

Electronic Supplementary Information

Nitrogen-doped Carbon Nanotubes with metal nanoparticles as Counter Electrode Materials of Dye-Sensitized Solar Cells

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Materials preparation.

Synthesis of nitrogen-doped carbon nanotubes with confinement of Co or Ni nanoparticles was carried out according to previous reported. [1] In brief, dicyandiamide (12 mmol) was mixed with cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.84 mmol). After grinding for 15 min, the homogeneous mixture was placed on an alumina boat and heated at 500 °C in a tube furnace for 2 h in N_2 atmosphere. The temperature in the tube furnace was further raised to 700 °C at a ramp of 10 °C/min and kept at 700 °C for 2 h in N_2 atmosphere. The resulting sample was treated in 1.0 M H_2SO_4 aqueous solution for 24 h, followed by washing in distilled water and ethanol, and drying at 80 °C for 24 h. NCNT-Ni were prepared according to the same procedures.

Sputtered Pt layer (~40 nm) on a FTO glass was used as the Pt CE in this study.

Fabrication of DSSC devices. The NCNT-metal materials obtained were ultrasonically dispersed in isopropanol for 30 mins, resulting in NCNT-Co slurry, which was subsequently sprayed onto FTO to form counter electrodes of DSSCs. The photoanodes made of mesoporous TiO_2 films on FTO glass substrate was commercially provided by OPV Tech Co., Ltd (Yingkou, China). Before use they were heated at 500 °C for 0.5h, then the temperature was cooled down to 70 °C. Susequently, the mesoporous TiO_2 films were immersed into a 0.3 mM of N719 dye (Solaronix SA, Switzerland) in acetonitrile/tert-butyl alcohol (1:1 volume ration) for

20 h. The TiO₂ photoanodes were assembled with various CEs to fabricate DSSCs. The dye-sensitized TiO₂ photoanode and the CE were separated by a hotmelt Surlyn film (60 μm thick) and sealed through hot-pressing. The redox electrolyte (0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in anhydrous acetonitrile) was injected into the interspace between the photoanode and CE. Finally, the holes on the back of the CE were sealed with a Surlyn film covered with a thin glass slide under heat. The as-fabricated DSSCs with an active area of 0.25 cm² were used for photovoltaic performance tests. A dummy cell was assembled with two identical counter electrodes in a sandwich fashion containing the same electrolyte as used in the DSSCs devices. The as-assembled symmetrical cell was used for the electrochemical impedance spectroscopy and Tafel polarization measurements.

Characterization.

Scanning electron microscopy (SEM) images were obtained from FEI Quanta 200F microscope operated at an accelerating voltage of 20 kV. Elemental analysis of the electrodes were conducted using an energy dispersive X-ray spectroscopy (EDS) analyzer (QUANTA 200FEG) attached to the FEI Quanta 200F SEM microscope. Transmission electron microscopy (TEM) and high resolution (HR) TEM were carried out with a FEI Tecnai F30 microscope and a G2 microscope operated at an accelerating voltage of 300 kV. X-ray diffraction (XRD) analysis were performed at a scanning rate of 1°/min on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation source ($\lambda = 1.54 \text{ \AA}$) operating at 40 kV and 200 mA. During X-ray photoelectron spectroscopy (XPS) measurement, Mg Kα radiation (1253.6 eV) with a power of 200 W and pass energy of 50.0 eV was used. Scanning electron microscopy (SEM) was conducted on Hitachi S5500 operated at 30 kV.

Cyclic voltammetry (CV) for the I⁻/I₃⁻ system was measured in an anhydrous acetonitrile solution consisting of 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂, and conducted over the potential range from -0.2 V to 0.9 V at a scanning rate of 20 mV s⁻¹, using a electrochemical workstation (CHI760C, Chenhua, Shanghai) in a three-electrode electrochemical system. The CV stability test for the CEs was conducted

