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Supporting Information

Organic Solar Cells Based on Cellulose Nanopaper from Tobacco Stalk of Agroforestry Residues with Efficiency >16% with Effective Wide-Angle Light Capturing

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Materials and characterizations

Raw tobacco stalk (TS) was obtained from Weifang in China in 2018. Before cooking, the roots and barks of TS were removed, and smashed under 20 mesh. Ammonium sulfite (90%) was bought from Macjlin (Shanghai, China). Sodium hydroxide (NaOH), dimethylacetamide (DMAC) and hydrogen peroxide (H_2O_2, 30 wt%) were obtained Sinopharm Chemical Reagent Co. The indium tin oxide glass sheet (0.7 mm thick, ≤12 Ω/square, transmittance >90%) was purchased from Jinghui Science and Techlogy Company, Ltd. Acetone, isopropanol, chloroform and methanol were purchased from

Sinopharm Chemical Reagent Co., Ltd. PEDOT:PSS was purchased from Heraeus, Germany. PM6 and Y6 were from Vizuchem. PDIN was purchased from Suna Tech In. The morphologies of the treated tobacco stalk were measured by using scanning electron microscope (SEM, Hitachi S-4800) and atomic force microscope (AFM, Agilent 5400), respectively. The crystallinity index (CrI) of CNP sample was tested using an X-ray diffractometer (XRD, Bruker Discover D8). The range of the scattering angle (2θ) was from 5 to 40 ° with a scan rate of 4 ° min^{-1} at 40 kV and 40 mA. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on an FTIR spectrometer (Nicolet 6700, Thermo Fisher Scientific Inc.) from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

Preparation of CNFs

Ammonium sulfite (AS) cooking of TS was carried out at 160ºC for 2 h using a rotating reactor system (VRD-42SD-A, China National Pulp and Paper Research institute, Ltd.) with the AS concentration of 2 wt.% to achieve delignification. The dosage of urea was 6% on the basis of the oven dried mass of TS for each cooking to maintain weak alkali conditions in AS treatment. Then, the AS-treated TS samples were collected by filtration and washed with deionized water until pH reached neutral.

In order to obtain the lignin-free sample, the AS-treated TS samples were bleached with 5% H_2O_2 (based on the oven dried mass of AS-treated TS sample) at 90 ºC for 2 h. The liquid-to-solid weight ratio was 10 and the pH of the mixture was 10.5 by adjusting with 1 M NaOH solution. This whole process was repeated 3 times until the snowy-white bleached TS sample was obtained. The bleached TS samples were dried at 75 ºC for 4 h.

Then, formic acid (FA) hydrolysis was conducted to further break down the bleached TS samples (each trial processed 10 g sample). The bleached TS sample was directly treated with FA (1:30, w/v) with the mechanical stirring of 300 rpm at 95 ºC for 6 h. The FA hydrolyzed cellulosic solid residue (FCSR) was rinsed with FA to remove the dissolved substances and then washed with water to neutralize pH for the removal of impurities. The lignin content of the resultant FCSR was less than 0.1 wt.%, and the remaining water in FCSR was removed by centrifugation and solvent exchange with DMAc (thrice). After that, the FCSR was homogenized at a concentration of 0.2 wt.% in DMAc passing through an ATH-BASIC homogenizer (ATH Engineering Limited, China) 3 times at 30 MPa and then 5 times at 100 MPa. At last, the CNF suspension in DMAc was obtained.

Fabrication of CNP

110 mL of CNF suspension with CNF concentration of 0.2 wt% in DMAc was used to fabricate CNP by vacuum filtration using a filter membrane (polypropylene, diameter of 10 cm, pore size of 0.44 μm). The obtained wet CNP was placed between two filter membranes and dried under vacuum at 70 ºC for 3 h. After drying, the resultant CNP was ready to be used as optical trapping for organic solar cells.

