

Supporting Information

for

Facile and Quick Preparation of Carbon Nanohorn-based Counter Electrodes for Efficient Dye-Sensitized Solar Cells

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Table of Contents

Materials	2
Dye-sensitized solar cell characterization	2
Transmission electron microscopy	3
Thermogravimetric analysis	4
Raman experiments	5
Profilometry	6
Scanning electron microscopy	7
Equivalent circuits for the EIS fittings	8
Charge transfer resistances from EIS	9
Figures-of-merit of CNH- and Pt-based CEs over time	10

Materials

All chemicals were purchased from chemical suppliers and used without further purification. TiCl_4 (0.09 M in HCl), guanidinium thiocyanate, ACN, *tert*-butyl alcohol, valeronitrile, *ortho*-dichlorobenzene, 4-*tert*-butylpyridine, 1-butyl-3-methylimidazolium iodide, cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutyl-ammonium), and $\text{H}_2\text{Cl}_6\text{Pt} \times \text{H}_2\text{O}$ were purchased from Sigma-Aldrich. TiO_2 paste (Ti-Nanoxide T/SP) and the sealing foil (Meltonix 1170-25) were purchased from Solaronix. CNHs were produced by Carbonium s.r.l., Padova (Italy) by direct graphite evaporation in Ar flow, according to a patented method and used without further purification.¹

Dye-sensitized solar cell characterization

The photocurrent measurements and electrochemical impedance spectroscopy (EIS) were performed using a 150 W lamp (Xenon lamp, calibrated to 1000 W m^{-2} under AM 1.5G conditions with a Si-Reference cell (Oriel SRC-1000-TC-K-KG5-N). Current-voltage measurements were measured by using a potentiostat/galvanostat (PGSTAT30N, Autolab equipped with a frequency response analyzer module – FRA) in the range of -0.9 to 0.2 V. DSSCs were measured by using a shading mask with an aperture size according to the literature.² EIS measurements for DSSCs were performed at the respective open-circuit voltage of the different devices at 1000 W m^{-2} and AM 1.5G conditions. The AC signal amplitude was set at 10 mV, modulated in a frequency range from 0.1 to 100000 Hz. The Nova ver. 1.11.2 software was used to obtain the parameters from the equivalent circuit.

The linear sweep voltammetry of the electrolytes in the FTO|CNH|electrolyte|CNH|FTO configuration measurements and were performed with an Autolab potentiostat/galvanostat (PGSTAT30, Autolab equipped with a frequency response analyzer module – FRA) in the range of -1 to 1 V. Here, EIS was performed without applying a potential. The AC signal amplitude was set at 10 mV, modulated in a frequency range from 0.1 to 100000 Hz. The Nova ver. 1.11.2 software was used to obtain the parameters deduced from the equivalent circuit and the Tafel plots.

Transmission electron microscopy

Transmission electron microscopy (TEM) was performed with a Zeiss Leo 912 at 80 kV equipped with an in-column electron energy filter and digital CC camera for image acquisition.