over the potential range from -0.2 V to 0.5 V using the same system. The resultant CEs acted as the working electrode, a Pt foil as the counter electrode, and a saturated calomel electrode as the reference electrode. The symmetrical dummy cells assembled with two identical CEs filled with the same electrolyte as used in the DSSCs were used for the electrochemical impedance spectroscopy (EIS) measurements and Tafel polarization tests. EIS experiments were carried out using an electro-chemical workstation (IM6 Zahner, Germany) at 0 V with a frequency range of 10 mHz ~ 400 kHz and a potential modulation of 20 mV under dark conditions. The resultant impedance spectra were analyzed with an appropriate equivalent circuit by means of Z-view software. The Tafel polarization curves were measured at a scanning rate of 10 mV/s. Photovoltaic measurement was recorded with a Newport Oriel class AAA solar simulator (model 92250A-1000) equipped with a class A 300 W xenon light source powered by a Newport power supply (model 69907). The power output of the lamp was calibrated to 1 Sun (AM1.5G, 100 mW cm⁻²) using a certified Si reference cell (SRC-1000-TC-QZ, VLSI standard, S/N 10510-0031). The current-voltage characteristics of each cell were recorded with a Keithley digital source meter (model 2400). Photovoltaic performance was measured using a metal mask displaying a round geography with the diameter of 3 mm.

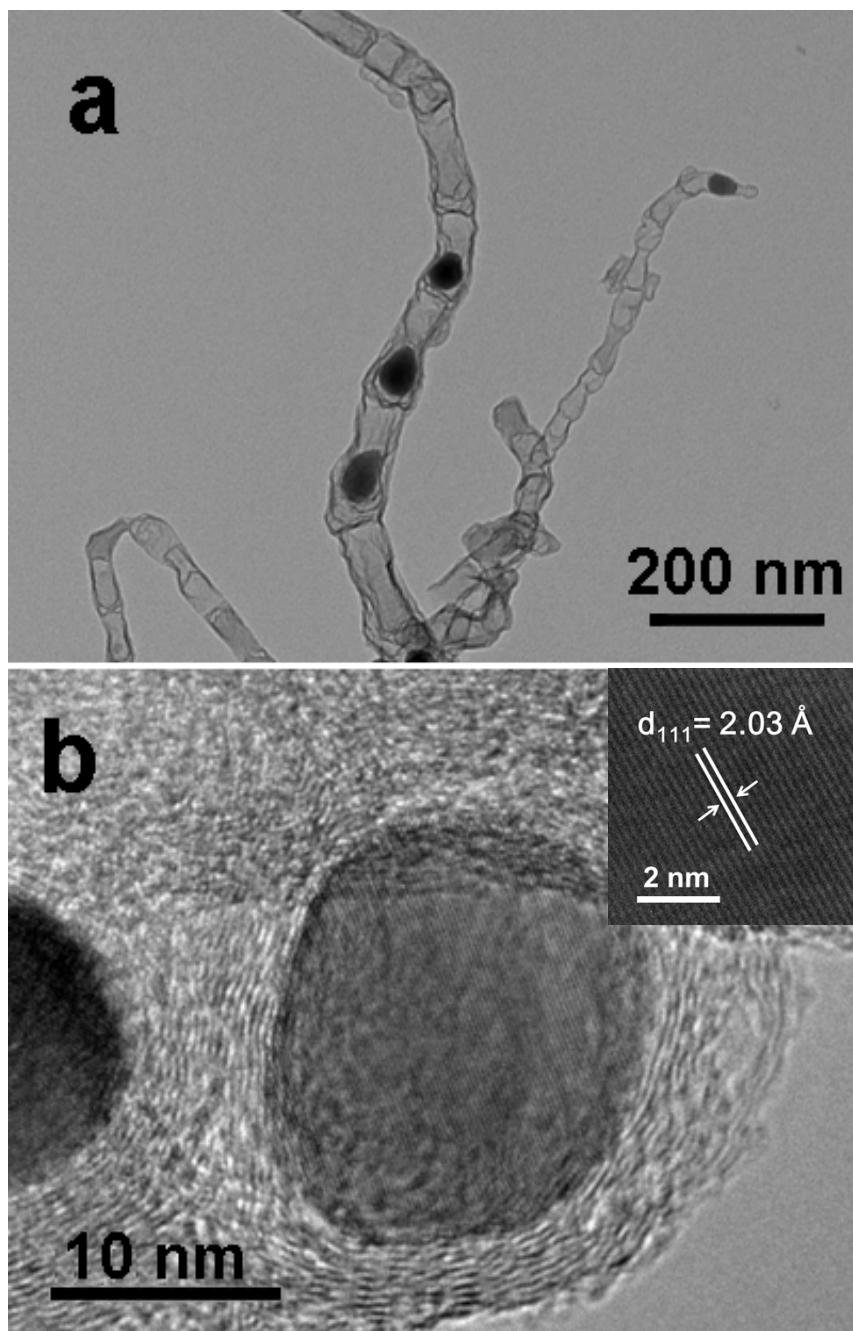


Fig. S1 (a) TEM image and (b) HRTEM for graphic walls and the encapsulated Ni nanoparticles (inset) of the sample NCNT-Ni.