UV-Vis measurement and Raman volume mapping of CNP

The transmittance and haze of CNPs was measured with UV-Vis spectroscopy (Lambda 750, Perkin Elmer). The transmittances of CNPs/ITO glass and ITO glass at different incident angles were characterized with customized optical moving platform (an interval of 5^o), light source (Wyoptics, IS50T), integrating spheres (Wyoptics, DH2000-LL), and detector (Ocean Optics, Maya 2000 Pro). For Raman measurement, the CNP was fixed onto glass slide by pasting its' edges with adhesive tape and placed onto the optical platform of Raman microscope (Renishaw, Invia Reflex). The Raman volume mapping was conducted using 532 nm laser excitation and suitable intensity on the volume of 15 μm^3 of CNPs (thickness of 47 μm), with an interval of 1 μm. The full spectra were achieved for each point, and the peak area ratio at 380 and 1092 cm^{-1} was selected to calculate the local crystalline index on each point.

Device fabrication

The conventional device structure was indium tin oxide (ITO)/ PEDOT: PSS/PM6:Y6/PDIN/Ag. The ITO glass was respectively ultrasonicated with an surface active cleaner, deionized water, acetone, and isopropanol for 20 minutes and then drying at 80 ^{o}C for one night. Then, the PDMS glue is used to paste the cellulose film on the back of the dried ITO glass, and the device can be manufactured after the glue is cured. After oxygen plasma treatment for 20 min, a thin layer of PEDOT:PSS was prepared by spin-coating , the PEDOT:PSS solution filtered through a 0.45 mm poly(tetrafluoro-ethylene) (PTFE) filter at 3000 rpm for 50 s on the ITO substrate. Then the PEDOT:PSS substrates were annealed at 140 ^{o}C in air for 10 min, and the thickness of the PEDOT:PSS layer was about 35 nm. The polymer PM6:Y6 (D:A = 1:1.2,16 mg mL^{-1} in total) was dissolved in chloroform (CF) with the solvent additive of 1-chloronaphthalene (CN) (0.5 %, v/v) and spin-cast at 4000 rpm for 50 s onto the PEDOT:PSS substrates, the thickness of the active layer is about 100nm and annealed at 100 ^{o}C for 5 min to prepare the active layers. Then the PDIN added acetic acid dissolved in methanol and then were spin-coated onto the active layers at 2200 rpm for 30 s. Finally, the equipment was evacuated to 10^{-4} to begin heating and evaporation, and about 100 nm of Ag was deposited on top of the cathode interface layer.

Water resistance of CNP

The water resistance was investigated by immersing these CNP films into water, the results showed little changes on width and length were found. It means that these CNP films were very stable in water.

J-V characterization and EQE measurement

The J-V characteristics and the J-V characteristics of a typical device with different incident illumination intensity of the OSCs was measured by a Keithley 2400 source measurement unit and an AM 1.5 G solar simulator (Newport-Oriel® Sol3A450W) in an Ar-filled glovebox, and the light intensity for J-V measurements was calibrated with a NREL certified silicon reference cell. The EQE was measured on a Newport-Oriel® OPSA500, which was calibrated by standard Si/Ge solar cell under illumination with monochromatic light from a Xe lamp at room temperature in air. In the meanwhile, the EQE with different angles were measured by tuning the incident light with required angles.

