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Facile and quick preparation of carbon nanohorn-based counter electrodes for efficient dye-sensitized solar cells†

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For the first time, Pt-free counter electrodes based on carbon nanohorns for highly efficient dye-sensitized solar cells were assembled by a facile and fast drop cast technique. These novel electrodes feature an effective catalytic behavior towards the reduction of I_3^- and, as such, afford even higher short-circuit current densities compared to Pt-based references. In a final device, solar cells with 7.7% efficiency were achieved.

The sun provides an enormous potential of energy, which implies that solar harvesting processes play a leading role in covering the world's current energy demand.¹ Efficient light harvesting accompanied by low-cost production still remains a major challenge. As such, research in the field of solar cells results in a vast variety of different solar energy conversion concepts. Among them, dye-sensitized solar cells (DSSC)² stand out due to their low-cost production and moderate power conversion efficiencies (PCE) of up to 13%.³

The usage of rare metals including platinum (Pt) in counter electrodes (CE) raises the overall production costs, and, as such, constitutes a major bottleneck in terms of its introduction into the market.^{4–6} There have been several attempts to substitute Pt, while still maintaining a good performance. Firstly, transition metal complexes (TMC) are widely used due to activities similar to that of Pt.⁷ For example, highly ordered TiN nanotube arrays on metallic Ti foil substrates resulted in an efficiency of 7.7%.⁸ In another approach, when $WO_{2.72}$ was the CE material for DSSCs, PCEs around 8.0% were achieved.⁹ TMCs are synthesized by a simple and facile one-pot method. However, the lack of control over the morphology and side-product formation has limited their applications so far.⁷ Secondly, conductive polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-propylenedioxythiophene) (PProDOT),

polypyrrole (PPy), and polyaniline (PANI), exhibit good catalytic activities towards the reduction of I_3^- , which render them a promising alternative to Pt-based CEs.¹⁰

By virtue of good conductivity and low-temperature processability PANI is the best candidate among the conductive polymers. For example, oriented PANI nanowire arrays have been successfully grown *in situ* on a glass substrate. For the latter, low charge transfer resistances (R_{CT}) of around 1 Ω , and, in turn, a good catalytic activity towards the reduction of I_3^- was noted.¹¹ The simple and straightforward preparation of PANI-based CEs is, however, hindered by its poor solubility in most organic solvents. In general, complex fabrication and stability issues are still major limitations for CEs based on conductive polymers.^{7,10}

Finally, nanocarbon-based CEs stand out due to their low production costs, high specific surface area, high conductivity, and good catalytic activity towards the reduction of I_3^- (low R_{CT}). There are several reports on the replacement of Pt by graphene derivatives, which feature high room-temperature carrier mobility ($\approx 20\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), high optical transparency, large surface area ($\approx 2600\text{ m}^2\text{ g}^{-1}$), and a high chemical stability.¹² Defect-free graphene is, however, hardly suitable for CEs in DSSCs, since they still suffer from poor thermal stability and large R_{CT} values.¹³ The latter relates to the reduction of I_3^- , which is promoted by defects and oxygen-containing functional groups at the edges of the graphene sheets.^{12,14} To overcome such setbacks, it should be considered that graphene is dopable to provide desirable electronic structures and higher catalytic activity. For example, Kim *et al.* synthesized N-doped graphene nanoplatelets (NGnP) in a two-step process, which were deposited onto fluorine-doped tin oxide (FTO) substrates by using an electrostatic spray technique. After a 9 min deposition, DSSCs with NGnP-based CEs featured PCEs of 9.05%.¹⁵ In contrast to N-doped graphene-based CEs, Baek *et al.*

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synthesized edge-fluorinated graphene nanoplatelets, which were also deposited by an electrostatic spray technique. The resulting graphene-based CE yielded PCEs of 10.01% in the final device, which is, to the best of our knowledge, the highest efficiency for graphene-based CEs.¹⁶ Similar PCEs of 10.04% for Pt-free CEs were achieved by the direct growth of carbon nanotubes (CNTs) onto FTO substrates using chemical vapor deposition (CVD).¹⁷ The fast electron transfer kinetics and the large surface area of multi-wall CNTs render them as a promising material for Pt-free CEs.¹⁸ Due to the aforementioned advantages of nanocarbons, they are considered as the most promising material for Pt-free CEs.

