

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Nitrogen-doped Carbon Nanotubes with Metal Nanoparticles as Counter Electrode Materials of Dye-Sensitized Solar Cells

Cite this: DOI: 10.1039/x0xx00000x

Received 00th February 2015,
Accepted 00th February 2015

DOI: 10.1039/x0xx00000x

Yedi Xing, Xiaojia Zheng, Yihui Wu, Mingrun Li, Wen-Hua Zhang,* and Can Li*^a

www.rsc.org/ChemComm

Nitrogen doped carbon nanotubes decorated with metal Co and Ni nanoparticles were assessed as counter electrodes (CEs) of dye-sensitized solar cells (DSSCs). These composites show good electrocatalytic activity toward the counter electrode reduction reaction ($I_3^- \rightarrow I^-$) in DSSCs. The resulting devices using these composites as CEs display photovoltaic performance as good as, or even better than Pt-based devices, indicating their application promise in DSSCs.

DSSCs are among the most promising photovoltaic devices to address the challenge for clean energy due to their cost-effective fabrication and relative high device performance.¹⁻³ The CE of DSSCs plays two key roles in a typical DSSC device: regeneration of I^- from I_3^- in the shuttle reaction via electrocatalytic reduction and collection of the electrons from the external circuit. Thus good CE materials should exhibit high catalytic activity toward the counter electrode reduction reaction and display good conductivity. Currently, noble metal Pt is the most useful CE in DSSCs, while it is limited in very rare resource and high cost. Therefore, it is highly desirable to explore low-cost and abundant materials to replace Pt as the CEs of DSSCs for future large-scale fabrication. To date, a number of new materials have been demonstrated to be useful as efficient CEs of DSSCs, such as metal,⁴ metal oxide,⁵⁻⁷ chalcogenides,⁸⁻¹¹ and carbon-based materials.¹²⁻¹⁹ Carbon materials are especially attractive because of their natural abundance, low-cost fabrication and good electrocatalytic activity. CNTs with chemical modification could endow them with special properties and great application potentials²⁰⁻²². We have recently demonstrated that nitrogen-doped carbon nanotubes (NCNTs) encapsulating FeNi alloy nanoparticles are ideal candidates for CE of DSSCs, showing excellent catalytic activity in the redox reaction of I^-/I_3^- shuttle and superior device efficiency in comparison with the Pt CE, while Fe NPs confined within CNTs did not exhibit sufficient activity in the CE reaction of DSSCs.¹⁸ Moreover, different metals can affect the electronic structure of the carbon nanotube surface in a significantly different way, which would have an important effect to the catalytic activity of the carbon surface.²³ Therefore, it is necessary to investigate the effect of different metals decorated carbon nanotubes on the activity of CE reaction, and the corresponding DSSCs performance, which will provide a rational way to guide the design of the CEs of DSSCs. In this

work, we have prepared nitrogen-doped carbon nanotubes confining Co or Ni nanoparticles within their tubes, which are correspondingly designated as NCNT-Co and NCNT-Ni, respectively, and further assessed their applicability as CEs of DSSCs. Experimental results indicate that both composites display high catalytic activity in the counter electrode reduction reaction (I_3^- to I^-) and good electrochemical stability. Moreover, the DSSC devices yield powder conversion efficiency (PCE or η) of 7.75% for the NCNT-Co system and 8.39% for the NCNT-Ni, which are comparable to or superior to the control device made of Pt CE (with efficiency of 7.67%), demonstrating their application promise in developing low-cost and high efficiency DSSCs.

