REVIEW

View Article Online
View Journal | View Issue

Recent advances in multifunctional nanocarbons used in dye-sensitized solar cells†

Rubén D. Costa, Fabian Lodermeier, Rubén Casillas and Dirk M. Guldi*

Cite this: *Energy Environ. Sci.*, 2014, 7, 1281

Received 17th October 2013
Accepted 20th January 2014

DOI: 10.1039/c3ee43458c

www.rsc.org/ees

Throughout recent years the implementation of nanocarbons into dye-sensitized solar cells (DSSC) has resulted in important breakthroughs. The most relevant of them in this context are (i) the enhancement of charge transport and charge collection in nanocarbon-doped electrodes, (ii) the introduction of nanocarbon interlayers that simultaneously reduce the charge recombination and increase the charge collection efficiency, (iii) the use of nanocarbon-based, iodine-free, solid-state electrolytes featuring excellent diffusion coefficients and catalytic efficiencies, (iv) the use of novel nanocarbon-based hybrid dyes, and (v) the use of nanocarbons towards platinum-free counter electrodes. The first four aforementioned aspects are thoroughly described in this review.

Broader context

Throughout recent years the implementation of nanocarbons into dye-sensitized solar cells (DSSC) has resulted in important breakthroughs. The most relevant of them in this context are (i) the enhancement of charge transport and charge collection in nanocarbon-doped electrodes, (ii) the introduction of nanocarbon interlayers that simultaneously reduce the charge recombination and increase the charge collection efficiency, (iii) the use of nanocarbon-based, iodine-free, solid-state electrolytes featuring excellent diffusion coefficients and catalytic efficiencies, (iv) the use of novel nanocarbon-based hybrid dyes, and (v) the use of nanocarbons towards platinum-free counter electrodes. The first four aforementioned aspects are thoroughly described in this review.

Introduction

Nowadays, one of humanity's major challenges is the development of renewable energy sources to secure our current lifestyle. As a matter of fact, solar irradiation is prone to take a leading role in covering the world's current energy demand. As such, photovoltaic devices are considered as a superior means towards supplying energy.^{1–3} The following covers a brief summary of the most important achievements.

First reports on photovoltaic concepts date back to the end of the XIX century with two major contributions, namely, on one hand, in solution by Alexander E. Becquerel in 1839,⁴ and, on the other hand, in the solid state by Willoughby Smith in 1873.⁵ Photovoltaic technologies gained, however, a major momentum six decades ago following pioneering breakthroughs in the area of mono-crystalline silicon-based solar cells.⁶ In 1954, Bell laboratories reported on the prototype manufacturing of a new solar battery and a year later the first Bell solar battery was used in a telephone carrier system. The aforementioned examples are considered as part of the first generation of solar cells, which currently dominate the market. Such first generation of solar

cells is either based on single-crystalline (sc-Si) or on multi-crystalline (poly-Si) silicon as well as on GaAs and InGaP semiconductors. Si, GaAs, and InGaP technologies are considered the most mature, especially in the context of high efficiencies, that is, >15%. The production costs of such modules are, however, very high, which motivated engineers and scientists to search for second generation solar cells by addressing factors such as easy and low-cost production as well as high performances. Owing to the development of cost-efficient thin-film technologies, second generation solar cells appeared in the early 60s. Leading examples are chemical vapor deposited (CVD) amorphous silicon (a-Si) as well as poly-crystalline CdS, InSe, CuInSe₂, and CdTe based devices.⁷ In these solar cells, lower production costs are, however, combined with lower efficiencies when compared to first generation solar cells. Some drawbacks, which evolve from the facts that the materials are not very abundant and are toxic, triggered research on third generation solar cells during the last two decades. In the latter, highly efficient solar cells are based on environmentally friendly materials that allow inexpensive solvent-based fabrication techniques. Leading examples are low-cost, thin-film solar cells based on novel concepts like hot carrier solar cells (HCSC), multiple exciton generation (MEG), and intermediate band solar cells. By means of these cells, the Shockley–Queisser limit as found in first generation solar cells is expected to be bypassed.^{8,9} Finally, dye-sensitized solar cells (DSSC)¹⁰ and organic photovoltaics (OPV), either in the form of bilayer or bulk heterojunction (BHJ) configurations,^{11,12} are

Department of Chemistry and Pharmacy, Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität, Erlangen-Nürnberg Egerlandstr. 3, 91058 Erlangen, Germany. E-mail: dirk.guldi@fau.de

† We would like to dedicate this paper to Prof. Dr. David Officer on the occasion of his 60th birthday.

Fig. 1 Chemical structures of fullerenes (upper left), graphene (upper central), single-walled carbon nanotubes (upper right), and single-walled carbon nanohorns (lower central).

considered as the third-generation of solar technology. Importantly, for OPV efficiencies beyond 10% have been achieved at very low production costs,^{13,14} while for DSSC efficiencies between 13–15% have been recently reported.^{15,16}

The scope of this review is to highlight DSSC technology, in general, and recent strategies to implement carbon nanomaterials – fullerenes, single- and multi-walled carbon nanotubes (SWCNT and MWCNT), single-walled carbon nanohorns (SWCNH), and graphene (Fig. 1) – into the different parts of DSSC, in particular. The physico-chemical features of carbon nanomaterials have been studied in great detail during recent decades.^{17–22} Carbon nanomaterials are the basic building blocks in materials science and are of utmost relevance in solar technology.^{20,21,23–29} As a matter of fact, they have been strongly linked to breakthroughs in OPV since the mid 90s, but they have only recently been implemented into DSSC. Going beyond the scope of the current work, we refer the interested reader to excellent reviews in the area of OPV,^{11,12} inorganic third generation solar cells,^{23–26} and DSSC²⁷ as well as two specific reviews about the use and interpretation of different techniques like time-resolved spectroscopy, incident and adsorbed photo-to-current conversion efficiency (IPCE and APCE, respectively), impedance spectroscopy, intensity-modulated photovoltage spectroscopy (IMVS), and intensity-modulated photocurrent spectroscopy (IMPS), which have been used to study the *modus operandi* in DSSC under different conditions.^{28,29}

Carbon nanomaterials

There is a wealth of carbon nanomaterials, but only four of them have lately driven the photovoltaic field.²¹ In particular, these are fullerenes, single- and multi-walled carbon nanotubes, single-walled nanohorns, and graphene.

The production of fullerenes has been well-known since 1990.^{20,21,30–34} They are best described as spherical carbon

nanomaterials that are composed of fused hexagons and pentagons – Fig. 1. The most outstanding feature of fullerenes is their electron acceptor property and their small reorganization energy in charge transfer reactions. Both are responsible for fast charge separation and slow charge recombination when fullerenes are integrated into covalently and/or non-covalently linked electron donor-acceptor systems.²⁰ Although the vast majority of fullerene applications are found in bilayer and BHJ organic solar cells, a few reports on their use in DSSC also exist.

Carbon nanotubes (CNT) in the form of multi- or single-walled carbon nanotubes (MWCNT and SWCNT) have also been well-known since 1991 – Fig. 1.^{21,35} They are considered as small strips of graphene sheets that have been rolled up to form a large variety of nanocylinders denoted by a pair of indices (n,m), which define the diameter and the chirality. Some of the most exciting features of CNT involve high Young's moduli and tensile strengths.^{36,37} Even more striking are their electrical charge transport properties. They are either metallic or semi-conducting, depending on their diameter and chirality. For instance, the electrical transport in both types of SWCNT is considered as ballistic, that is, no loss of energy by thermal effects, allowing current densities approximately 1000 times higher than that of a typical copper wire.^{38,39} This phenomenon is ascribed to the lack of electrical resistance, owing to the extended but directional network of delocalized π -orbitals.

Single-walled carbon nanohorns (SWCNH) are yet largely unexplored. They consist of tubular structures – 2 to 5 nm in diameter and 30 to 50 nm in length – that associate into roundish aggregates of 100 nm diameter – Fig. 1. Similar to the above mentioned SWCNT, SWCNH are semiconducting and provide films with large surface areas.^{34,40,41} They differ, however, with respect to their synthesis. SWCNH are synthesized metal-free by means of CO₂ laser induced ablation of graphite targets, which proceeds in high yields and high purities.^{42,43} Until this point, their applications have been mainly limited to hydrogen and methane storage, biosensing, solar thermal collectors, drug delivery systems, and super-capacitor electrodes.^{34,40,44,45}