The major bottlenecks in large-scale application of nanocarbons are their bundling affinity in solution and their poor solubility. Furthermore, time-consuming or complicated techniques such as electrostatic spray or CVD are often necessary for high-performance nanocarbon CEs.^{15–17} To circumvent the aforementioned obstacles, different approaches, such as screen printing, doctor blading, or spin coating techniques have been successfully applied leading to PCEs of 3.34, 8.57, and 9.06%, respectively.^{13,19,20} Nevertheless, all the aforementioned techniques comprise an annealing process under inert gas conditions, which might hamper their introduction into industrial production processes.

Herein, we report for the first time the exclusive use of carbon nanohorns (CNHs) as a replacement for Pt as a CE material by a facile and fast drop cast technique. Furthermore, our approach does not comprise any post-treatment such as annealing, which, for example, is also a crucial step for Pt-based CEs. By avoiding time- and money-consuming assembly processes, CNH-based CEs could facilitate the introduction of DSSCs into the market.

CNHs are conical structures with diameters between 2 and 5 nm and a length from 30 to 50 nm, while the angle of the conical tip is calculated to be around 20° (Fig. 1).^{21,22} In solution, they tend to associate and form round-shaped and loosely bound aggregates of around 100 nm. Due to their large surface area and porosity they are readily dispersible in organic solvents in high concentrations. Recently, the interest

in CNHs has been intensified given their metal-free synthesis *via* CO₂ laser ablation, semiconducting character, and relatively easy suspendability in organic solvents. As a consequence, CNHs were successfully implemented as dopants for TiO₂-based photoanodes²³ and used as buffer layers between the FTO and TiO₂.²⁴ Additionally, CNHs were already effectively tested as catalytic supportive material inside a quasi-solid state redox electrolyte. As a consequence of the higher ionic conductivity inside the electrolyte and quasi-zero distance between the CE and the electrolyte, the device performance was greatly improved from 1.3 to 7.8%.²⁵ Recently, PEDOT:PSS/CNH hybrids were used for Pt-free CEs featuring efficiencies of up to 4.7%, which are well below the efficiencies of Pt-based CEs of 5.5%.²⁶ When Pt is, for example, present in CNH/Pt hybrid CEs, the corresponding PCEs are 3.08%, which is similar to 3.09% seen for the Pt reference. This study suggests that CNHs fail to impact the device performance when used as CE materials.²⁷ However, we report herein that CNHs can effectively substitute Pt as a catalytic material featuring similar efficiencies as the Pt-based CE reference based on their good catalytic behavior.

CNHs were characterized by means of various methods. Fig. S1† shows the transmission electron microscopy (TEM) images of dahlia-shaped CNH-bundles. Thermogravimetric analysis (TGA) was applied to investigate their stability upon heating. From Fig. S2† we conclude the lack of significant mass losses up to temperatures of 800 °C, suggesting no decomposition of CNHs upon heating.

Next, Raman experiments revealed that the G-mode, which relates to the E_{2g} mode at the Γ -point, is at 1584 cm⁻¹ (Fig. S3†). The G-band arises from the stretching of C–C bonds in graphitic materials and is commonly found in all sp²-carbon systems. Localized vibrational modes, due to impurities, may interact with the extended phonon modes of CNHs resulting in a splitting of the G band. The absence of the D'-peak, which normally is seen around 1620 cm⁻¹, corroborates the pristine nature of the CNHs as already seen in the TGA experiments. Furthermore, like other sp²-carbon systems, CNHs feature a 2D-band around 2655 cm⁻¹. This is a second-order two-phonon process and exhibits a strong frequency dependence on the excitation laser energy. More interesting is, however, the high intensity of the D-band at 1333 cm⁻¹. It is of A_{1g} symmetry and is induced by defects or edges.²⁸ As already shown in previous investigations, CNHs exhibit a high D/G ratio due to defects.^{25,29}

