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Pt-free Transparent Counter Electrodes for Dye-Sensitized Solar Cells Prepared from Carbon Nanotube Micro-balls

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Supplementary Information

Experimental Details

Preparation of CNT micro-balls

Multi-walled carbon nanotubes designed for electrochemical electrodes and prepared by chemical vapor deposition, were purchased from Applied Carbon Nano, Inc. Some 1 g of CNTs was dispersed in 100 ml of distilled water by ball milling for 24 h. 100 mg of carboxymethylcellulose (CMC) was then added as a condensation and dispersion agent. After further ball-milling, 400 ml of water was added to and sonicated for 40 min using a horn-type ultrasonicator.

The prepared CNT suspensions were spray-dried using an ultrasonic sprayer with a spraying pressure of 130 kPa and an inlet air temperature of 200^{o}C. The outlet air temperature was 60^{o}C and the blow rate was 0.13 cm^{3}/min.

Preparation of counter electrode

The CNT micro-ball counter electrode was prepared by both spraying and application of a paste, using a Dr. Blade procedure. The CNT micro-ball paste was prepared by mixing 10-50 mg of CNT micro-balls with 10 ml of ethanol to which was added 1 g of terpineol and 1 g of 5 wt% ethylcellulose in ethanol. This mixture was sonicated for 30 min in a bath-type ultrasonic cleaner and the ethanol evaporated *in vacuo* for 2 h. For spraying, 20 mg of CNT micro-balls were dispersed in 20 ml of ethanol by ultra-sonication and then sprayed on FTO-coated glass, using a hand sprayer. After deposition, the electrodes were heat treated at 380^{o}C for 2 h in air to remove the CMC.

The Pt counter electrode was prepared using Pt paste purchased from Solaronix SA and deposited on the FTO glass using a Dr. Blade, followed by heat treatment at 400^{o}C for 3 min.

DSSC unit cell preparation

Fabrication methods are described elsewhere. We used N719 Ru-based dye and an acetonitrile-based electrolyte (Solaronix, AN 50). The active area of the unit cell was 0.36 cm^{2} and the photovoltaic performance was measured by a solar simulator in 1.5 AM, 1 sun conditions. The efficiency of DSC cell was measured using

solar simulator produced by Abet Technologies, model Sun 2000 (1000W Xe source) and Keithley 2400 source meter. The 1sun condition was calibrated on each measurement by KG-3 filter and NREL-certified Si reference cell. At least 4 unit cells were prepared for each set of electrode conditions and the results averaged. In some cases, 8-10 cells were prepared.

Figure S1. SEM micrograph of raw MWNT used in this study.

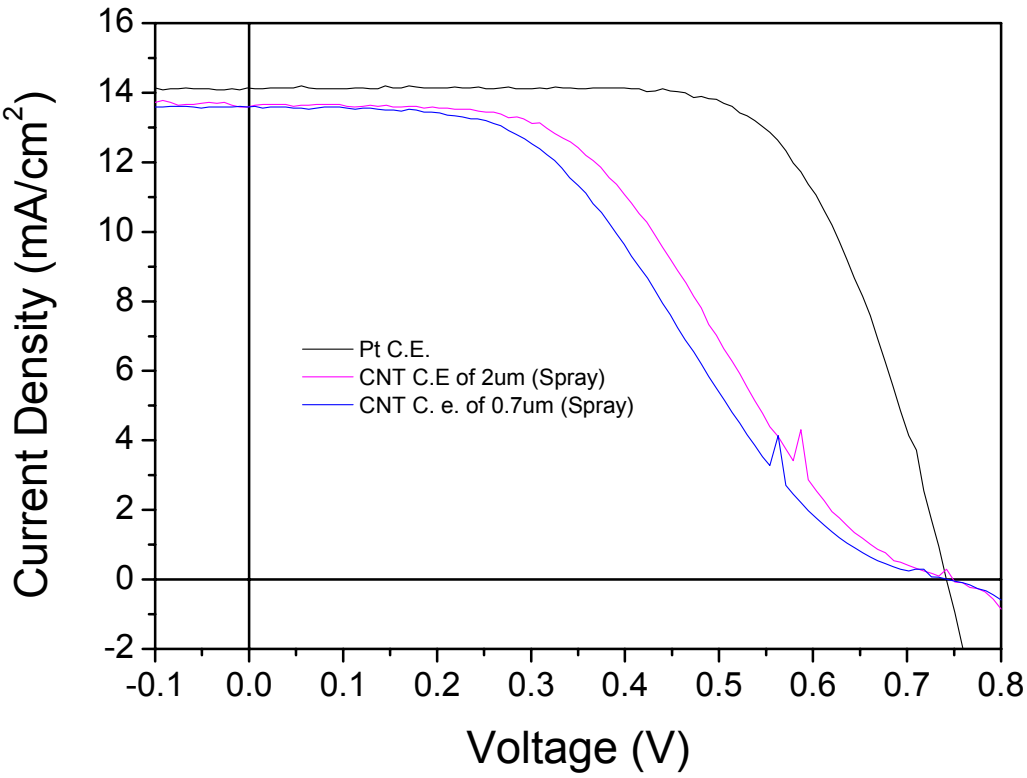

Figure S2. The current density-voltage relationship (I-V curve) for DSSC with CNT counter electrode of various thickness