The NCNT-Co and NCNT-Ni composites were prepared on the basis of reported process with modification²⁴ using dicyandiamide as nitrogen and carbon source along with $NiCl_2$

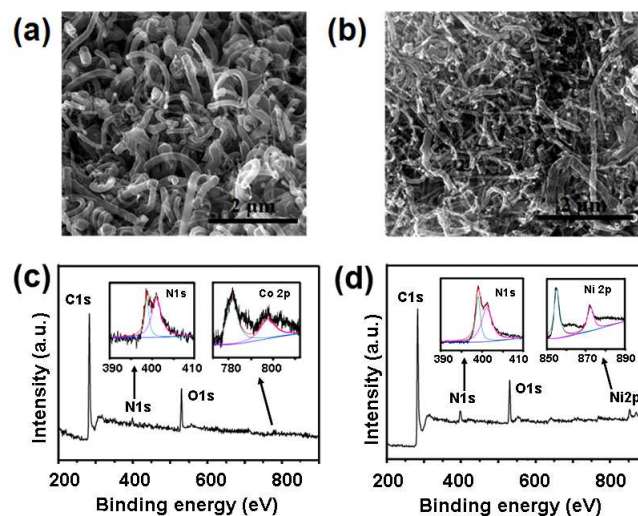


Fig. 1 SEM images for (a) NCNT-Co and (b) NCNT-Ni. The scale bar is 2 μ m. XPS spectra of the NCNT-Co (c) and NCNT-Ni (d). The binding energy in the XPS spectra is calibrated by C1s (285.0 eV) and $CoCl_2$ as catalysts via calcination at 700 $^{\circ}C$ in N_2 atmosphere. The resulting samples were treated in 1.0 M H_2SO_4 aqueous solution to remove the metal residues on the external

surface of the resulting products, yielding the composites for use as CEs of DSSCs. Scanning electron microscopy (SEM) images in Fig. 1a and 1b reveal respectively the ensembles of the NCNT-Co and NCNT-Ni, consisting of a large number of nanotubes. X-ray photoelectron spectroscopy (XPS) was performed to gain information of elements in the composite. As observed in both Fig. 1c and 1d, the XPS spectra show the presence of two types of nitrogen species, which can be attributed to pyridinic (~398.8 eV) and quaternary (~401.0 eV) nitrogen atoms,¹⁹ respectively. The doping of nitrogen into the walls of CNTs can improve their catalytic activity in reduction reaction and to enhance wettability to polar solvent, thus is very favourable to improve the performance as counter electrode of DSSC devices.¹⁸ The signal intensities of metal Co and Ni are very small in the survey plots of XPS, showing the contents of both metal are likely very low. Considering the fact that XPS is a tool sensitive to the surface elements, the very low signal intensity of Co and Ni can also be attributed to the removal of the metal residues on the external surface of nanotubes due to the H₂SO₄ washing process in this study. High-resolution XPS displays the peaks with binding energies of 781.8 eV and 797.7

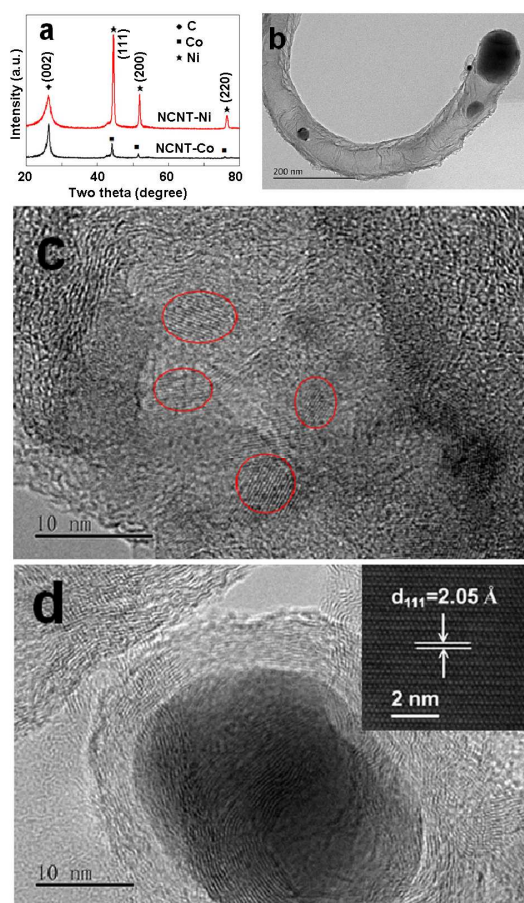


Fig.2 (a) XRD pattern of the NCNT-Co and NCNT-Ni composites. (b) TEM images for the NCNT-Co. (c) HRTEM for small Co nanoparticles on NCNT walls. (d) HRTEM for graphic walls and the encapsulated Co nanoparticles (inset) of the sample NCNT-Co.