This figure reveals the graphic walls of the CNTs. HRTEM shown as inset clearly discloses the metal nanoparticles encapsulated within tubes show an interplanar lattice spacing (d) of 0.203nm, corresponding to the (111) plane of metal Ni.

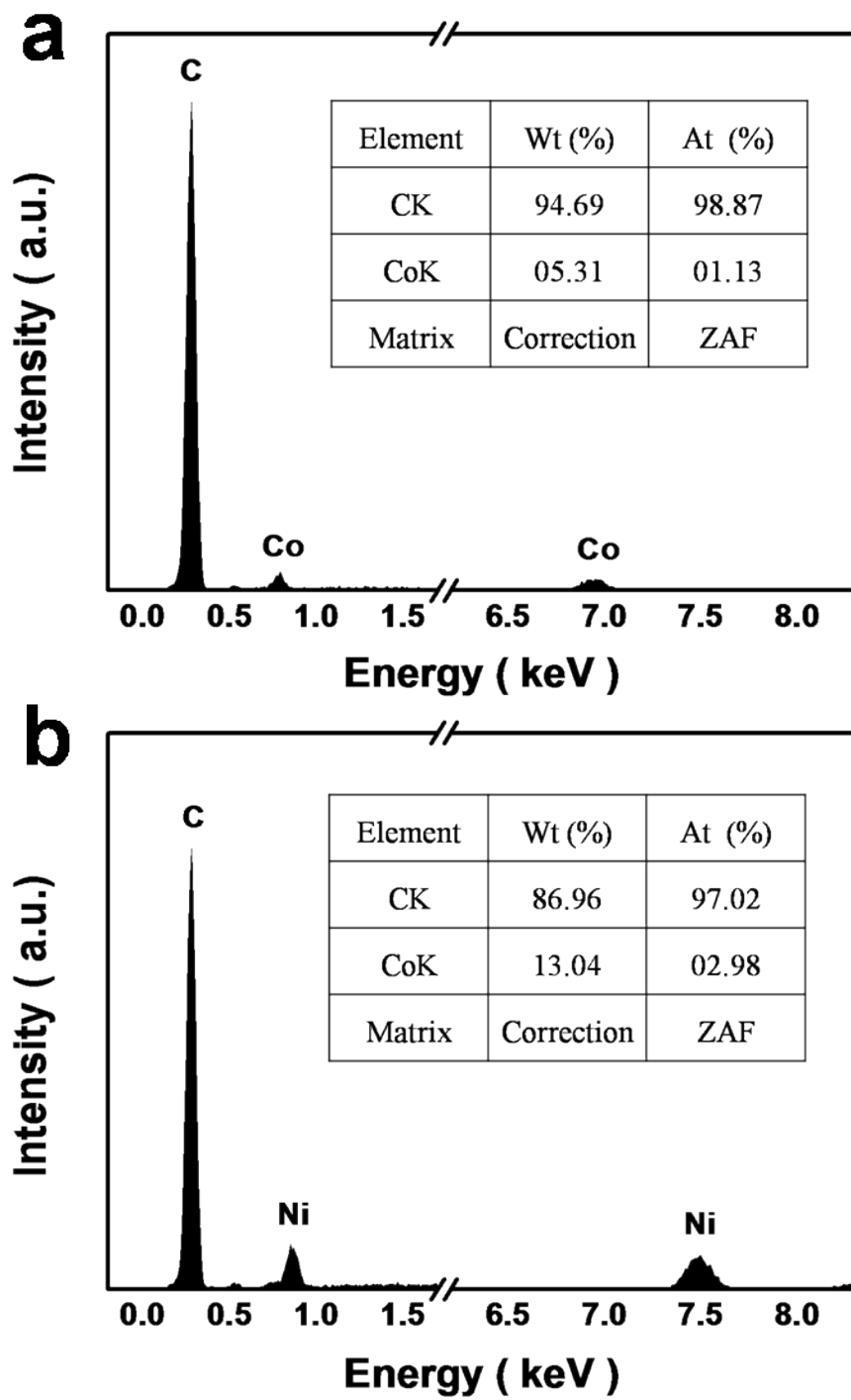


Fig. S2 EDS analysis for (a) NCNT-Co and (b) NCNT-Ni, respectively.

