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## **Spatial Arrangement of Carbon Nanotubes in TiO<sub>2</sub> Photoelectrodes to Enhance the Efficiency of Dye-Sensitized Solar Cells**

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### *Electrochemical deposition of multi-walled carbon nanotubes (MWCNTs)-layer on FTO*

Chemical vapour deposition (CVD)-grown MWCNTs (*ca.* 5~10  $\mu\text{m}$  in length), tetraoctylammonium bromide (TOAB), and tetrahydrofuran (THF) were obtained from Sigma-Aldrich. MWCNTs were first oxidized in a mixture of concentrated sulfuric and nitric acid (95% H<sub>2</sub>SO<sub>4</sub>/65% HNO<sub>3</sub> = 3/1, v/v) for 1 h to open the ends of the tubes and for shortening up to 0.5~1  $\mu\text{m}$ .<sup>s1</sup> After collection following centrifugation and repeated washing to remove excess acid, 40 mg of completely dried CNTs were dissolved in 100 ml THF with 0.52 g TOAB to form a stable dark suspension following 30 min sonication. CNTs, recollected by centrifugation, were washed to remove unbound TOAB and dried at 60°C for 8 h. They were dissolved in 25 ml THF, followed by sonication for 20 min, to prepare highly dispersed CNT solution, which was used for the electrophoretic deposition of CNTs after further dilution by THF up to the factor of 5.25 V (dc), applied for 10 min across the two pieces of FTO (15  $\times$  50 mm, 15  $\Omega$  , Pilkington Co. Ltd.). They were then dipped into the solution 4–5 mm apart in parallel to deposit CNTs electrophoretically.

### *Preparation of TiO<sub>2</sub> colloidal mixture*

TiO<sub>2</sub> colloidal mixture was prepared using 25 nm commercially available nanoparticles (P25; Degusa, Germany) by mixing with 50 % (w/w) of hydroxypropyl cellulose (HPC) (Aldrich) after pretreatment with acetylacetone as previously reported.<sup>s1-s3</sup> MWCNTs in 0.2, 0.025, and 0.01% by weight solutions were added to form a CNT-dispersed TiO<sub>2</sub> colloidal mixture.

### *Fabrication of device*

The electrodes were dipped into 0.3 mM ethanolic solution of *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis-tetrabutylammonium dye (N719) for 18 h. The counter electrodes were prepared by spin coating of 5 mM ethanolic solution of chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) on FTO and sintered at 380°C for 20 min. The dye loaded photoelectrodes (active area *ca.* 0.16 cm<sup>2</sup>) and platinized counter electrodes were sandwiched with 20 μm thick Surlyn film as a spacer and sealing agent at 110°C for 10 min. The electrolyte solution composed of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.1 M I<sub>2</sub>, and 0.5 M 4-*tert*-butylpyridine (*t*BP) in 3-methoxypropionitrile (MPN) was injected into the cell through the drilled holes on the counter electrode. They were sealed with a transparent scotch tape.<sup>s1</sup>

### *Measurements*

A solar simulator equipped with a 200 W Xenon lamp (Polaronix<sup>®</sup> K201, McScience) was used to generate simulated light of AM1.5. A photovoltaic power meter (Polaronix<sup>®</sup> K101 LAB20, McScience) was used to measure the *J-V* curves. The incident light intensity was adjusted to 100 mWcm<sup>-2</sup> (1 sun) by a standard mono-Si solar cell (PVM 396, PV Measurement), certified by

National Renewable Energy Laboratory (NREL). Electrochemical impedance spectra (EIS) were obtained under open circuit and dark conditions in the frequency range of  $10^5$ –0.1 Hz with the ac amplitude of 10 mV (IM6ex, Zahner-Elektrik GmbH & Co. KG).

Voltammetric analysis was performed with CHI 430A electrochemical workstation (CH Instrument, Inc. USA). A conventional three electrode system was used with platinum wire and Ag/AgCl as counter and reference electrode, respectively.

## Notes and references

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