We started elucidating the optimum thickness and roughness of the CNH layers to implement CNH-based CEs into DSSCs. In general, the higher the roughness of the nanocarbon CE layer is, the more catalytically active sites are present.^{30,31} Therefore, it is important to determine the optimum threshold between the CNH layer thickness and roughness prior to device assembly. To control the layer thicknesses, 13.32, 26.64, 53.28, and 106.65 μ L of a CNH dispersion (3.6 μ g μ L⁻¹ in *o*DCB) were drop cast onto FTO substrates. The devices are referred to as **1**, **2**, **3**, and **4**. The thicknesses gradually increased from 1.52, to 3.38, to 6.26, and to 8.91 μ m for **1**,

Fig. 1 Schematic representation of a single CNH (top) and a dahlia shaped aggregate (bottom).

Fig. 2 SEM images of drop cast CNHs onto a FTO glass slide. The thickness of the CNH layer is around 6 μm .

Fig. 3 Left: Tafel polarization curves of symmetric cells with CEs 1 (black), 2 (red), 3 (green), 4 (blue), and Pt (cyan). Right: corresponding Nyquist plots measured at 0 V (dots) and corresponding fittings (lines).

2, 3, and 4, respectively (Fig. S4†). A similar trend is noted for the roughness factor and, as a consequence, more catalytically active sites should be expected.³¹

Fig. 2 depicts SEM images of drop cast CNHs, onto FTO glass. The FTO surface is homogeneously covered by CNH leaving no bare FTO sites free. A good coverage of the FTO surface is crucial, since electrons are likely to recombine with the electrolyte at the bare FTO|electrolyte interface.^{32,33} At low magnifications, cracks in the CNH layers are observed, which are particularly evident for the thicker CNH layers with nm-sized gaps (Fig. S5†). As such, an increased roughness is concluded for thicker CNH-based CEs.

To evaluate their catalytic activity and the charge transfer resistances symmetric devices FTO|CNH|electrolyte|CNH|FTO were assembled. The interfacial charge-transfer properties of the I_3^-/I^- redox couple on the CNH surface were probed by Tafel polarization measurements and electrochemical impedance spectroscopy (EIS). Fig. 3 shows the semilogarithmic Tafel plots regarding the current density (J) as a function of the voltage (V) for symmetric devices 1, 2, 3, and 4. In theory, the Tafel curves are divided into three zones *via* the value of overpotential.³⁴ Firstly, the polarization zone at low overpotentials ($|U| < 120$ mV), secondly, the Tafel zone with a sharp slope at middle overpotentials, and, thirdly, the diffusion zone at high overpotentials. From the Tafel and diffusion zones, the

Table 1 Figures-of-merit for CNH-based CEs deduced from Tafel plots and EIS

CE	J_{lim} [mA cm ⁻²]	J_0 [mA cm ⁻²]	R_{CT} [Ω]	R_{diff} [Ω]	D_{diff} [$\times 10^{-10}$ m ² s ⁻¹]
1	67.00	27.29	2.43	132.53	1.10
2	69.00	32.06	2.77	65.19	2.23
3	79.76	41.64	3.05	32.30	4.50
4	91.63	42.85	3.19	16.00	9.09
Pt	64.60	35.12	5.00	1.68	86.57

exchange current density (J_0) and the limiting diffusion current density (J_{lim}), are deduced. Both parameters relate to the catalytic activity of CNHs.^{30,31} Table 1 summarizes the figures-of-merit deduced from the Tafel experiments. CEs 2 exhibit a J_{lim} similar to that of 1. But, a steep slope indicates a higher catalytic activity due to more catalytically active sites (Fig. 3). For thicker layers, both J_{lim} and J_0 rise as a reflection of enhanced catalytic activities. While J_{lim} rises continuously, J_0 plateaus for the thicker layers yielding similar catalytic activities for CEs 3 and 4.