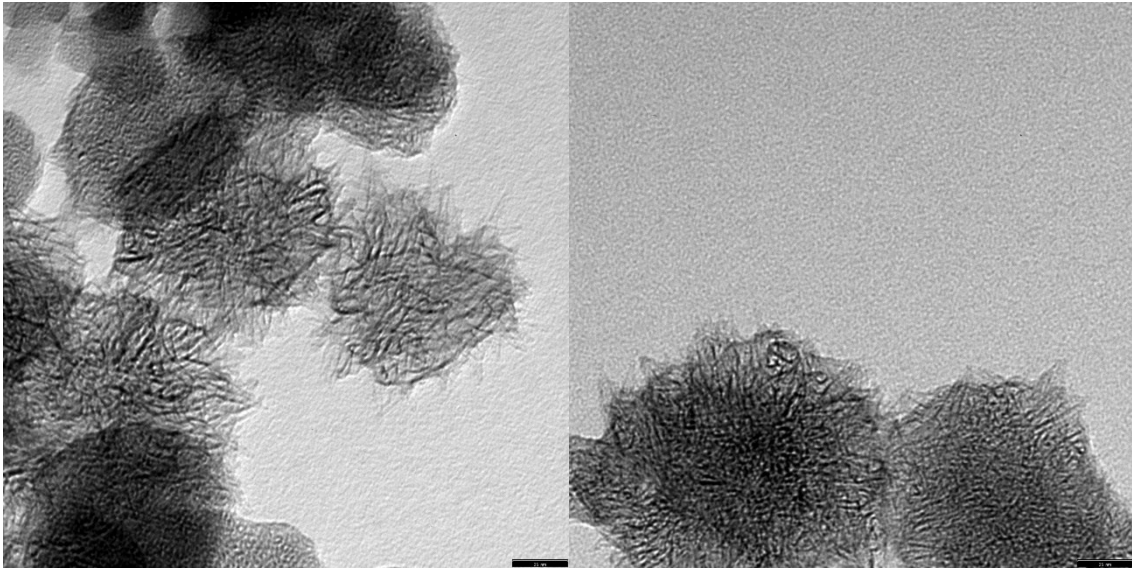


Figure S1. TEM images of a drop casted dispersion of CNH in *ortho*-dichlorobenzene onto a lacey carbon grid. Scale bar: 25 nm.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed with a NetzschTG 209 F1 Libra at 10 °C/min under nitrogen.

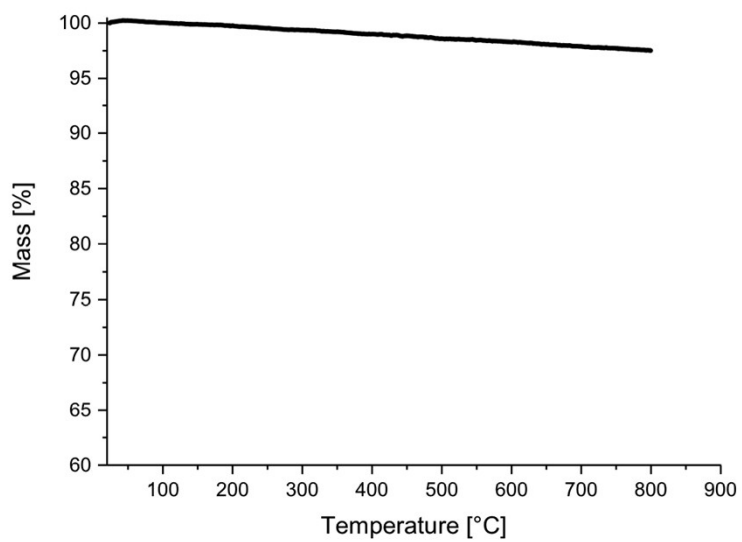


Figure S2. TGA analysis profile of CNHs measured under nitrogen conditions.

Raman experiments

Raman experiments were performed using Horiba Jobin Yvon LabRAM Aramis confocal Raman microscope with an excitation wavelength of 532 nm. The spot size was about 1 μm using an Olympus LMPlanFI 100, NA 0.80 objective in backscattering geometry.