Finally, single graphene layers (Fig. 1) first appeared in 2004 by mechanical exfoliation of graphite using scotch tape.⁴⁶ Graphene is best described as a flat monolayer of sp² hybridized carbon atoms tightly packed into 2D honeycomb crystal lattices. Graphite consists of single graphene layers that stack on top of each other forming a bulk material. This material is mechanically and chemically stable and has remarkable features in terms of transmittance (>97%) and mobility of holes/electrons at room temperature.^{47,48} Currently, the most critical bottleneck is its production.⁴⁹ In the early days of graphene research, solution processing by means of oxidation of graphite to graphite oxide (GO) was performed to shed light on the structure and constitution of graphite.⁵⁰ Exfoliation at basic pH affords monolayers of GO, whose stability is favored by coulombic repulsions, in high yields. Nevertheless, the final step, that is, reduction of GO, fails to completely remove the introduced oxygen atoms and to reinstate the lattice of graphene. As a matter of fact, the resulting reduced GO (rGO) features properties different from those predicted for pure

graphene.^{51,52} Alternative solution approaches include intercalation of graphite with alkali metals,⁵³ chemical post-treatment with electrophile yielding materials, in which aggregation and material properties are largely governed by the functional groups^{54,55} and the break-off of π - π interactions between individual layers by using ultrasound.^{56,57} The latter also leads to interesting electronic features when, for example, electron donating chromophores like phthalocyanines,⁵⁸ porphyrins,⁵⁹ *etc.* are utilized. Finally, solid-state production includes graphitization of SiC, chemical vapor deposition (CVD), and roll-to-roll production of films grown on copper foils.⁶⁰⁻⁶²

All of the aforementioned nanocarbons show, however, very different photophysical and electrochemical features, which exert a rather unique impact on functions like, for example, light harvesting, charge separation, and catalysis. This aspect is mainly related to their preparation procedure and their nano-scale self-ordering/self-assembling features. More details regarding this topic are found in a recent review.⁶³

Dye-sensitized solar cells

Since the first highly efficient DSSC reported in 1991,¹⁰ much effort has been focused on the development of DSSC. Here, the use of cheap materials, the ease of device fabrication, the high stability, and the efficiency of around 15% as state-of-the-art^{15,16,27,64-66} have fueled the interest. For example, G24 Innovation Ltd. uses a low-cost, roll-to-roll process to fabricate flexible DSSC modules, which feature 0.5 W of power under sunlight illumination.⁶⁷ First demonstrators, which were displayed at the 1st International Photovoltaic Power Generation Expo in 2008, are based on 2.1 m $\times$ 0.8 m DSSC modules with conversion efficiencies of around 3%. More relevant are recent breakthroughs announced by Sony and Apple, which implement DSSC in our daily life like decoration, iPads, *etc.*^{68,69}

Fig. 2 illustrates a typical DSSC architecture. In particular, DSSC consist of two electrodes, that is, the photoelectrode and the counter-electrode, which are brought together in a sandwich-like architecture. On one hand, the photoelectrode consists of a highly porous, nanocrystalline, wide-band gap, metal oxide based semiconductor layer. The latter is modified with a light harvesting dye that is adsorbed onto the electrode. Typical semiconductor materials are TiO₂ or ZnO (n-type) and NiO (p-type) in the form of nanoparticles. Notably, the possibility of integrating both types of electrodes into single DSSC has evoked the potential of developing tandem DSSC, which feature better overall device performances compared to just n- or p-type based DSSC – Fig. 3.⁷⁰⁻⁷⁶ On

the other hand, substrates used for counter-electrodes are covered with a thin catalytic platinum layer. Finally, a redox mediator – most commonly I^-/I_3^- – is used as an electrolyte to close the circuit. The electrolyte is either a liquid or a solid with different additives to enhance the charge diffusion between the electrodes and to prevent changes of the Fermi level of the electrodes.

The *modus operandi* under illumination conditions of DSSC involves four well-defined steps as summarized in Fig. 3. Initially, light is absorbed by a dye, which is anchored to the surface of either n- or p-type semiconductor mesoporous electrodes. Subsequently, charge separation takes place across the dye/n-type electrode interface by means of electron injection from the photoexcited dye into the conduction band (cb) of the semiconductor.^{27,29,77,78} A different mechanism governs p-type DSSC.⁷⁹⁻⁸² Here, once the dye is photoexcited, electrons are driven from the valence band (vb) of the semiconductor to the photoexcited dye, increasing the hole density in the electrode. In both DSSC, the injected charge is driven through the external circuit to the counter-electrode, where the charge is reintroduced by means of a platinum-assisted catalytic reaction of the electrolyte at the electrode surface. Finally, the electrolyte regenerates the ground state of the dye. In n-type devices, the electrolyte reduces the oxidized dye to its original form. In contrast, the electrolyte oxidizes the photoexcited reduced dye in p-type DSSC. Several charge loss pathways are known under device operation conditions. Firstly, radiative and non-radiative relaxations of the excited dyes to their ground state compete with charge injection. Secondly, the injected charges recombine at the photoactive electrode with the redox mediator as well as the reduced or oxidized dyes. As a matter of fact, this lowers the charge density in the photoactive electrode and reduces the overall DSSC efficiency.

The performance of a solar cell is determined by means of standard characterization methods, in which the applied voltage (V) is linearly swept and the corresponding current density (J) is measured under either illumination or dark conditions. Here, the open-circuit voltage (V_{oc}) represents the maximum voltage that a device might feature and, as such, relates to the energetic difference between the Fermi levels (E_{F}) of electrons at the two contacts – Fig. 3. The Fermi levels in the dark must be equal for all DSSC components, since the cell is always at electrochemical equilibrium. Under illumination and open-circuit conditions, electrons are injected into the semiconductor, where they reach a steady state concentration (n_{light}). This is governed by the balance between charge injection and charge recombination processes. The increase of the semiconductor Fermi level under illumination defines V_{oc} , which is the ratio of free electron concentration in the semiconductor under illumination and under dark conditions as illustrated in eqn (1):

$$V_{\text{OC}} = \frac{1}{q} E_{\text{F}} - E_{\text{F,redox}} = \frac{K_{\text{B}} T}{q} \ln \frac{n_{\text{light}}}{n_{\text{dark}}} \quad (1)$$

where q is the electric charge, K_{B} is the Boltzmann constant, and T is the temperature.

The short-circuit current density (J_{sc}) relates to the maximum current flowing in the absence of an applied voltage. It depends mostly on the yields of charge injection, charge collection, and dye regeneration, that is, η_{inj} , η_{coll} , and η_{reg} , respectively, at the

Fig. 2 Sketch of a typical DSSC.

Fig. 3 *Modus operandi* of n-type (top left), p-type (top right), and tandem DSSC (bottom). S, E_F , cb, and vb are the dye ground and excited state, Fermi level, conduction band, and valence band, respectively. e^- and h^+ refer to electrons and holes, respectively.

electrodes, and the light harvesting efficiency of the electrode (LHE). The incident photon-to-current conversion efficiency (IPCE) represents the current response at each wavelength. It is considered as the total balance of the quantum yields as illustrated in eqn (2):

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda)\eta_{\text{coll}}\eta_{\text{reg}}\eta_{\text{inj}} \quad (2)$$

The IPCE spectrum commonly matches the absorbance spectrum of the dye used in the solar cell. The short-circuit current density (J_{sc}) is the integrated overlap between the IPCE spectrum and the solar irradiance spectrum at any given wavelength – see eqn (3):

$$J_{\text{sc}} = q \int I_0(\lambda) \text{IPCE}(\lambda) d\lambda \quad (3)$$

where I_0 is the solar photon flux and q is the electric charge.

The fill factor (FF) is the ratio of the maximum power that is observed relative to its theoretical maximum, given by eqn (4).

$$\text{FF} = \frac{J_{\text{M}} V_{\text{M}}}{J_{\text{sc}} V_{\text{oc}}} \quad (4)$$

where J_{M} is the maximum power point current density and V_{M} is the maximum power point voltage.

A FF less than unity indicates losses within the solar cell, which originate from inherent characteristics under operation conditions. Such losses are best described in terms of series resistance (R_{s}) and parallel shunt resistance (R_{SH}). On one hand, R_{s} is caused by the bulk resistance from the different components of the device, namely the semiconductor, the electrodes, and the different interfaces. On the other hand, R_{SH} is composed of leakages across the junction, that is, at the edges of the cell, near crystal defects, and contaminants.

The power conversion efficiency (η) is the maximum power density achievable in an operating cell per incident light power density (P_{s}). η is an overall balance between all of the aforementioned figures-of-merit and relates to V_{oc} , J_{sc} , and FF as shown in eqn (5):

$$\eta = \frac{V_{\text{oc}} J_{\text{sc}} \text{FF}}{P_{\text{s}}} \quad (5)$$

Implementing multifunctional nanocarbons into DSSC

Despite the plethora of outstanding contributions to the field of DSSC, contemporary science is driven by five grand challenges.

These are categorized in terms of device components, that is, the development of (i) photoelectrodes with high charge collection yields, (ii) solid-state electrolytes with excellent ion diffusion and conductivity features, (iii) efficient iodine-free electrolytes, (iv) panchromatic dyes, and (v) efficient and platinum-free counter-electrodes. In recent years, the implementation of nanocarbons into each of the above-mentioned device components together with the development of nanocarbon-based dyes have emerged as a powerful strategy to tackle these challenges. This primarily relates to the multifunctionality of nanocarbons. The latter impacts the device mechanism in terms of, for example, simultaneous enhancement of charge transport across electrodes and charge collection at electrodes as well as ionic diffusions and catalytic efficiencies in electrolytes.