Next, the symmetric cells with the configuration FTO|CNH|electrolyte|CNH|FTO were investigated by EIS as a means to shed light into the charge transfer resistance across the different interfaces.³⁵ Fig. 3 depicts the Nyquist plots fit to the corresponding equivalent electrical circuit model (Fig. S6†). Two semicircles are discernable – each at clearly distinct frequencies. On the one hand, the semicircle at frequencies between 1000 and 100 000 Hz relates to the charge transfer resistance (R_{CT}) and the corresponding Helmholtz capacitance (C_{CT}) at the FTO|CNH|electrolyte interface. On the other hand, the 0.1–100 Hz semicircle correlates with the resistance of the Warburg diffusion of I_3^- in the bulk electrolyte (R_{diff}). With this data in hand, the effective diffusion coefficient (D_{diff}) in the bulk of the electrolyte is calculated by eqn (1):³⁵

$$D_{\text{diff}} = (k_{\text{B}} \times T) / (m^2 \times q^2 \times N \times [\text{I}_3^-] \times R_{\text{diff}} \times \delta) \quad (1)$$

Here, k_{B} is the Boltzmann constant, T the absolute temperature, m the number of transferred electrons in the reaction, q the elementary charge, and N the Avogadro constant.

From the EIS analysis of the symmetric cells, we deduce an increasing amount of catalytically active sites derived from R_{diff} values, whereas the R_{CT} values are too low for a meaningful interpretation. Fig. S7† reveals that the R_{CT} values are more or less in the same range of around 3 Ω . In stark contrast, the Warburg diffusion resistance is affected by the CNH layer thickness. In particular, R_{diff} gradually reduces from 132.53 to 65.19, to 32.30, and to 16.00 Ω for devices 1, 2, 3, and 4, respectively. This trend relates to increasing J_0 s deduced from the Tafel plots owing to the fact that the catalytic activity is increased (Table 1 and Fig. 2). As a consequence, D_{diff} – as deduced from eqn (1) – increases gradually for devices 1, 2, 3, and 4 from 1.10×10^{-10} to 2.23×10^{-10} , to 4.50×10^{-10} , and to 9.09×10^{-10} m² s⁻¹, respectively. At this point we conclude that more catalytically active sites are available for the reduction of

Fig. 4 Left: J - V curves of DSSCs with CNH-based CEs 1 (black), 2 (red), 3 (green), 4 (blue), and Pt-based CEs (cyan) under 1 sun and AM 1.5 G conditions. Right: corresponding Nyquist plots measured under V_{OC} conditions (dots) and corresponding fittings (lines).

Table 2 DSSC performance and EIS parameters obtained under AM1.5 G conditions and 1 sun illumination. EIS was performed under V_{OC} conditions

CE	J_{SC} [mA cm ⁻²]	V_{OC} [V]	FF	η [%]	R_{CT} [Ω]	R_{diff} [Ω]	D_{diff} [× 10 ⁻¹⁰ m ² s ⁻¹]
1	14.15	0.79	0.47	5.21	0.55	181.59	0.80
2	15.09	0.77	0.56	6.43	0.74	36.10	4.03
3	16.14	0.79	0.61	7.70	1.07	17.62	8.26
4	14.43	0.74	0.61	6.55	1.21	23.50	6.19
Pt	15.58	0.79	0.65	7.92	7.31	8.43	17.26

I_3^- when the CNH layer thickness and roughness is increased. Note that upon increasing the CNH layer thickness the total distance of the electrolyte ($\delta = 18 \mu\text{m}$) is not reduced due to the design of the device. R_{diff} of symmetric Pt devices is well below that of CNH-based devices. We relate the difference to less effective I_3^- diffusion – *vide infra*. In terms of R_{CT} and J_0 , Pt-based devices give rise to higher and lower values, respectively, indicating higher catalytic activity of CNHs towards I_3^- when compared to Pt.

