmer, *Adv. Energy Mater.* **2011**, 1, 599.