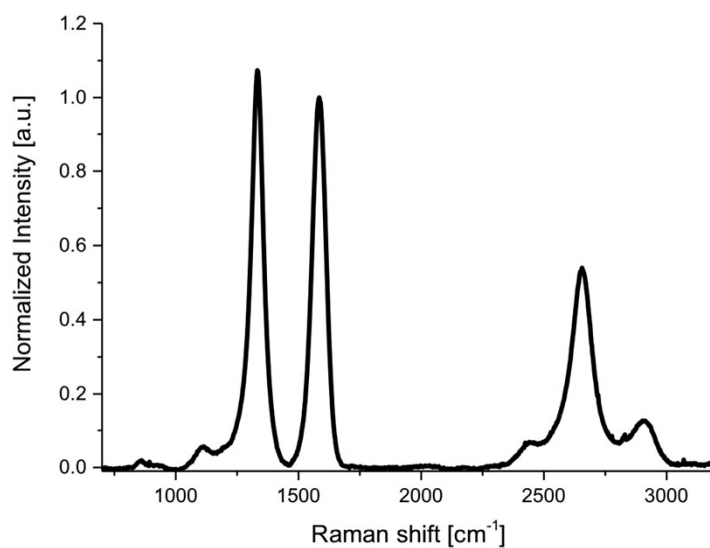


Figure S3. Normalized Raman spectrum of CNHs measured in solid state at 532 nm excitation.

Profilometry

For alpha-step thickness measurements and roughness determination of the CNH-based CEs a Dektak XT profilometer from Bruker was utilized.

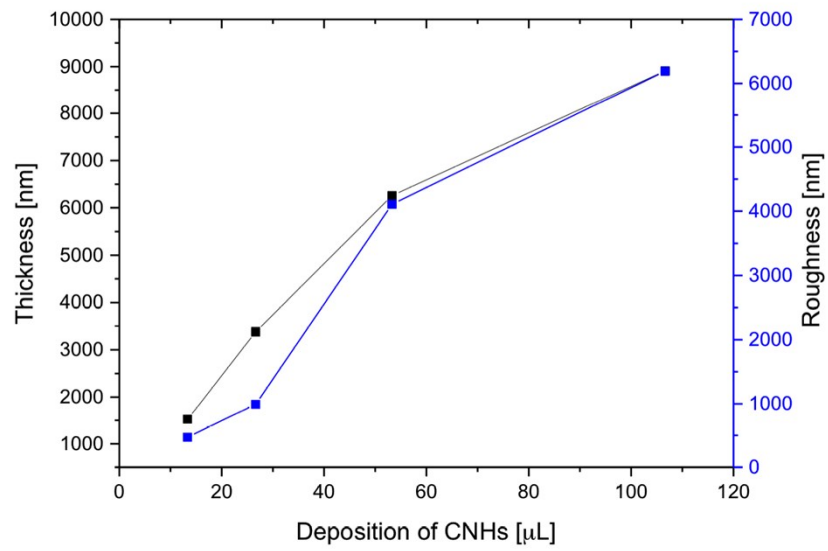


Figure S4. Thickness and average roughness of the CNH-based CEs.

Scanning electron microscopy

Scanning electron microscopy (SEM) was conducted on an AURIGA with a GEMINI column (Zeiss).