In this section, the milestones associated with these challenges are briefly described. This is followed by three sections, which feature a detailed description regarding the implementation, characterization, and impact of nanocarbons on photoelectrodes and solid-state electrolytes with and without iodine, as well as nanocarbon-based dyes.

Firstly, the optimization of electron transport within the semiconductor photoelectrode and the reduction of the charge transfer resistance across the different interfaces are of utmost relevance. The photoelectrode is an essential part of DSSC in terms of dye adsorption, charge transport, charge collection, and diffusion processes.^{27,65,66,83} Notable, charge transport competes with charge recombination and/or charge transfer involving the dyes and/or the electrolyte, respectively. To overcome such bottlenecks, the implementation of multifunctional nanocarbons either as interlayers or as dopants into the mesoporous semiconductor photoelectrodes has emerged as a viable strategy.

Secondly, solvent-based electrolytes are unstable over time, owing to solvent leakages, evaporation processes under indoor and outdoor operation conditions, and sealant corrosion.^{84–86} In addition, industrial large-scale production by, for example, roll-to-roll processes is very inefficient when liquid electrolytes are used. Promising solutions involve the fabrication of solid-state DSSC (ssDSSC). Leading examples are organic ionic plastic crystal electrolytes,⁸⁷ organic hole conductors,^{88–94} polymer gel electrolytes,^{95,96} light-trapping schemes adding nematic liquid crystals,⁹⁷ physically cross-linked gelators,^{98,99} and ionic liquid (IL) based electrolytes.^{95,100–104} Still, the rather poor pore filling of mesoporous semiconductor electrodes, the low charge mobility, and the moderate charge diffusivity constitute major obstacles *en route* towards highly efficient ssDSSC. In recent years, the introduction of multifunctional nanocarbons into solid-state electrolytes based on ionic liquids has been established as an easy and elegant strategy to circumvent some of the aforementioned problems.

Thirdly, much design work towards iodine-free redox electrolytes has been performed.¹⁰⁵ To date, the most widely used and efficient electrolyte is the I^-/I_3^- redox couple. But, this electrolyte imposes severe limitations, namely rather high Nernst potential, absorption features in the visible region, rapid mass losses of I_2 , enhanced charge recombination processes

due to I_3^- ion pair formation in the proximity of the electrodes, and corrosion that limits the DSSC stability. Practical alternatives are cobalt(II/III) and copper(I/II) complexes,^{106,107} ferrocene,^{108,109} inorganic materials,¹¹⁰ and organic compounds.¹¹¹ Among all of them, cobalt complexes stand out, owing to their excellent DSSC performance.¹¹² Nevertheless, it has recently been demonstrated that multifunctional nanocarbons function as electrolytes in ssDSSC without the needs of I_2 .

Fourthly, the use of environmentally friendly, organic dyes with panchromatic absorption features should be considered. To this end, a myriad of efforts have focused on the synthesis and implementation of perylenediimides, squarines, thiophenes, porphyrins, and phthalocyanines, featuring absorption cross-sections that span from the ultraviolet to the near infrared regions of the solar spectrum.^{27,113,114} Among all of them, the use of push–pull porphyrins has led to a breakthrough in the device efficiency with a value of 13%.¹⁵

Fifthly, platinum-free counter-electrodes, such as PEDOT and ITO, are at the focal point of development.^{27,115–124} Although platinum is the superior catalyst in DSSC, drawbacks including high price, rarity, and susceptibility to corrosion by iodide stimulate the search for new counter-electrodes. To this end, several low-cost materials – multifunctional nanocarbons,^{125–131} metal oxide,¹³² and transition metal carbides and sulfides^{133–135} – have been probed as alternatives. The number of publications in the field of multifunctional nanocarbon based counter-electrodes for DSSC is staggering. As such, we wish to refer to two excellent reviews in the area.^{123,124}

Hybrid semiconducting electrodes based on multifunctional nanocarbons

Throughout the last five years, different approaches have been developed to implement multifunctional nanocarbons either as interlayers on the bottom and/or on the top of the mesoporous films or as dopants inside the electrode networks – Fig. 4. Regardless, both approaches have improved the charge collection yields under operation conditions.

Charge recombination processes in DSSC mainly occur across FTO/electrode/electrolyte and the electrode/dye/electrolyte interfaces. In the case of TiO_2 -based DSSC, charge recombination is greatly reduced upon depositing a thin film of TiO_2 on the bottom and on the top of the electrode *via* hydrolyzing aqueous solutions of TiCl_4 .²⁷ Although the benefits of such a buffer layer – Fig. 4 – are undisputed, important drawbacks, such as high production and recycling costs, low stability of TiCl_4 solutions, and toxic waste of the initial material, still evolve.^{136,137} One of the most challenging topics in DSSC research is the search for a universal buffer layer, which is applicable to any type of electrode.

The first example of multifunctional nanocarbon-based buffer layers was reported by Kim *et al.* in 2009.¹³⁸ In this context, buffer layers define thin films placed between FTO substrates and photoelectrodes as sketched in Fig. 4. They mixed graphene oxide (GO) with TiO_2 nanoparticles (Degussa P25) followed by ultraviolet light irradiation treatment – a 450 W

Fig. 4 Upper part – scheme of multifunctional nanocarbon-based interlayers used in DSSC. Lower part – J – V curves of DSSC with and without TiCl_4 treatment (light-grey solid line and black dotted line, respectively) as well as with SWCNH interlayers of 15 and 30 nm (black solid line and dark-grey solid line, respectively).

xenon arc lamp for about 2 hours – to reduce GO. Impedance spectroscopy was used to demonstrate that the presence of a thin GO layer assists in effectively reducing the charge recombination processes, leading to better FF and V_{oc} and, in turn, to an overall efficiency improvement of around 10%.

Chen *et al.* have recently developed a strategy to form graphene-based interlayers that consist of few layer graphene sheets with sizes ranging from 0.5 to 3 μm .¹³⁹ They used spin-coating of ethanol dispersions of chemically reduced GO. Impedance spectroscopic measurements suggested that the charge transfer resistance across the electrode/FTO interface is greatly reduced, affording rates for electron collection that are enhanced. The graphene sheets are likely to block the backward electron flow, that is, to the TiO_2 electrode. The most valuable finding is that the overall DSSC efficiency increases from 7.54 to 8.13% in devices featuring thin TiO_2 electrodes without and with reduced GO interlayers, respectively.

On the same note, Casillas *et al.* demonstrated that single-walled carbon nanohorn-based buffer layers impact the overall device performance.¹⁴⁰ Device features similar to those treated with TiCl_4 were found (Fig. 4). The authors deposited buffer layers of pristine SWCNH of variable thicknesses by using a spin-coating technique. They noted that the best device

performance was achieved when an interlayer of around 15–20 nm was utilized. Importantly, even thicker layers led to substantial decreases of the device performance in terms of FF and J_{sc} , due to the less conductive nature of the interlayers. Independent support for this assumption came from impedance measurements. The latter confirm that recombination processes are successfully suppressed, since the electron lifetime is similar to that noted in control electrodes. In addition, studies under dark and illumination conditions lead to charge collection efficiencies of 47 to 80% for devices without and with SWCNH interlayers, respectively. In short, the authors presented a viable approach to replace the TiCl_4 treatment by a spin-coated layer of SWCNH without, however, impacting the device performance.

Regarding better electrode/dye/electrolyte interfaces, a similar sort of interlayer has recently been used towards enhancing photocurrents and FFs in TiO_2 -based DSSC.^{141–149} Song *et al.* used, for example, GO to form a GO– TiO_2 Schottky junction that blocks recombination processes.¹⁴¹ Both the electron transport through the TiO_2 network and the adsorption of the dye by means of π – π interactions were found to be improved. The Schottky junction was prepared by spray-coating GO aqueous solutions at 120 °C until a thin layer of GO is formed on top of the TiO_2 electrode. A direct comparison between a control device and of a modified device by means of impedance spectroscopy, that is, looking at charge transfer and recombination processes, led to the conclusion that the overall device resistances were reduced and the electron lifetimes were increased. Notably, higher FFs and larger photocurrents resulted in a moderate efficiency enhancement of 10%.

The implementation of multifunctional nanocarbons into the mesoporous electrode was firstly reported in the form of SWCNT-doped TiO_2 electrodes. They were prepared by dispersing SWCNT on top of carbon fiber electrodes *via* electrophoresis followed by depositing bare TiO_2 nanoparticles – Fig. 5.^{150,151} On one hand, the resulting devices gave rise to efficiencies twice as high as those seen in reference devices lacking SWCNT. On the other hand, once a $\text{Ru}^{\text{II}}(\text{bpy})_2(\text{dcbpy})$ photosensitizer was immobilized the overall improvement was marginal. This is rationalized on the basis of lower V_{oc} , owing to the low Fermi level of SWCNT.¹⁵¹ Nevertheless, the authors demonstrated that the benefits of doping originate from a better charge separation in the excited state and a better charge transport and charge collection at the photoelectrode. With the help of steady-state and time-resolved photophysical measurements the charge injection processes were recorded and were shown not to be affected by the presence of SWCNT.