eV, respectively assigned to 2p_{3/2} and 2p_{1/2} of Co (inset of Fig.1c), while the peaks at 855.2 eV and 872.5 eV correspond to the 2p_{3/2} and 2p_{1/2} of Ni (Fig.1d).²⁴ These results confirm the metallic nature of Co and Ni in the composites prepared in this

study. EDS analyses further confirm the presence of metal Co and Ni in these nanotube-composites with higher Ni content than Co, as provided in Fig.S2, ESI†.

X-ray diffraction (XRD) pattern of the NCNT-Co sample show diffraction peaks located at 2θ degrees of 26.4, which is attributed to the (002) lattice planes of graphite (JCPDS 41-1487). The peaks at 43.7, 51.0 and 74.7 arise from the diffraction of the (111), (200) and (220) planes of the Co (JCPDS 150806) (Fig.2a), respectively. These results prove that carbon nanotubes with graphitic walls were formed, endowing them with high conductivity. Low-magnification transmission microscopy (Fig.2b) shows that some relative large metal nanoparticles are encapsulated within carbon nanotubes, and high-resolution (HR) TEM in Fig.2c discloses that a number of very small metal nanoparticles distributed randomly on the inner walls of the CNTs. Fig.2d clearly reveals the graphic walls of the CNTs, and the metal nanoparticles encapsulated within tubes show an interplanar lattice spacing (d) of 0.205 nm, corresponding to the (111) plane of metal Co (inset of Fig.2d). Similar scenario occurs for the NCNT-Ni materials (Fig.S1, ESI†). The presence of metal nanoparticles within CNTs could promote electron transfer from metal to the carbon walls, decreasing the surface work function of carbon walls,^{18,25} thereby improving the reduction ability in chemical reaction, such as the counter electrode reduction reaction in DSSCs.

To assess the electrocatalytic activity of the NCNT-Co and NCNT-Ni as counter electrodes to reduce I₃⁻ to I⁻ in the DSSC system, cyclic voltammetry (C-V) was first measured with sputtered Pt electrode as the control sample. Two typical pairs of oxidation/reduction peaks were observed for all of these electrodes. The left pair (A) in the C-V plots is assigned to the oxidation and reduction of I₃⁻, which occurs at the surface of or within the counter electrodes. The right pair (B) is attributed to the oxidation and reduction of I₃⁻/I₂.¹⁸ Thus the left pair of peaks in C-V curves is closely correlated with the catalytic ability of a counter electrode of DSSCs in reduction of I₃⁻ to I⁻, and further study was focused on it. The peak current density can reflect the catalytic activity of a CE, and larger current density means higher catalytic activity. Fig.3a shows obviously that the peak current density of the three counter electrodes is in order of Pt < NCNT-Co < NCNT-Ni, suggesting the catalytic activity of the reduction reaction occurred at counter electrodes is in the same order. Moreover, peak separation between the anodic and cathodic peaks (E_{pp}) is another factor to evaluate the catalytic activity of a material in the CE reaction. E_{pp} is negatively correlated with the standard electrochemical rate constant of a redox reaction. The NCNT-Co electrode displays an E_{pp} value of 131 mV, and the NCNT-Ni shows E_{pp} of 119 mV, both of which are smaller than the Pt electrodes (with E_{pp} of 243 mV). These results suggest that both the NCNT-Co and NCNT-Ni electrodes show excellent catalytic activity in reduction of I₃⁻ to I⁻ in comparison with the widely used Pt electrode, which is critical to achieve DSSC device with competitive efficiency.