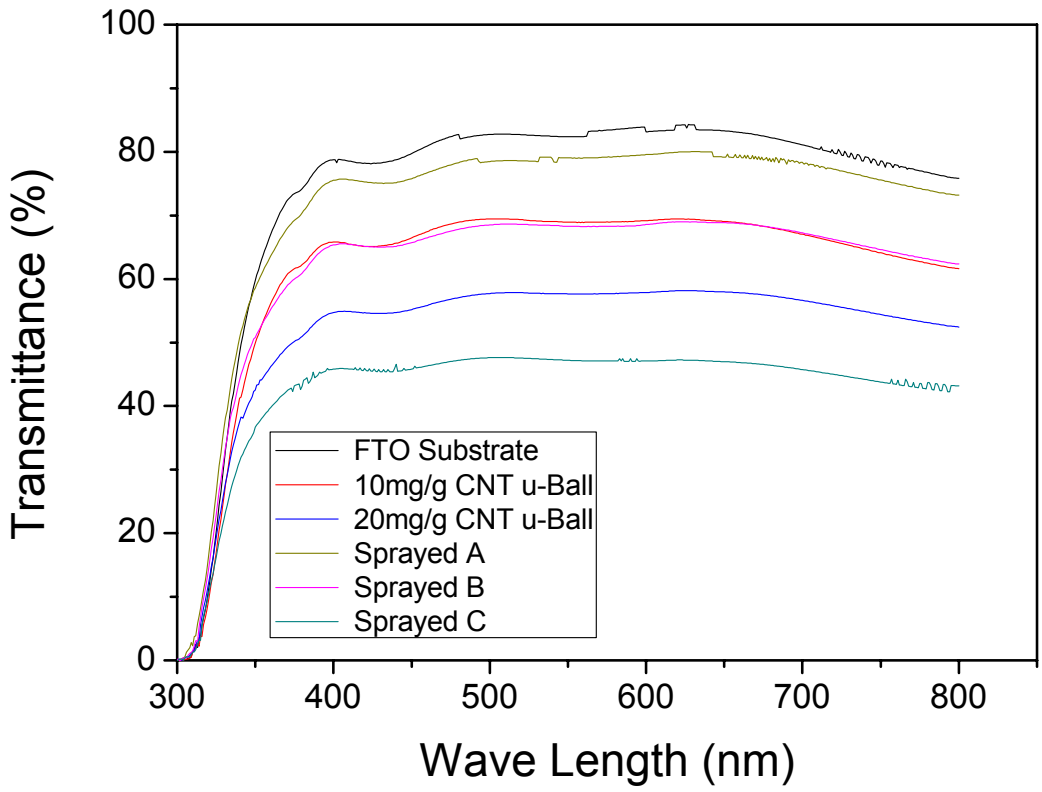

Figure S3. The relationship between transmittance of CNT micro-ball counter electrode on FTO glass and wavelength.

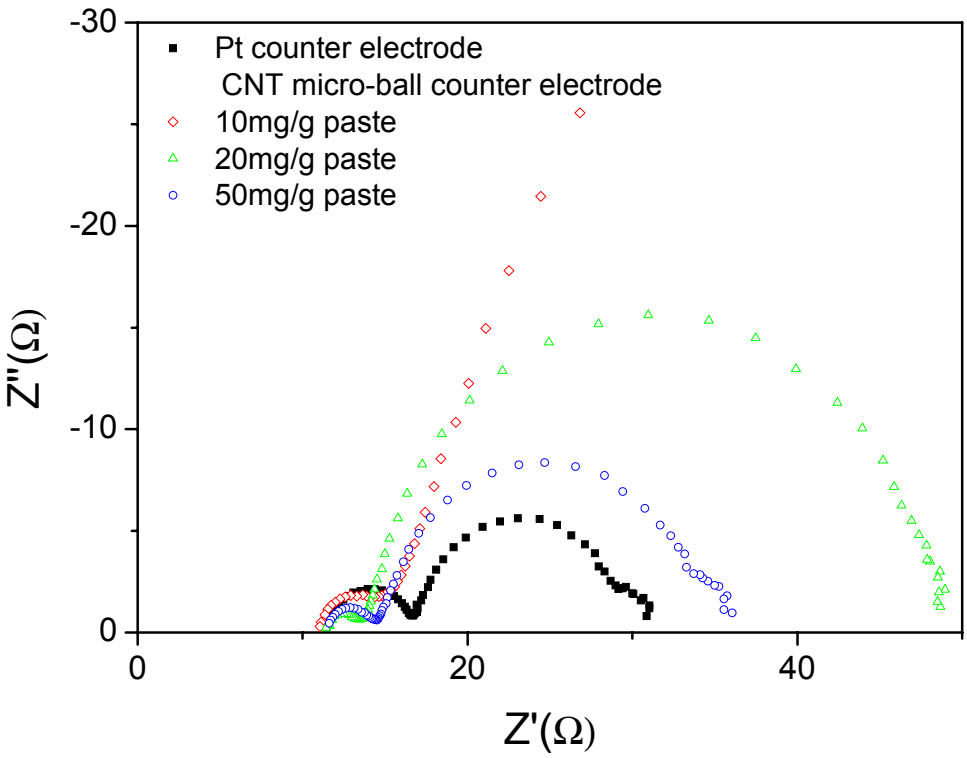

Figure S4. Nyquist Plot for DSSC cells near Voc using various counter electrode. (1sun 1.5AM)