After this contribution, the benefits of using MWCNT in ZnO and TiO_2 electrodes were demonstrated.^{152–156} Here, MWCNT containing photoanodes were fabricated either by a modified acid-catalyzed sol-gel procedure¹⁵⁵ or by a step-wise mixture of oxidized MWCNT dispersions in metal-oxide particle pastes.¹⁵⁶ A common trend is that doping with MWCNT increases the electrode roughness and decreases the charge recombination rate. The earlier has a consequence that more dye is adsorbed and that higher photocurrents are realized, while the latter assists in improving the overall charge collection yield. The

Fig. 5 Upper part – scheme of multifunctional nanocarbon-doped electrodes used in DSSC. Lower part – J - V characteristics of DSSC prepared with the different multifunctional nanocarbons/ TiO_2 photoelectrodes – reference (black solid), 0.5 wt% pristine SWCNH (black dashed), 0.2 wt% oxidized SWCNH (black dotted), 0.1 wt% graphene (dark grey solid), 0.5 wt% partially reduced graphene oxide (dark grey dashed), 0.1 wt% pristine SWCNT (dark grey dotted), and 0.1 wt% oxidized SWCNT (light grey solid).

synergy stemming from both aspects enhances the efficiency to around 30 and 50% for ZnO - and TiO_2 -based devices, respectively.

Recently, Yang *et al.* have demonstrated the implementation of MWCNT into TiO_2 nanorods.¹⁵⁷ Two different sets of experiments, in which the thickness of the electrodes was changed, were performed. In both cases, FFs increased from 50 up to 76% for devices without and with MWCNT in the TiO_2 nanorods, respectively. However, upon doping with more MWCNT, J_{SC} s dropped, owing to lower amounts of adsorbed dye on the electrodes. Overall, higher FFs are rationalized on the basis of lower charge recombination due to the presence of MWCNT.

Not surprisingly, graphene derivatives have also been used to dope ZnO , TiO_2 , and NiO electrodes, owing to their high conductivity and high surface contact – Fig. 5.^{158–167} Intermolecular forces such as physisorption, electrostatic binding, and charge transfer govern the mutual interactions between metal oxides and graphene. To this date, three different procedures have been developed to prepare graphene doped composites. Firstly, GO and nanoparticles were mixed in solution and irradiated with ultraviolet light to reduce GO.^{158,159} Secondly, single

and few layer graphene flake suspensions were prepared by chemical exfoliation under either oxidative or reductive conditions^{160,161,165} or by ultrasonication with Nafion as a stabilizer.¹⁶² Thirdly, nanographene suspensions were prepared by direct exfoliation of graphite by means of stabilizers such as pyrene derivatives.^{166,168} In a subsequent step, the prepared suspensions were mixed with ZnO , TiO_2 and NiO .

Similar to what has been documented for CNT-doped electrodes, the presence of graphene enhances the charge transport and inhibits the charge recombination. In addition, rougher surfaces evolved as a consequence of doping, which is shown in Fig. 6. The latter leads to better light trapping and a more efficient dye uptake. Interestingly, high graphene loading seems to promote nanocarbon aggregation, which, in turn, compromises the morphology of the electrodes. Still, photocurrents are greatly increased (40–60%), while a slight loss of V_{OC} is noted – Fig. 5.^{158–167} Interesting is the observation by Li *et al.*, who showed that V_{OC} increases upon graphene doping from 73 to 105 mV in NiO -based devices.¹⁶⁵ This fact was ascribed to lower hole densities, since graphene traps and transports holes. Regardless of the type of electrode, the overall device efficiency was greatly improved. The use of graphene rather

Fig. 6 Upper part – SEM images of pristine (left) and oxidized (right) nanocarbon/ TiO_2 films. The TiO_2 films are doped with 0.5 wt% SWCNH (top), 0.5 wt% graphene (middle), and 0.1 wt% SWCNT (bottom). The SEM image of the reference TiO_2 electrode (bottom middle) is also shown for comparison.

than SWCNT to dope DSSC evokes a higher device performance enhancement – Fig. 5.

Noteworthy, pristine and oxidized SWCNH were evaluated as DSSC dopants.¹⁶⁶ Here, the composite preparation was realized by mixing SWCNH and TiO₂ pastes by means of ultrasonication. Similar to the aforementioned, features – including surface roughness, quantity of adsorbed dye, light trapping, electrical resistance, *etc.* – were impacted by the doping with SWCNH – Fig. 6. Additional measurements based on impedance and nanosecond transient absorption spectroscopy led to a charge recombination that was suppressed, on one hand, and to a charge collection efficiency that was enhanced, on the other hand. Taking these facts into account, higher photocurrent and efficiency values evolved – Fig. 5. In this work, doping with pristine SWCNT, oxidized SWCNT, partially reduced graphene, and exfoliated graphene was also probed. The results indicated that SWCNH and graphene doping resulted in similarly performing devices, which were, however, superior in terms of performance relative to SWCNT doped devices – Fig. 5.

Solid-state electrolytes based on multifunctional nanocarbons

One of the few grand challenges in ssDSSC is the development of iodine-free, solid-state electrolytes that feature good contact with the mesoporous electrode, high ionic mobility, and good diffusion. A fairly popular approach implements the use of inorganic p-type semiconductors – CuI, CuSCN, *etc.*^{169,170} – and/or organic hole transporting materials – thiophenes, polypyrroles, polyanilines, *etc.*^{88–94,171,172} In this regard, state-of-the-art efficiencies of around 10% have been reached.⁸⁴ Very recently, the implementation of multifunctional nanocarbons has emerged as a viable alternative to prepare solid-state electrolytes as well as iodine-free electrolytes.

The first example of fullerene-based electrolyte was reported by Jung *et al.*¹⁷³ They focused their work on a set of fullerene derivatives as primary components for iodine-free, solid-state electrolytes – Fig. 7. The preparation of these novel electrolytes involves a number of steps. Firstly, the fullerene derivatives were dissolved in ethylene carbonate (EC)/propylene carbonate (PC) in a 4 : 1 (v/v) ratio and were deposited on top of TiO₂ electrodes by means of drop-casting. Secondly, the residual solvent was removed at 55 °C. Important characteristics of the fullerene-based electrodes are less pronounced absorption features in the visible region in sharp contrast to iodine-based electrolytes and the efficient regeneration of ruthenium dyes. Devices using these fullerene-based electrolytes gave rise to efficiency values of up to 2%. In addition, the authors indicated that control devices with the iodine-based electrolyte perform poorly over longer periods of time. To this date, only one more example, in which fullerenes are implemented into the electrolyte, has been reported.¹⁷⁴ Here, fullerenes act as a secondary electron shuttle in I[–]/I₃[–] based liquid electrolytes. The main impact is, however, the appreciable enhancement of the device photocurrents.

Fig. 7 Upper part – chemical structures of the set of fullerene derivatives serving as hole transport materials in electrolytes. Central part – chemical structures of poly(oxyethylene)-segmented (POE) and poly(oxyethylene)-segmented oligo(amide-imides) polymer derivatives (POEM). Lower left part – chemical structure of 15-crown-5-functionalized SWCNT. Lower right part – chemical structure of 1-(2-acryloxy-ethyl)-2-methyl-benzimidazol-1-ium iodide (AMImI).

Carbon nanotubes were firstly added to liquid electrolytes by mixing them with ionic liquids such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI), 1-ethyl-3-methylimidazolium iodide (EMIm-I), and the lithium iodide (LiI)/iodine (I₂) redox shuttle.¹⁷⁵ Using the new electrolytes resulted in enhanced viscosity and ionic conductivity values, which, as a consequence, led to better device performances. Overall, a clear relationship between CNT-doping and device features, namely FF and V_{oc}, was established. The benefits were reflected in an efficiency that was 13% higher than in reference devices lacking CNT. Following this pioneering work, Ikeda *et al.* focused on developing iodine-free, CNT-based, solid-state electrolytes.¹⁷⁶ In fact, the composition of this new type of solid-state electrolyte was a mixture of clay-like conductive materials, SWCNT, and imidazolium iodide. Efficiencies of 1.63 and 2.3% emerged under 1 and 0.25 sun illuminations, respectively.

The field picked up additional momentum with the contribution by Akhatar *et al.*, who explored a new hybrid electrolyte consisting of a dispersion of MWCNT and polyethylene oxide (PEO).¹⁷⁷ LiI and I₂ were added by means of sonication and stirring. Similar to the results noted for solvent-based

electrolytes, the viscosity and ionic conductivity were changed. As such, better interfacial contacts with the electrode and more favorable I_3^- diffusion resulted in an IPCE, which was improved by around 50% relative to a control device when 1% MWCNT/PEO was present.