Electrochemical impedance analyses (EIS) was then performed to further elucidate the catalytic activity of the present NCNT-metal composites using symmetrical cells consisting of two identical CEs. The high frequency intercept on the real axis reflect the series resistance (R_s) of the device. The three counter electrodes studied here present similar R_s, indicating that they influence the cell performance to similar extents. The left semicircle in the high-frequency range reveals the charge transfer resistance (R_{ct}) at the electrode/electrolyte interface due to the I₃⁻ reduction. Qualitatively, small arc is favourable for the charge transfer between electrode/electrolyte, which is irrespective of high catalytic activity in CE reduction reaction and could lead to lower series resistance and improving

the efficiency of a DSSC device. The right semicircle in the low-frequency range reflects the property of the Nernst diffusion impedance (Z_N), representing the redox couple transport in the electrolyte. A CE with higher activity can reduce I_3^- to I^- faster than that with lower activity, thus the electrolyte should diffuse with a higher speed within a cell with a better CE, thereby showing smaller Z_N . This scenario was indeed happened in our case, as shown in table 1. As Pt CE have show high catalytic activity in the CE reduction reaction, all of the three Z_N in this study do not show significant difference. The Nyquist plots for the three CEs were fitted by the Z-view software with an equivalent circuit diagram (shown in Fig.3b), giving rise to R_{ct} of 1.43, 0.78 and 0.50 Ωcm^2 for the electrodes of Pt, NCNT-Co, and NCNT-Ni, respectively. These results once again reveal the superior electrocatalytic activity of the NCNT-Co and NCNT-Ni in the counter electrode reduction reaction of I_3^- to I^- , making them suitable for use as CEs of DSSCs.

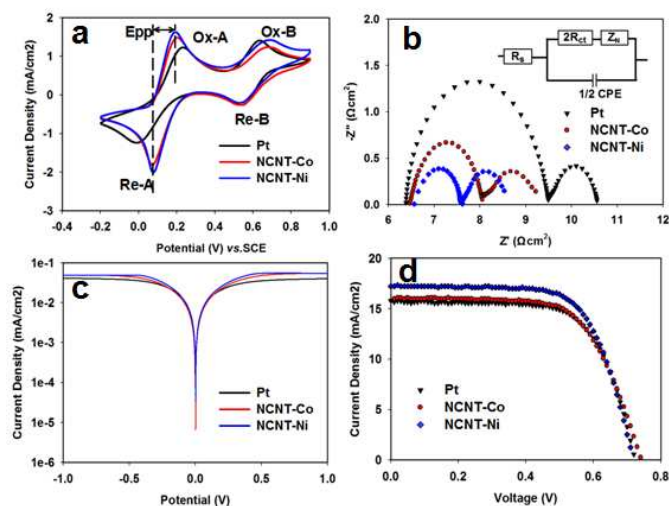


Fig.3 (a) The cyclic voltammograms (C-V) of the NCNT-Co, NCNT-Ni and Pt. (b) The EIS (c) The Tafel polarization curves of symmetrical cells. (d) J-V characteristics of DSSCs with different CEs, measured at AM1.5G illumination (100 mW cm^{-2}).

To further characterize the catalytic activity of the NCNT-metal composites as CEs for DSSCs, Tafel polarization was then carried out using the symmetrical cells. Fig.3c shows the Tafel curves of the devices made of the NCNT-Co, NCNT-Ni and Pt electrodes. On the basis of equation (1), one can gain information on the exchange current density (J_0) in the Tafel zone, and according to equation (2), the limiting diffusion current density (J_{lim}) can be analyzed in the diffusion zone. Both of J_0 and J_{lim} correlate closely with the catalytic activity of the catalysts^{18,26} It can be observed in Fig.3c that both the anodic and cathodic branches of the Tafel curves shows slopes in order of the NCNT-Ni > NCNT-Co > Pt in the Tafel polarization zone, indicative of the same order for J_0 obtained on these electrodes. Moreover, the NCNT-Ni exhibits very similar limiting diffusion current density than the NCNT-Co, which is a little higher than the Pt electrodes. These results suggest that the NCNT-Co and NCNT-Ni can effectively catalyze the reduction reaction of triiodide to iodide around the counter electrodes, showing catalytic ability comparable to or even a little better the standard Pt electrode.

$$J_0 = \frac{RT}{nFR_{ct}} \quad (1)$$

$$D = \frac{l}{2nFC} J_{lim} \quad (2)$$

where R is the gas constant, T is the temperature, F is Faraday's constant, n is the number of electrons involved in the reduction of I_3^- at the electrode, and R_{ct} is the charge transfer, D is the diffusion coefficient of the I_3^- , l is the spacer thickness, and C is the triiodide concentration.