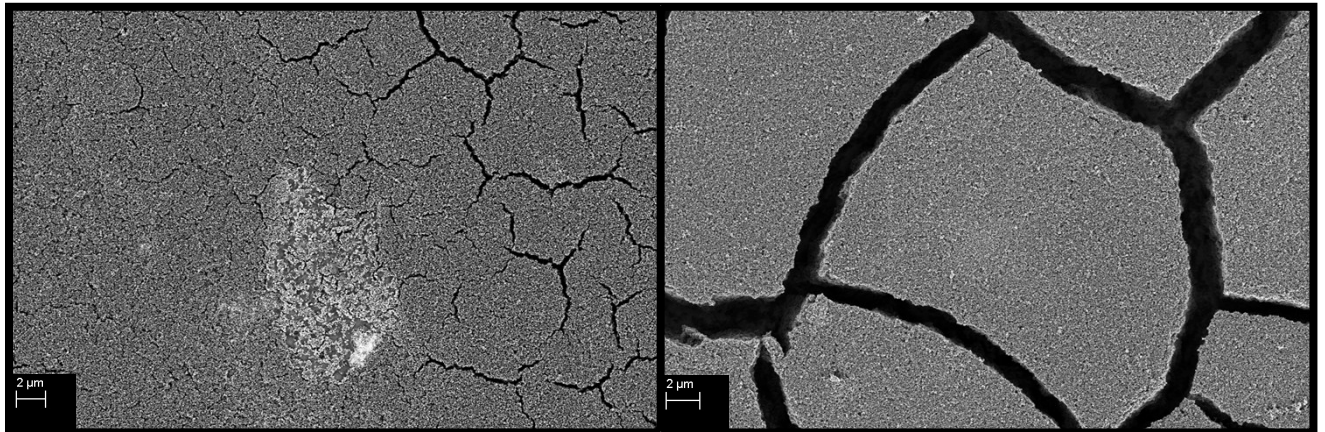


Figure S5. SEM images of drop casted CNHs onto a FTO glass slide with a thickness of 1.52 (left) and 6.26 (right) μm .

Equivalent circuits for the EIS fittings

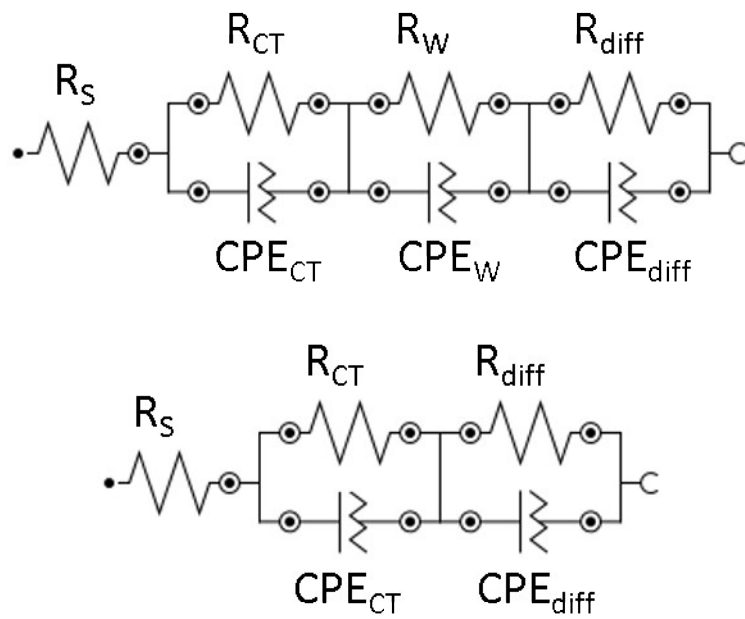


Figure S6. Equivalent circuits for the EIS fittings for DSSCs (top) and symmetric cells (bottom). R_s , R_{CT} , R_W , and R_{diff} represent the series resistance, charge transfer resistance at the CE, electron transport resistance in the TiO_2 , and diffusion resistance in the bulk electrolyte, respectively. CPE_{CT} , CPE_W , and CPE_{diff} represent the corresponding constant phase elements.