Soon after the above-mentioned contribution, Lin and Ho *et al.* pursued two approaches to achieve a better CNT dispersibility in solid-state electrolytes.^{178,179} They documented that the use of either poly(oxyethylene)-segmented amides, imides polymer derivatives (POEM), or 1-(2-acryloyloxy-ethyl)-2-methylbenzimidazol-1-ium iodide (AMImI) facilitated the dispersion of MWCNT without notable signs of aggregation – Fig. 7. Both solid-state electrolytes were prepared in the same manner. In brief, the dispersed MWCNT were added to acetonitrile solutions containing the I^-/I_3^- couple together with different additives by means of continuous ultrasonication. Finally, acetonitrile was removed under vacuum. Independent of the stabilizer to disperse MWCNT, the diffusion rate of I^- and I_3^- increased in the electrolyte under operation conditions. With the help of impedance spectroscopic and linear sweep voltammetric assays the photocurrents were correlated with the ionic diffusion. Owing to the fact that V_{oc} s and FFs remain nearly unchanged, enhanced photocurrents are the main reason for improving the efficiencies with values as high as 6.86% (POEM) and 3.6% (AMImI). For comparison, reference devices feature efficiencies of 4.63 and 1.16%, respectively.

Oxidized MWCNT have recently been tested in solid-state electrolytes by Zhang *et al.*¹⁸⁰ A direct comparison between pristine and oxidized MWCNT led to the conclusion that the latter are better miscible with ionic liquids in the electrolyte and, in turn, improve the gel formation. In particular, devices with oxidized MWCNT outperformed those with pristine MWCNT and reference devices in terms of photocurrent, V_{oc} , and efficiencies. Another important factor was the excellent device stability of around 100 days, that is, less than a 10% drop in efficiency, when oxidized MWCNT-based electrolytes are utilized. The lack of phase separation in oxidized MWCNT-based electrolytes is likely to contribute to the trends.

Additional benefits were noted when functionalized MWCNT were added to solid-state electrolytes. For instance, the presence of Li^+ ions limits the I^- diffusion by electrostatic interactions. As demonstrated by Lin and Ho *et al.* in 2011,¹⁸¹ Li^+ ions that are present in the electrolyte are subjected to crown ether complexation when using 15-crown-5-functionalized MWCNT as the dopant material – Fig. 7. The electrolyte mixture was prepared in MeOH by ultrasonication, followed by solvent removal under vacuum once the electrode is covered. In this manner, the presence of MWCNT and the immobilization of Li^+ ions were at force to optimize ionic diffusion in the solid-state electrolyte. As a matter of fact, corresponding devices obtained efficiencies of 2.11% and stabilities of 1200 hours at 100 mW cm^{-2} .

Concerning the development of iodine-free electrolytes based on CNT, Ho *et al.* mixed SWCNT, MWCNT, and carbon black materials with 1-ethyl-3-methylimidazolium iodide (EMII) and crystal growth inhibitors.^{182,183} In initial work, ssDSSC featuring SWCNT–EMII electrolytes showed efficiency values of

3.5% under 1 sun illumination.¹⁸² Assays, which were based on impedance spectroscopy and laser-induced photovoltage transient spectroscopy, shed light on interfacial charge recombination, ionic charge transport, and catalytic I_3^- reduction. All of the benefits come from the addition of SWCNT. Additionally, the latter acts as a filler for the physical gelation of the electrolyte and, as such, assists in improving the contact with the electrode. In follow-up work, they reported a comparison between SWCNT, MWCNT, and carbon black as dopants.¹⁸³ SWCNT devices outperformed MWCNT and carbon black devices featuring efficiency values of 4.01, 3.53, and 3.09%, respectively. Notable are stabilities of more than 1000 hours under room temperature and 1 sun illumination.

Regarding the use of single or few layer graphene flakes in iodine-free, solid-state electrolytes, only two studies are known to this day. Firstly, Gun'ko *et al.* prepared a series of quasi-solid electrolytes by blending pre-exfoliated graphene with 1-methyl-3-propylimidazolium iodide (PMII), on one hand, and electrolytes containing SWCNT and a mixture of pre-exfoliated graphene and SWCNT, on the other hand.¹⁸⁴ Common features were excellent thermal stabilities until 300 °C and better ionic conductivities when compared to the reference PMII-based electrolyte. The impact of graphene as a superior doping material was clearly corroborated by device efficiencies that improved by factors of around 13 and 15 relative to reference devices when graphene and graphene-SWCNT electrolytes were used, respectively. At the heart of this effect is a mechanism, which involves efficient charge transfer and shorter charge diffusion length. In addition, it was postulated that graphene plays an active role in the catalytic reduction of I_3^- . Secondly, Jung *et al.* reported a strategy to introduce partially reduced graphene oxide into electrolytes.¹⁸⁵ In particular, positively charged 1-octyl-2,3-dimethylimidazolium iodide (ODI) was used as a reducing and stabilizing agent for single or few layer graphene suspensions based on GO. ODI was mixed in water with GO and mutual electrostatic interactions afforded the reduction of GO as indicated by Raman assays. Ultimately, the presence of ODI assisted in stabilizing partially reduced GO *via* π – π interactions. Devices prepared with ODI-graphene gave rise to much better performance relative to those that only featured ODI-based electrolytes. To this end, higher photocurrents, open-circuit voltages, and efficiencies were discernible. Although there is neither an experimental confirmation nor a theoretical modeling, the authors postulated that graphene is responsible for the ionic diffusion *via* delocalizing the generated charges.

Novel types of dyes based on multifunctional nanocarbons

It is safe to say that the chemical functionalization of fullerenes is one of the most active fields in chemistry for more than 20 years.^{22,186} This fact has transcended to DSSC, in which well-known dyes were functionalized with fullerenes to tune the device performance. In 2007, Kim *et al.* reported the first example of fullerene-based dyes. This novel dye consisted of a fullerene attached *via* diaminohydrocarbon linkers of different

Fig. 8 Upper and central parts – chemical structures of fullerene derivatives applied in n-type DSSC. Lower part – chemical structures of fullerene derivatives applied in p-type DSSC.

alkyl chains to the N3 dye – (*cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium(II)) – Fig. 8.¹⁸⁷ The use of this dye increased the V_{oc} by around 20 mV, while the photocurrents were maintained with respect to N3 devices. As a consequence, the overall efficiency increased from 4.0 to 4.5% for devices without and with fullerene-based dyes, respectively. On one hand, the TiO_2 Fermi levels shift towards more negative values due to changes in the basicity caused by the linkers. On the other hand, fullerenes create a hydrophobic layer around TiO_2 and, in turn, retard the recombination between injected electrons in the TiO_2 electrode and I_3^- . The synergy of both aspects impacts V_{oc} and FF. Following this work, Shiga *et al.* reported on fullerenes bearing several carboxylic acid groups to graft TiO_2 nanoparticles – Fig. 8.¹⁸⁸ The successful charge mediation *via* the fullerene was demonstrated by assays regarding the incident photon-to-current efficiency, in which the Soret band was clearly observed. Although the efficiencies were very low (0.53%), the stability was exceptionally with values up to 3000 hours.

A final example came from Pleux *et al.* in 2011.¹⁸⁹ They tested a set of three different perylene monoimides (PMI) linked to either naphthalene diimide (NDI) or fullerene with the aim to enhance the efficiency in NiO-based DSSC – Fig. 8. Transient

absorption measurements in the nanosecond regime revealed that the presence of fullerenes extends the charge separated state lifetime compared to just PMI. Pleux *et al.* corroborated a flow of electrons from the valence band of NiO to PMI and, finally, to the fullerene. Such a cascade of electron transfer is likely to support device efficiencies with values reaching 0.04 and 0.06% when Co^{II}/Co^{III} and I^-/I_3^- electrolytes were utilized, respectively. More striking than the efficiencies is the remarkable incident photon-to-current efficiency, which features values of up to 57% combined with photocurrent densities of 1.88 mA cm^{-2} .

The first graphene derivative used as a dye in DSSC was reported by Yan *et al.* in 2010.¹⁹⁰ It shows a well-defined molecular size, high extinction coefficients of around $1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 591 nm, and excellent solubility owing to the peripheral 1,3,5-trialkyl-substituted phenyl substituents – Fig. 9. Notable is the lack of a linker to attach to the TiO_2 electrodes. In line with this comes the observation that by just immersing the electrode into toluene/ethanol solutions at 50°C for 96 hours the electrodes were barely colored reaching optical densities of only 0.2 at 591 nm. This led to poor photocurrent densities of around $200 \text{ }\mu\text{A cm}^{-2}$ and V_{oc} s of 0.48 V. The low photocurrents were attributed to the weak electronic coupling

Fig. 9 Upper part – chemical structure of a graphene derivative used as a dye in DSSC. Lower part – chemical structures of porphyrin (left) and porphycene (right) derivatives used to prepare graphene hybrids.

between the graphene dye and the TiO_2 electrode. Nevertheless, the authors concluded that the use of carboxylic groups as linkers to protect the graphene core and to interact with TiO_2 might enhance the device performance.

Kiessling *et al.* have recently demonstrated another way to explore nanographene-based dyes.^{191,192} Their approach is based on the direct formation of nanographene hybrids *via* exfoliation of single and few graphene sheets from graphite using a planar photoactive stabilizer that, in addition, provides the necessary linker for the electrodes. To this end, they used electron donating porphyrins and electron accepting porphycenes with carboxylic and catechol linkers, respectively – Fig. 9. The preparation of nanographene hybrids involves a number of steps.