An excellent CE of DSSCs should be highly stable in a working device. So we have further checked the electrochemical stability of the NCNT-Co and NCNT-Ni by measuring sequential CV up to 150 cycles for the three CEs in this study. As shown in Fig.S3 ESI[†], the current densities and the Epp had experienced negligible change subject to C-V measurement for all of the CEs studied, indicative of the superior stability of the NCNT-Co and NCNT-Ni in comparison with Pt CE. This is understandable considering the fact that the metal NPs were confined within the nanotubes and surrounded by multilayers of CNTs (shown by HRTEM in Fig.2d and Fig.S1b, ESI[†]), thus preventing them from directly contact with corrosive electrolyte.

Finally, the DSSC devices were fabricated using the NCNT-Co and NCNT-Ni as CEs of DSSCs along with the sputter Pt electrodes as a control (detail please see ESI[†]). Fig.3d comparatively presents the photocurrent density-voltage (J-V) curves of the devices studied here, and the corresponding photovoltaic parameters are summarized in Table 1. The control

Table 1. Photovoltaic performance of the DSSCs and electrochemical parameters for the symmetrical cells made of the NCN-Co, NCNT-Ni and Pt electrodes.

Sample	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	Z_N (Ωcm^2)	Epp (mV)
Pt	15.74	0.72	0.68	7.67	6.38	1.43	1.12	243
NCNT-Co	16.03	0.74	0.65	7.75	6.46	0.78	1.09	131
NCNT-Ni	17.22	0.71	0.69	8.39	6.58	0.50	0.97	119

Pt-based device displays power conversion efficiency (PCE, η) of 7.67% (with J_{sc} of 15.74 mA/cm^2 , V_{oc} of 0.72 V and fill factor (FF) of 0.68). In contrast, the NCNT-Co formed cell shows a PCE of 7.75%, very similar to the Pt-based cell. It is very interesting to find that the DSSC device made of the NCNT-Ni CE exhibits an impressive PCE of 8.39%, which is superior to the Pt device. The high performance of the present NCNT-metal (metal = Co and Ni) composites can be attributed to several factors: (a) the graphitic nature of the carbon nanotube walls ensures its high conductivity; (b) the doping of nitrogen into the walls of carbon nanotubes can enhance its catalytic activity toward reduction reaction and wettability to polar solvent; and (c) the encapsulation of metal nanoparticles inside carbon nanotubes endow them with improved reduction ability in the counter electrode reaction. Therefore, the NCNT-metal composites obtained here present great promise as high-efficient CE materials for DSSC to achieve good device performance.

In summary, we have demonstrated that, as counter electrodes of DSSCs, the nitrogen-doped carbon nanotubes confining metal Co and Ni nanoparticles exhibit excellent activity in the reduction reaction of I/I_3^- couple. The corresponding photovoltaic devices made from the NCNT-Co and NCNT-Ni displayed efficiencies of 7.75% and 8.39%, respectively, which are comparable to or superior to the control sputtered Pt-based

device with PCE of 7.67%. These results may provide a new route to design high-efficient counter electrodes of DSSCs with environmental friendliness and cost-effective fabrication, an important step to achieve large-scale adoption of DSSCs.

We acknowledge the “Hundred Talents Program” of the Chinese Academy of Sciences, the National Science Foundation of China (Grant No. NSFC 20873141) for the financial support.