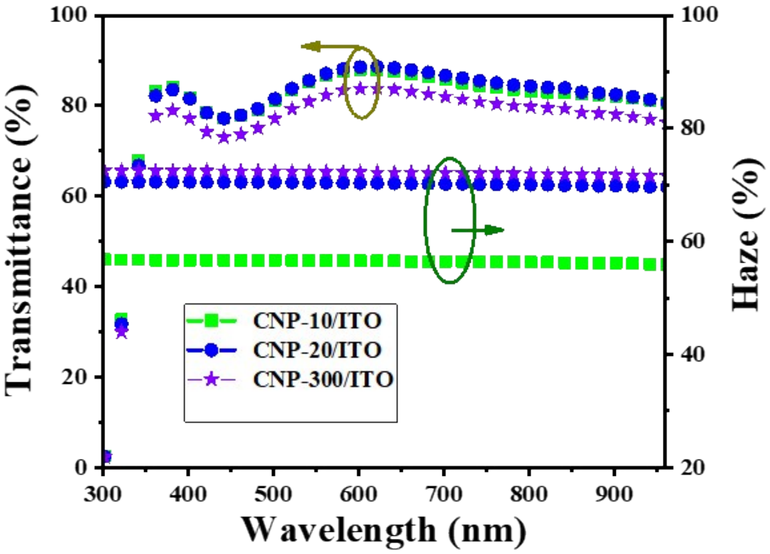

Figure S1. The Transmittance and haze of CNP-10, CNP-20, and CNP-30

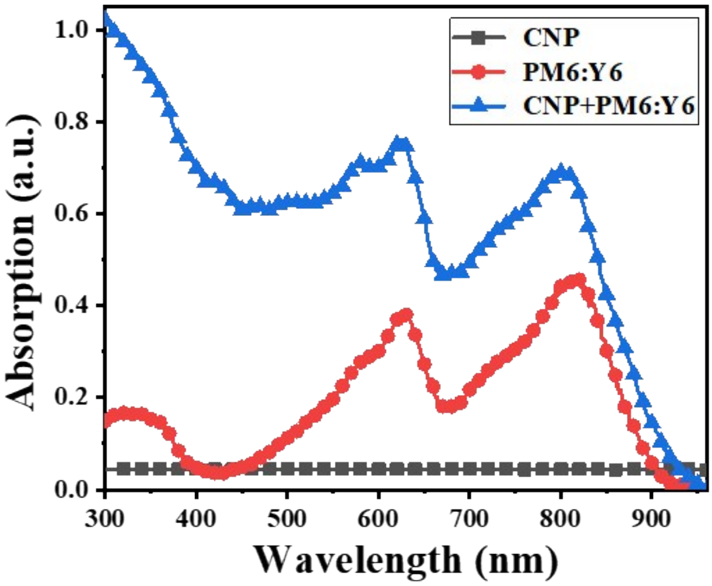

Figure S2. The absorption of PM6:Y6, CNP+ PM6:Y6, and CNP-20

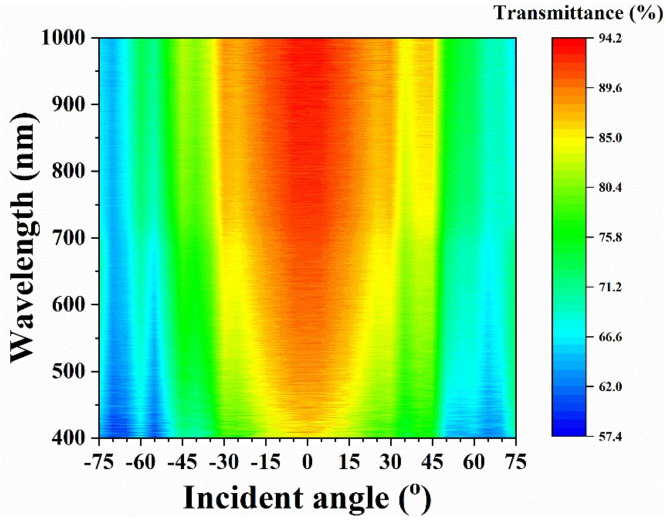

Figure S3. Transmittance of ITO-glass at different incident angles and wavelengths