Firstly, graphite is added to porphyrin/porphycene solutions and the mixtures are ultrasonicated between 30 min and 1 hour. Secondly, to remove all graphitic particles, the suspension is centrifuged. When an increase of the nanographene hybrid concentration is required, more graphite is added to the supernatant and the aforementioned steps are repeated. As a matter of fact, such a treatment resulted in the direct exfoliation of graphite, owing to the immobilization of the porphyrin/porphycene onto the basal plane of graphene sheets. To prove the presence of nanographene, Raman, AFM, TEM, and femto-second transient absorption spectroscopy techniques – Fig. 10 – were employed. Although the presence of single layer nanographene is *per se* a relevant finding, the most valuable results

Fig. 10 Upper part – TEM image of a drop-casted dispersion of a porphyrin/nanographene (left) and porphycene/nanographene (right) hybrids onto a lacey carbon grid with scale bars of 250 and 100 nm, respectively. Central part – Raman spectra of porphyrin/nanographene (left) and porphycene/nanographene (right) hybrids drop-coated onto silicon oxide wafers upon laser excitation at 532 nm. Lower part – differential absorption spectra (visible and near-infrared) obtained upon pump probe experiments (387 nm) of porphyrin/nanographene (left) and porphycene/nanographene (right) hybrids in argon saturated THF at room temperature – the time is stated in ps.

came from transient absorption experiments. The latter indicated that the immobilization of porphyrins or porphycenes onto the basal plane of graphene leads to chemical doping of graphene. For instance, electron donating porphyrins caused an electron density shift to graphene that is revealed once excited by the generation of the one electron oxidized radical cation of the porphyrin (*i.e.*, positive bands at 490 and 625 nm) and conduction band electrons in nanographene (*i.e.*, negative bands at 890 and 1025 nm) – Fig. 10. In stark contrast, the use of an electron accepting porphycene induced an electron density shift from graphene. In this case, the characteristics of the electron transfer product relate to the one electron reduced radical anion of porphycene (*i.e.*, positive band at 840 nm) and valence band holes generated in nanographene (*i.e.*, negative band at 1000 nm), respectively – Fig. 10. Importantly, this example is the first one, in which the electron donor feature of graphene is shown in solution.

As a complement, the authors demonstrated that the unique electronic features of the nanographene hybrids are a real asset with regard to improving the device performance in DSSC. Importantly, SEM images of the modified electrodes revealed that the linker is operative to attach to the electrodes. Devices, which were fabricated using porphyrin/nanographene hybrids, performed superiorly, that is, 50% higher efficiency, compared to reference devices fabricated with the respective porphyrin.¹⁹¹ The graphene flakes prevent aggregation, which is beneficial for the charge regeneration process with the porphyrin, on one hand, and act as a Schottky barrier reducing the charge recombination processes, on the other hand.¹⁹¹

In contrast, porphycene/nanographene was implemented in two types of electrodes, that is, ZnO and NiO-based electrodes.¹⁹² In this manner, the benefits that stem from the unique electronic features of this hybrid were demonstrated. ZnO-based devices prepared with the new hybrid outperformed devices with only the porphycenes. In NiO-based devices an opposite scenario emerged. In ZnO-based devices, a cascade of electron transfer from the nanographene to the porphycene and, finally, to the ZnO is operative, since the latter acts as an electron accepting electrode. In NiO-based devices, which are an electron donating material, a disruption of the electron flow is at force, since graphene acts as electron donating material and, in turn, competes with NiO in the overall reduction of the porphycene.

Conclusion and outlook

All the achievements reached by implementing multifunctional nanocarbons into the different parts of DSSC have led to a new momentum in the field. So far the major benefits include better charge transport and higher charge collection yields in nanocarbon-based electrodes, improved ionic diffusion and regeneration in solid-state electrolytes when nanocarbons are used as integrative components, and designing cascades of electron transfer in nanocarbon-based hybrid dyes to tune the device performance. In addition, transparent and flexible electrodes based on multifunctional nanocarbons are currently investigated as a viable alternative to traditional ITO and FTO

electrodes. For more details in this regard, we recommend these two excellent reviews that complement this work.^{123,124}

No doubt, the improvement by means of implementing multifunctional nanocarbons has been clearly demonstrated. Still, the highest efficiencies reported for nanocarbon-based DSSC are appreciably lower than those found for optimized DSSC, namely porphyrins in combination with cobalt complex based electrolytes.¹⁵ It is, however, important to emphasize that nanocarbons have not yet been introduced into the latter, which underpins their prospect even more.

To date, there are, at least, three major current challenges to tackle in the field of nanocarbon-based DSSC. Firstly, a more sound understanding regarding the nature of the nanocarbon/metal oxide interfaces and the control over charge transfer, charge trapping, and charge transport processes is crucial. In this context, the impact of nanocarbons functionalized with, for example, different linkers such as carboxyl, pyridine, *etc.* is a viable strategy. Secondly, in the case of nanocarbon-based, solid-state, and iodine-free electrolytes, the impact of multifunctional nanocarbons on the electrolyte regeneration at the counter-electrode interface is not settled. In any of the reported examples platinum-based counter-electrodes have been utilized without screening the individual steps of the catalytic cycle. Therefore, the best counter-electrode for nanocarbon-based electrolytes remains at this point undetermined. In addition, the impact of multifunctional nanocarbons on other solid-state electrolytes has not yet been explored. Thirdly, in-depth investigations on inter- and intramolecular electron transfer, electron injection into the electrode, dye regeneration, and electron recombination at the electrode interface should guide future design of new nanocarbon-based dyes towards better operating devices. Equally important aspects that remain to be explored are the right electrode architecture in terms of materials, pore distribution, thickness, *etc.* as well as the right type of electrolytes.

Besides the above-mentioned aspects, it is important to consider up-scaling techniques used by the industry, namely roll-to-roll printing, *etc.* As a matter of fact, DSSC are easily fabricated by using well-established printing techniques on flexible plastics or metal foils. Owing to the compatibility of multifunctional nanocarbons with all sorts of substrates, it is expected that printable nanocarbon-based DSSC should be easily achieved. Recent examples aimed at the reduction of hazard components used in device fabrication. For instance, graphene and carbon nanohorn interlayers have emerged as viable alternatives to TiCl_4 -based interlayers without compromising device performances. Notably, all of the aforementioned are not only applicable to DSSC but also to other optoelectronic devices, H_2 -production, and battery technologies.

The prospect of multifunctional nanocarbons, in general, and graphene, in particular, seems to be unsurpassable. Nevertheless, the exploration of ways to master them for solution process techniques, on one hand, and to control their properties through chemical functionalization, on the other hand, constitutes a major challenge. For instance, the synthesis of soluble/processable graphene-type molecules as models for large area graphene sheets is still in its infancy. In this context, a few prominent

examples have demonstrated possible strategies. Firstly, the introduction of alkyl-substituents provides soluble graphene hybrids with a large aromatic core. Nevertheless, a clear relationship between materials properties and device performance has to be established. Secondly, exfoliating nanographene by means of ultrasonication in combination with molecular stabilizers like porphyrins, phthalocyanines, porphycenes, *etc.* constitutes another promising strategy to handle graphene for solution-based process techniques. There are, however, open questions regarding the control over the exfoliation in terms of flake sizes, the relationship between size and stability in solution as well as those with the device performance, *etc.*

Taking all of the aforementioned into account, the use of multifunctional nanocarbons in DSSC has evolved into an emerging field ready to realize necessary breakthroughs. Once appropriate means to handle and to control the electronic features of multifunctional nanocarbons in solution have been established by the scientific community, the industrial production of carbon-based printable DSSC might become a reality in the not so distant future.

Acknowledgements

For financial support the DFG (Cluster of Excellence – Engineering of Advanced Materials), ICMM, and GSMS are gratefully acknowledged. R.D.C. acknowledges the Humboldt Foundation for support. We would like to convey our most sincere gratitude to the reviewers for their accurate and valuable revisions and suggestions.