Notes and references

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian 116023, China
E-mail: whzhang@dicp.ac.cn, canli@dicp.ac.cn

† Electronic Supplementary Information (ESI) available: Experimental details, See DOI: 10.1039/b000000x/

- 1 B. Oregan, M. Grätzel, *Nature*, 1991, 353, 737.
- 2 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.*, 2010, 110, 6595.
- 3 J. H. Yum, E. Baranoff, F. Kessler, T. Moehl, S. Ahmad, T. Bessho, A. Marchioro, E. Ghadiri, J. E. Moser, C. Y. Yi, Md. K. Nazeeruddin, M. Grätzel, *Nature Communications*, 2012, 3, 631.
- 4 J. Wan, G. Fang, H. Yin, X. Liu, D. Liu, M. Zhao, W. Ke, H. Tao, Z. Tang, *Adv. Mater.* 2014, 26, 8101.
- 5 Y. Hou, D. Wang, X. H. Yang, W. Q. Fang, B. Zhang, H. F. Wang, G. Z. Lu, P. Hu, H. J. Zhao, H. G. Yang, *Nat. Commun.* 2013, 4, 1583;
- 6 M. Wu, X. Lin, Y. Wang, L. Wang, W. Guo, D. Qi, X. Peng, A. Hagfeldt, M. Grätzel, T. Ma, *J. Am. Chem. Soc.* 2012, 134, 3419.
- 7 F. Gong, H. Wang, X. Xu, G. Zhou, Z.-S. Wang, *J. Am. Chem. Soc.*, 2012, 134, 10953.
- 8 Y. Duan, Q. Tang, J. Liu, B. He, L. Yu, *Angew. Chem. Int. Ed.*, 2014, 53, 14569.
- 9 X. Zheng, J. Guo, Y. Shi, F. Xiong, W.-H. Zhang, T. Ma, C. Li, *Chem. Commun.*, 2013, 49, 9645.
- 10 X. Xin, M. He, W. Han, J. Jung, Z. Lin, *Angew. Chem. Int. Ed.* 2011, 50, 11739.
- 11 D. W. Zhang, X. D. Li, H. B. Li, S. Chen, Z. Sun, X. J. Yin, S. M. Huang, *Carbon*, 2011, 49, 5382.
- 12 M. Wu, X. Lin, T. Wang, J. Qiu, T. Ma, *Energy Environ. Sci.*, 2011, 4, 2308.
- 13 Z. Yang, M. Liu, C. Zhang, W. W. Tjiu, T. Liu, H. Peng, *Angew. Chem. Int. Ed.* 2013, 52, 3996.
- 14 Y. Xue, J. Liu, H. Chen, R. Wang, D. Li, J. Qu, L. Dai, *Angew. Chem. Int. Ed.* 2012, 51, 12124.
- 15 L. Kavan, J.-H. Yum, M. K. Nazeeruddin, M. Grätzel, *Acs Nano* 2011, 5, 9171.
- 16 F. Malara, M. Manca, M. Lanza, C. Huebner, E. Piperopoulos, G. Gigli, *Energy Environ. Sci.* 2012, 5, 8377.
- 17 E. Bi, H. Chen, X. Yang, W. Peng, M. Grätzel, L. Han, *Energy Environ. Sci.* 2015, 7, 2637.
- 18 X. Zheng, J. Deng, N. Wang, D. Deng, W.-H. Zhang, X. Bao, C. Li, *Angew. Chem. Int. Ed.*, 2014, 53, 7023.
- 19 S. Hou, X. Cai, H. Wu, X. Yu, M. Peng, K. Yan, D. Zou, *Energy Environ. Sci.* 2013, 6, 3356.
- 20 K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* 2009, 323, 760.
- 21 N. Karousis, N. Tagmatarchis, *Chem. Rev.* 2010, 110, 5366.
- 22 K. Balasubramanian, M. Burghard, *Small*. 2005, 1, 180.
- 23 J. Deng, P. Ren, D. Deng, L. Yu, F. Yang, X. Bao, *Energy Environ. Sci.*, 2014, 7, 1919.
- 24 X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova, T. Asefa, *Angew. Chem. Int. Ed.*, 2014, 53, 4372.
- 25 D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun, X. Bao, *Angew. Chem. Int. Ed.*, 2013, 52, 371.
- 26 M. Wu, X. Lin, A. Hagfeldt, T. Ma, *Chem. Commun.* 2011, 47, 4535.

Table of contents

Nitrogen-doped carbon nanotubes confining Co and Ni nanoparticles are employed as counter electrodes (CEs) of dye-sensitized solar cells, showing photovoltaic performance compared to or superior to the devices with sputtered platinum as CE.