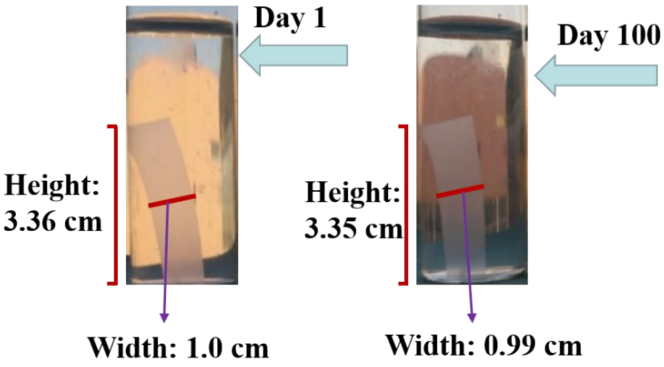

Figure S4. The size of CNP in water one day and 100 days

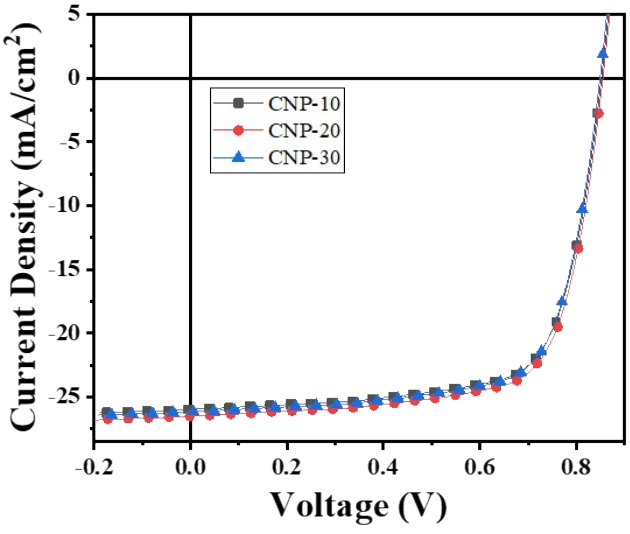

Figure S5. *J*-V curves of CNP-10, CNP-20, and CNP-30/Glass/ITO-based devices

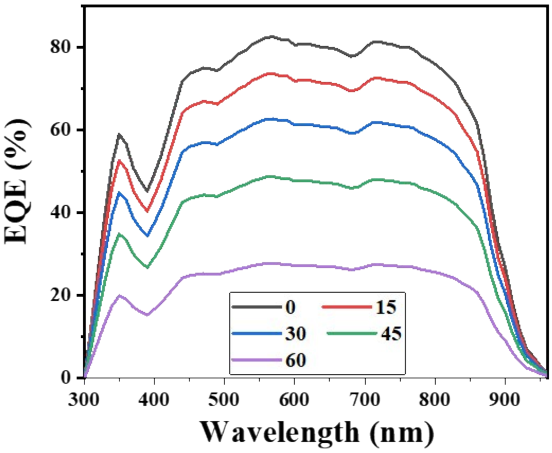

Figure S6. EQE with different incident angles of Glass/ITO-based devices

Table S1. Some parameters for OSCs with light-trapping of CNP at different light intensities (device area: 4.0 mm^2)

Light Intensities (AM)	J_{SC} (mA/cm^2)	V$_{OC}$ (V)	FF (%)	PCE (%)
1.1	28.02	0.862	71.08	17.16
1.0	25.51	0.862	73.41	16.14
0.9	23.44	0.860	70.49	14.21
0.7	18.23	0.851	66.56	10.33
0.5	12.92	0.842	71.86	7.81
0.3	8.00	0.824	66.96	4.41
0.1	2.63	0.791	67.05	1.39

Table S2. The parameters for OSCs with/without light-trapping of CNP at different incident light angles (device area: 4.0 mm^2)

Angle (°)	CNP-20	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
0	w/o	25.61	0.856	70.28	15.41
	w	26.48	0.858	71.17	16.17
15	w/o	22.84	0.853	71.98	14.02
	w	25.72	0.852	71.96	15.77
30	w/o	19.46	0.851	71.48	11.84
	w	24.67	0.851	71.46	15.00
45	w/o	15.11	0.850	71.01	9.12
	w	21.18	0.850	70.99	12.78
60	w/o	8.61	0.838	68.33	4.93
	w	10.99	0.838	68.21	6.28

Table S3. The parameters for OSCs with/without light-trapping of CNP-10, CNP-20, and CNP-30 at different incident light angles (device area: 4.0 mm^2)

Angle (°)	CNPs	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)
0	CNP-10	25.94	0.855	70.92	15.73
	CNP-20	26.48	0.858	71.17	16.17
	CNP-30	26.13	0.852	71.03	15.81
15	CNP-10	24.75	0.853	71.74	15.14
	CNP-20	25.72	0.852	71.96	15.77
	CNP-30	25.35	0.853	71.83	15.53
30	CNP-10	23.58	0.851	71.39	14.32
	CNP-20	24.67	0.851	71.46	15.00
	CNP-30	24.13	0.852	71.49	14.70
45	CNP-10	19.30	0.850	71.03	11.65
	CNP-20	21.18	0.850	70.99	12.78
	CNP-30	20.44	0.850	70.91	12.32
60	CNP-10	8.99	0.835	68.33	5.13
	CNP-20	10.99	0.838	68.21	6.28
	CNP-30	9.58	0.836	68.62	5.49