Notes and references

- 1 N. Armaroli and V. Balzani, *Angew. Chem., Int. Ed.*, 2007, **46**, 52.
- 2 O. Morton, *Nature*, 2006, **443**, 19.
- 3 R. F. Service, *Science*, 2005, **309**, 548.
- 4 E. Becquerel, *Comptes Rendus*, 1839, **9**, 561.
- 5 W. Smith, *Nature*, 1873, **7**, 303.
- 6 R. Ohl, *US Pat.*, 2402662, USA, 1941.
- 7 M. A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon and R. Noufi, *Prog. Photovoltaics*, 1999, **7**, 311.
- 8 C. A. Nelson, N. R. Monahan and X.-Y. Zhu, *Energy Environ. Sci.*, 2013, **6**, 3508.
- 9 M. A. Green, *Third Generation Photovoltaics*, Springer-Verlag, Berlin, 2003.
- 10 B. O'Regan and M. Gratzel, *Nature*, 1991, **353**, 737.
- 11 G. Dennler, M. C. Scharber and C. J. Brabec, *Adv. Mater.*, 2009, **21**, 1323.
- 12 C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. J. Jia and S. P. Williams, *Adv. Mater.*, 2010, **22**, 3839.
- 13 http://www.konarka.com/index.php/site/pressreleasedetail/konarka_technologies_advances_award_winning_power_plastic_solar_cell_effici.
- 14 http://www.heliatek.com/newscenter/latest_news/heliatek-erzielt-mit-107-effizienz-neuen-weltrekord-fur-seine-organische-tandemzelle/?lang=en.
- 15 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diao, C. Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629.
- 16 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, **499**, 316.
- 17 D. Tasis, N. Tagmatarchis, A. Bianco and M. Prato, *Chem. Rev.*, 2006, **106**, 1105.
- 18 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
- 19 A. K. Geim, *Science*, 2009, **324**, 1530.
- 20 D. M. Guldi, G. G. A. Rahman, V. Sgobba and C. Ehli, *Chem. Soc. Rev.*, 2006, **35**, 471.
- 21 D. M. Guldi and N. Martín, *Carbon Nanotubes and Related Structures*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010.
- 22 D. M. Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski and N. Martín, *Chem. Soc. Rev.*, 2009, **38**, 1587.
- 23 S. E. Habas, H. A. S. Platt, M. F. A. M. van Hest and D. S. Ginley, *Chem. Rev.*, 2010, **110**, 6571.
- 24 M. A. Green, *Prog. Photovoltaics*, 2001, **9**, 123.
- 25 M. Morgano, I. Perez-Wurfl and S. Binetti, *Sci. Adv. Mater.*, 2011, **3**, 388.
- 26 G. Conibeer, M. Green, R. Corkish, Y. Cho, E. C. Cho, C. W. Jiang, T. Fangsuwannarak, E. Pink, Y. D. Huang, T. Puzzer, T. Trupke, B. Richards, A. Shalav and K. L. Lin, *Thin Solid Films*, 2006, **511**, 654.
- 27 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.
- 28 P. R. F. Barnes, K. Miettinen, X. E. Li, A. Y. Anderson, T. Bessho, M. Gratzel and B. C. O'Regan, *Adv. Mater.*, 2013, **25**, 1881.
- 29 A. Listorti, B. O'Regan and J. R. Durrant, *Chem. Mater.*, 2011, **23**, 3381.
- 30 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.
- 31 R. S. Ruoff and K. M. Kadish, *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Pennington, 1999.
- 32 P. V. Kamat, *Fullerenes and Nanotubes: Materials for the New Chemical Frontier: Proceedings of the International Symposium on Fullerenes, Nanotubes, and Carbon Nanoclusters*, Electrochemical Society, Pennington, 2005.
- 33 N. Martín, L. Sanchez, B. Illescas and I. Perez, *Chem. Rev.*, 1998, **98**, 2527.
- 34 D. M. Guldi and V. Sgobba, *Chem. Commun.*, 2011, **47**, 606.
- 35 S. Iijima, *Nature*, 1991, **354**, 56.
- 36 M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly and R. S. Ruoff, *Science*, 2000, **287**, 637.
- 37 M. F. Yu, B. S. Files, S. Arepalli and R. S. Ruoff, *Phys. Rev. Lett.*, 2000, **84**, 5552.
- 38 J. Robertson, *Mater. Today*, 2004, **7**, 46.
- 39 P. G. Collins and P. Avouris, *Sci. Am.*, 2000, **283**, 62.
- 40 S. Zhu and G. Xu, *Nanoscale*, 2010, **2**, 2538.
- 41 M. Yudasaka, S. Iijima and V. Crespi, *Carbon Nanotubes*, Springer, Berlin, Heidelberg, 2008.
- 42 S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai and K. Takahashi, *Chem. Phys. Lett.*, 1999, **309**, 165.

- 43 T. Azami, D. Kasuya, R. Yuge, M. Yudasaka, S. Iijima, T. Yoshitake and Y. Kubo, *J. Phys. Chem. C*, 2008, **112**, 1330.
- 44 E. Sani, L. Mercatelli, S. Barison, C. Pagura, F. Agresti, L. Colla and P. Sansoni, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 2994.
- 45 A. Izadi-Najafabadi, T. Yamada, D. N. Futaba, M. Yudasaka, H. Takagi, H. Hatori, S. Iijima and K. Hata, *ACS Nano*, 2011, **5**, 811.
- 46 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
- 47 Y. Zhang, Y.-W. Tan, H. L. Stormer and P. Kim, *Nature*, 2005, **438**, 201.
- 48 R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres and A. K. Geim, *Science*, 2008, **320**, 5881.
- 49 D. K. James and J. M. Tour, *Acc. Chem. Res.*, 2012, **46**, 2307.
- 50 U. Hofmann and A. Frenzel, *Ber. Dtsch. Chem. Ges. B*, 1930, **63**, 1248.
- 51 C. Gómez-Navarro, R. T. Weitz, A. M. Bittner, M. Scolari, A. Mews, M. Burghard and K. Kern, *Nano Lett.*, 2007, **7**, 3499.
- 52 C. Drahl, *Chem. Eng. News*, 2010, **88**, 8.
- 53 K. Fredenhagen and H. Suck, *Z. Anorg. Allg. Chem.*, 1929, **178**, 353.
- 54 J. M. Englert, C. Dotzer, G. Yang, M. Schmid, C. Papp, J. M. Gottfried, H.-P. Steinrück, E. Spiecker, F. Hauke and A. Hirsch, *Nat. Chem.*, 2011, **3**, 279.
- 55 M. Quintana, E. Vazquez and M. Prato, *Acc. Chem. Res.*, 2013, **46**, 138.
- 56 Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nat. Nanotechnol.*, 2008, **3**, 563.
- 57 J. M. Englert, J. Röhr, C. D. Schmidt, R. Graupner, M. Hundhausen, F. Hauke and A. Hirsch, *Adv. Mater.*, 2009, **21**, 4265.
- 58 J. Malig, N. Jux, D. Kiessling, J.-J. Cid, P. Vázquez, T. Torres and D. M. Guldi, *Angew. Chem., Int. Ed.*, 2011, **50**, 3561.
- 59 J. Malig, A. W. I. Stephenson, P. Wagner, G. G. Wallace, D. L. Officer and D. M. Guldi, *Chem. Commun.*, 2012, **48**, 8745.
- 60 I. Forbeaux, J. M. Themlin and J. M. Debever, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **58**, 16396.
- 61 K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov and A. K. Geim, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 10451.
- 62 S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong and S. Iijima, *Nat. Nanotechnol.*, 2010, **5**, 574.
- 63 D. M. Guldi and R. D. Costa, *J. Phys. Chem. Lett.*, 2013, **4**, 1489.
- 64 M. Grätzel, *Nature*, 2001, **414**, 338.
- 65 M. Grätzel, *Pure Appl. Chem.*, 2001, **73**, 459.
- 66 M. Grätzel, *Acc. Chem. Res.*, 2009, **42**, 1788.
- 67 <http://www.g24i.com/>.
- 68 <http://www.materialsviews.com/graetzel-dsscs-used-in-new-ipad-keyboard/>.
- 69 http://www.sony.net/SonyInfo/csr/SonyEnvironment/technology/solar_cells.html.
- 70 M. Durr, A. Bamedi, A. Yasuda and G. Nelles, *Appl. Phys. Lett.*, 2004, **84**, 3397.
- 71 K. Uzaki, S. S. Pandey and S. Hayase, *J. Photochem. Photobiol., A*, 2010, **216**, 104.
- 72 J. Usagawa, M. Kaya, Y. Ogomi, S. S. Pandey and S. Hayase, *J. Photonics Energy*, 2011, **1**, 011110.
- 73 N. Andrew, F. Michael, K. Robert, C. Yi-Bing and B. Udo, *Nanotechnology*, 2008, **19**, 295304.
- 74 A. Nattestad, A. J. Mozer, M. K. R. Fischer, Y.-B. Cheng, A. Mishra, P. Bäuerle and U. Bach, *Nat. Mater.*, 2010, **9**, 31.
- 75 J. He, H. Lindström, A. Hagfeldt and S.-E. Lindquist, *Sol. Energy Mater. Sol. Cells*, 2000, **62**, 265.
- 76 F. Odobel, L. C. Le Pleux, Y. Pellegrin and E. Blart, *Acc. Chem. Res.*, 2010, **43**, 1063.
- 77 J. A. Anta, E. Guillén and R. Tena-Zaera, *J. Phys. Chem. C*, 2012, **116**, 11413.
- 78 J. R. Durrant, S. A. Haque and E. Palomares, *Coord. Chem. Rev.*, 2004, **248**, 1247.
- 79 E. A. Gibson, L. Le Pleux, J. Fortage, Y. Pellegrin, E. Blart, F. Odobel, A. Hagfeldt and G. Boschloo, *Langmuir*, 2012, **28**, 6485.
- 80 P. Qin, J. Wiberg, E. A. Gibson, M. Linder, L. Li, T. Brinck, A. Hagfeldt, B. Albinsson and L. Sun, *J. Phys. Chem. C*, 2010, **114**, 4738.
- 81 E. A. Gibson, A. L. Smeigh, L. Le Pleux, J. Fortage, G. Boschloo, E. Blart, Y. Pellegrin, F. Odobel, A. Hagfeldt and L. Hammarström, *Angew. Chem., Int. Ed.*, 2009, **48**, 4402.
- 82 L. Le Pleux, A. L. Smeigh, E. Gibson, Y. Pellegrin, E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarstrom and F. Odobel, *Energy Environ. Sci.*, 2011, **4**, 2075.
- 83 M. K. Nazeeruddin, E. Baranoff and M. Graetzel, *Sol. Energy*, 2011, **85**, 1172.
- 84 D. Li, D. Qin, M. Deng, Y. Luo and Q. Meng, *Energy Environ. Sci.*, 2009, **2**, 283.
- 85 S. M. Zakeruddin and M. Grätzel, *Adv. Funct. Mater.*, 2009, **19**, 2187.
- 86 J. N. de Freitas, A. F. Nogueira and M.-A. De Paoli, *J. Mater. Chem.*, 2009, **19**, 5279.
- 87 Q. Li, J. Zhao, B. Sun, B. I. Lin, L. Qiu, Y. Zhang, X. Chen, J. Lu and F. Yan, *Adv. Mater.*, 2012, **24**, 945.
- 88 P. Docampo, S. Guldin, M. Stefiak, P. Tiwana, M. C. Orilall, S. Hüttner, H. Sai, U. Wiesner, U. Steiner and H. J. Snaith, *Adv. Funct. Mater.*, 2010, **20**, 1787.
- 89 Y. Saito, T. Azechi, T. Kitamura, Y. Hasegawa, Y. Wada and S. Yanagida, *Coord. Chem. Rev.*, 2004, **248**, 1469.
- 90 C. S. Karthikeyan, H. Wietasch and M. Thelakkat, *Adv. Mater.*, 2007, **19**, 1091.
- 91 T. Leijtens, I.-K. Ding, T. Giovenzana, J. T. Bloking, M. D. McGehee and A. Sellinger, *Nano Lett.*, 2012, **6**, 1455.
- 92 J. K. Koh, J. Kim, B. Kim, J. H. Kim and E. Kim, *Adv. Mater.*, 2011, **23**, 1641.