To validate our findings, we assembled TiO_2 -based DSSCs with *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetra-butylammonium) (N719) using the abovementioned CNH-based CEs. Fig. 4 depicts current density-voltage (J - V) dependencies and Table 2 lists the figures-of-merit deduced from the J - V and EIS measurements.

DSSCs with CE 1 exhibit low fill factors (FF) and moderate short-circuit current densities (J_{SC}). Upon increasing the CNH layer thickness, FFs gradually increase – a finding that is rationalized by more catalytically active sites and increasing D_{diff} (*vide supra*). In detail, FFs enhance from 0.47, to 0.56, to 0.61, and culminate at 0.61 for CE 1, 2, 3, and 4, respectively. Low FFs mainly arise from a high series resistance based on the incomplete regeneration of the redox couple.³⁶ DSSCs with CEs 3 and 4 exhibit similar FFs, which suggest that further increasing of D_{diff} – as deduced from the symmetric cells – does not result in better electrolyte regeneration.

The open-circuit potentials (V_{OC}) exhibit no clear trend, since high series resistance as in the case of the thin CEs hinders meaningful interpretations. Nonetheless, J_{SC} values rise

from 14.15 (CE 1), to 15.09 (CE 2), and to 16.14 (CE 3), before decreasing to 15.58 (CE 4) mA cm⁻² upon increasing the layer thickness. As a result, the efficiencies (η) of 5.20, 6.43, 7.70, and 6.55% for CEs 1, 2, 3, and 4, respectively, were achieved as a reflection of the trends seen for FF and J_{SC} . Please note that DSSCs with CE 3 exhibit comparable figures-of-merit as DSSCs with Pt-based CEs ($\eta = 7.92\%$).

To gather additional insights into the processes occurring during device operation, EIS assays of DSSCs with CEs 1, 2, 3, and 4 were performed at open-circuit and 1 sun AM 1.5 G conditions.^{35,37} Fig. 4 depicts the corresponding Nyquist plots and Table 2 summarizes the results from the fitting of the equivalent circuit (Fig. S6†). As already seen in the symmetric devices, R_{CT} values of around 1 Ω are well below those seen for Pt-based CEs of 7.31 Ω. This suggests that CNHs are more active in the catalytic reduction of I_3^- , which is in sound agreement with previous work on nanocarbon-based CEs.^{38–40} As already discussed for the symmetric devices, the low resistance hinders a good fit according to the equivalent circuit (Fig. S7†). As a consequence, R_{CT} values are disregarded from any further interpretations. However, R_{diff} s for CNH-based CEs, which are in the range of around 20–30 Ω, exceed those of Pt-based CEs with values of around 8 Ω. Most likely, migration of I_3^- ions inside the porous CNH network is hindered and, as a consequence, D_{diff} decreases relative to Pt-based CEs. In Pt-based CEs the diffusion of I_3^- ions is, however, unhindered due to only nanometer-sized Pt-layers. Interestingly, the lowest R_{diff} s for CNH-based CEs of 17.62 Ω were found in CE 3. Although CEs 4 have larger surface area and higher roughness (*vide supra*), they feature a higher R_{diff} of 23.50 Ω and, as a consequence, a lower D_{diff} of 17.26×10^{-10} m² s⁻¹ than DSSCs with CEs 3. A likely rationale implies that in the thick nanocarbon network of CE 4 a larger fraction of I_3^- ions than in CEs 3 is trapped. This hinders them to take part in the overall regeneration inside the electrolyte. Seemingly, the threshold for thickness/roughness is around 6 μm, that is, in CEs 3. Please note that DSSCs with CEs 3 and 4 feature the same FFs and, in turn, similar electrolyte regeneration activities. Also, similar exchange current densities of 41.64 mA cm⁻² for CEs 3 and 42.85 mA cm⁻² for 4 were derived from the Tafel plots.