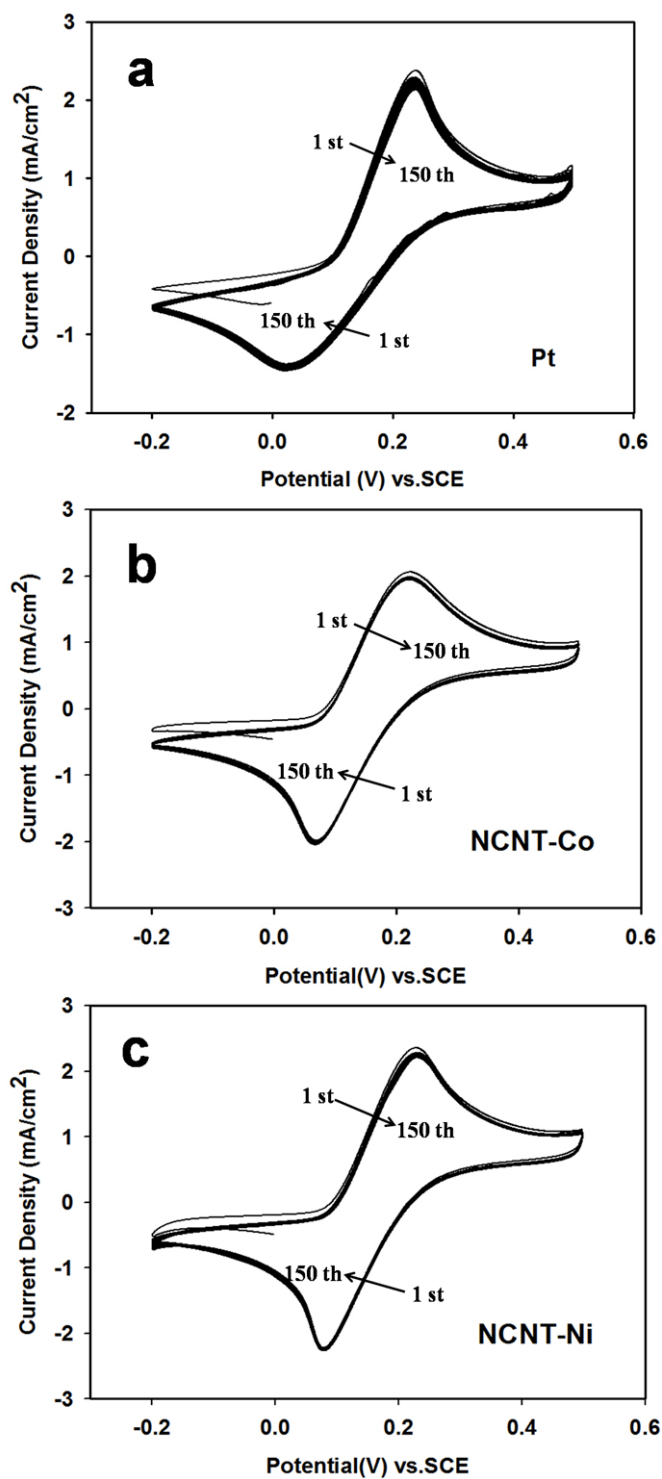


Fig. S3 A total of 150 consecutive cyclic voltammograms for the I^-/I_3^- system at a scanning rate of 20 mV s^{-1} for (a) Pt (b) NCNT-Co and (c) NCNT-Ni, respectively.

These results demonstrate that both NCNT-Co and NCNT-Ni exhibit electrochemical stability as comparable to, and even superior to the standard Pt CE.

Reference

- [1] X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova, T. Asefa, *Angew. Chem. Int. Ed.* 2014, **53**, 4372.