Charge transfer resistances from EIS

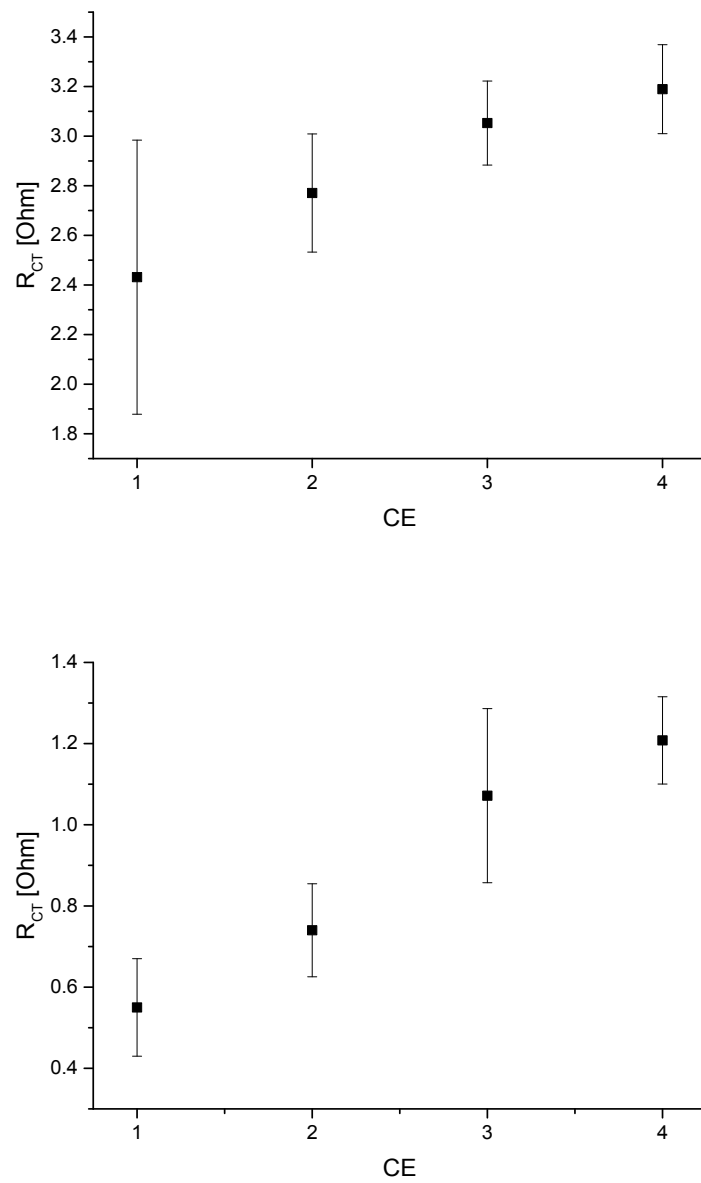


Figure S7. Charge transfer resistances deduced from EIS measurements of CEs **1**, **2**, **3**, and **4** with corresponding error bars of the symmetric devices (upper part) and of DSSCs (lower part).

Figures-of-merit of CNH- and Pt-based CEs over time

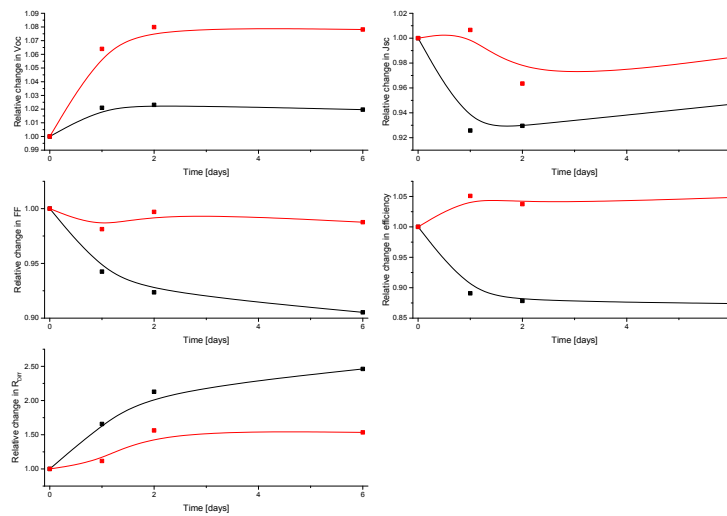


Figure S8. Relative changes of the figures-of-merit of DSSCs with CEs based on CNHs (black) and Pt (red) derived from J-V measurements and EIS over time.

- 1 M. Schiavon, *US Patent 7,125,525*, 2006, **2**.
- 2 S. Ito, M. K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Péchy, M. Jirousek, A. Kay, S. M. Zakeeruddin and M. Grätzel, *Progress in Photovoltaics: Research and Applications*, 2006, **14**, 589–601.