Preliminary time-dependent assays on the device performance revealed a rather similar behavior, when comparing CNH- and Pt-based CEs (Fig. S8†). In detail, the rise over time in both, J_{SC} and V_{OC} values, is similar for both CEs. The efficiency stabilizes for both CEs after six days. The fact that CNH-based CEs only exhibit 90% of the initial efficiency is due to a gradual decrease in the FFs. This can be rationalized with a gradual increase in R_{Diff} for CNH-based CEs, whereas Pt-based CEs show an initial 1.5-fold increase in R_{Diff} but plateau after six days. In the case of the former the 2.5-fold increase after six days could be explained with more I_3^- ions being trapped inside the nanocarbon network over time. This could be circumvented with alternative CE-assemblies, such as the implementation of binders to improve the adhesion and change the morphology of those CEs.

In summary, we have developed for the first time CNH-based CE by a facile and fast drop cast technique. In our approach we avoid the necessity of a sintering process, which, on one hand, simplifies the assembly process and, on the other hand, facilitates the introduction of DSSCs into the market. CNH-based CE feature considerably lower R_{CT} than Pt-based CE. Nevertheless, CNH-based CE require a relatively large thickness and roughness to compete with Pt-based CE. In this context, increasing the layer thickness leads unambiguously to more catalytically active sites. This is, however, compromised at a certain thickness – a finding that is explained by the trapping of I_3^- inside the nanocarbon network. As a final result, DSSCs with optimized CNH-based CE and with Pt-based CE feature comparable figures-of-merit. Ongoing work focuses on transient absorption spectroscopy to reveal the individual steps in the regeneration processes under device operation conditions and the use of different binders, which should increase the overall long-term stability of CNH-based CE.

Experimental section

Carbon nanohorns were purchased from Carbonium srl (Padova, Italy) and used without further purification. FTO substrates were sonicated for 15 min with a detergent solution, washed with deionized water, and again sonicated in isopropyl alcohol for 15 min. FTOs were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. Treated substrates were sintered at 450 °C for 30 min. The transparent nanocrystalline TiO_2 layer (Ti-Nan-oxide T/SP, Solaronix) was prepared on FTO glass plates for DSSCs by using a doctor blade technique and pre-dried at 125 °C for 6 min. The TiO_2 anodes were gradually heated under air flow to 325 °C and held for 5 min, further heated to 375 °C and held for 5 min, heated to 450 °C and held for 30 min, and finally sintered at 500 °C for 15 min. The final TiO_2 layers had an average thickness of 7 μm . The sintered films were immersed overnight into a 0.5 mM solution of *cis*-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N719) in ACN/*tert*-butyl alcohol (50 : 50 vol%). For the counter electrodes two holes (0.1 mm) were drilled into FTOs *via* sandblasting prior to the cleaning procedure (*vide supra*). For Pt-based CE, FTOs were coated with a thin film of chloroplatinic solution (4.88 mM, 26 μL) in isopropyl alcohol. Then, the slides were annealed to 390 °C for 15 min. CNH-based CE were prepared by drop casting a CNH dispersion at 90 °C onto a FTO, whereas the covered area was predefined by a hole ($A = 28.27 \text{ mm}^2$) cut into Scotch Tape. CNH-based CE were placed in a vacuum chamber to ensure complete drying from *o*DCB. The photoanodes and the counter-electrodes were assembled into a sealed sandwich-type cell by heating at 150 °C with a controlled pressure using a hot-melt sealing film. Afterwards, the electrolyte was filled into the cell *via* capillary forces. The electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium

iodide, 0.05 M I_2 , 0.1 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in a mixture of acetonitrile/valeronitrile (85 : 15, v/v). For every experiment four cells were assembled to prove good reproducibility.

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