- 93 X. Z. Liu, W. Zhang, S. Uchida, L. P. Cai, B. Liu and S. Ramakrishna, *Adv. Energy Mater.*, 2010, **22**, E150.
- 94 S. Ferrere and B. A. Gregg, *J. Phys. Chem. B*, 2001, **105**, 7602.
- 95 J. Zhao, X. Shen, F. Yan, L. Qiu, S. Lee and B. Sun, *J. Mater. Chem.*, 2011, **21**, 7326.
- 96 J. H. Wu, S. C. Hao, Z. Lan, J. M. Lin, M. L. Huang, Y. F. Huang, P. J. Li, S. Yin and T. Sato, *J. Am. Chem. Soc.*, 2008, **130**, 11568.
- 97 M. Wang, X. Pan, X. Fang, L. Guo, W. Liu, C. Zhang, Y. Huang, L. Hu and S. Dai, *Adv. Mater.*, 2010, **22**, 5526.
- 98 P. Wang, S. M. Zakkeeruddin, I. Exnar and M. Grätzel, *Chem. Commun.*, 2002, 2972.
- 99 Y. Zhou, W. Xiang, S. Chen, S. Fang, X. Zhou, J. Zhou and Y. Lin, *Chem. Commun.*, 2009, 3895.
- 100 P. Wang, S. M. Zakeeruddin, R. Humphry-Baker and M. Grätzel, *Chem. Mater.*, 2004, **16**, 2694.
- 101 N. Yamanaka, R. Kawano, W. Kubo, N. Masaki, T. Kitamura, Y. Wada, M. Watanabe and S. Yanagida, *J. Phys. Chem. B*, 2007, **111**, 4763.
- 102 H. Wang, X. Zhang, F. Gong, G. Zhou and Z.-S. Wang, *Adv. Mater.*, 2012, **24**, 121.
- 103 Y. Zhao, J. Zhai, J. L. He, X. Chen, L. Chen, L. B. Zhang, Y. X. Tian, L. Jiang and D. B. Zhu, *Chem. Mater.*, 2008, **20**, 6022.
- 104 N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe and S. Yanagida, *Chem. Commun.*, 2005, 740.
- 105 H. Tian and L. Sun, *J. Mater. Chem.*, 2011, **21**, 10592.
- 106 L. E. Polander, A. Yella, B. F. E. Curchod, N. Ashari Astani, J. Teuscher, R. Scopelliti, P. Gao, S. Mathew, J.-E. Moser, I. Tavernelli, U. Rothlisberger, M. Grätzel, M. K. Nazeeruddin and J. Frey, *Angew. Chem., Int. Ed.*, 2013, **52**, 8731.
- 107 Y. Bai, Q. Yu, N. Cai, Y. Wang, M. Zhang and P. Wang, *Chem. Commun.*, 2011, **47**, 4376.
- 108 T. Daeneke, A. J. Mozer, T. H. Kwon, N. W. Duffy, A. B. Holmes, U. Bach and L. Spiccia, *Energy Environ. Sci.*, 2012, **5**, 7090.
- 109 T. Daeneke, T.-H. Kwon, A. B. Holmes, N. W. Duffy, U. Bach and L. Spiccia, *Nat. Chem.*, 2011, **3**, 211.
- 110 P. Wang, S. M. Zakeeruddin, J.-E. Moser, R. Humphry-Baker and M. Grätzel, *J. Am. Chem. Soc.*, 2004, **126**, 7164.
- 111 Z. Zhang, P. Chen, T. N. Murakami, S. M. Zakeeruddin and M. Grätzel, *Adv. Funct. Mater.*, 2008, **18**, 341.
- 112 J.-H. Yum, E. Baranoff, F. Kessler, T. Moehl, S. Ahmad, T. Bessho, A. Marchioro, E. Ghadiri, J.-E. Moser, C. Yi, M. K. Nazeeruddin and M. Grätzel, *Nat. Commun.*, 2012, **3**, 631.
- 113 Y.-S. Yen, H.-H. Chou, Y.-C. Chen, C.-Y. Hsu and J. T. Lin, *J. Mater. Chem.*, 2012, **22**, 8734.
- 114 M. V. Martínez-Díaz, G. de la Torre and T. Torres, *Chem. Commun.*, 2010, **46**, 7090.
- 115 M.-H. Yeh, C.-L. Sun, J.-S. Su, L.-Y. Lin, C.-P. Lee, C.-Y. Chen, C.-G. Wu, R. Vittal and K.-C. Ho, *Carbon*, 2012, **50**, 4192.
- 116 Y. Xiao, J. Wu, C. Cheng, Y. Chen, G. Yue, J. Lin, M. Huang, L. Fan and Z. Lan, *Chin. Sci. Bull.*, 2012, **57**, 2329.
- 117 H. Ellis, N. Vlachopoulos, L. Häggman, C. Perruchot, M. Jouini, G. Boschloo and A. Hagfeldt, *Electrochim. Acta*, 2013, **107**, 45.
- 118 Y. Wang, C. Zhao, D. Qin, M. Wu, W. Liu and T. Ma, *J. Mater. Chem.*, 2012, **22**, 22155.
- 119 W. Wei, H. Wang and Y. H. Hu, *J. Mater. Chem. A*, 2013, **1**, 14350.
- 120 Y.-F. Chiang, C.-H. Tsai, P. Chen and T.-F. Guo, *Sol. Energy*, 2012, **86**, 1967.
- 121 G. H. Guai, Q. L. Song, C. X. Guo, Z. S. Lu, T. Chen, C. M. Ng and C. M. Li, *Sol. Energy*, 2012, **86**, 2041.
- 122 R. Trevisan, M. Döbbelin, P. P. Boix, E. M. Barea, R. Tena-Zaera, I. Mora-Seró and J. Bisquert, *Adv. Energy Mater.*, 2011, **1**, 781.
- 123 L. J. Brennan, M. T. Byrne, M. Bari and Y. K. Gunko, *Adv. Energy Mater.*, 2011, **1**, 472.
- 124 H. Wang and Y. H. Hu, *Energy Environ. Sci.*, 2012, **5**, 8182.
- 125 E. Ramasamy, W. J. Lee, D. Y. Lee and J. S. Song, *Appl. Phys. Lett.*, 2007, **90**, 173103.
- 126 W. J. Lee, E. Ramasamy, D. Y. Lee and J. S. Song, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 814.
- 127 C. T. Hsieh, B. H. Yang and J. Y. Lin, *Carbon*, 2011, **49**, 3092.
- 128 D. W. Zhang, X. D. Li, H. B. Li, S. Chen, Z. Sun, X. J. Yin and S. M. Huang, *Carbon*, 2011, **49**, 5382.
- 129 L. Kavan, J.-H. Yum and M. Grätzel, *Nano Lett.*, 2011, **11**, 5501.
- 130 L. Kavan, J.-H. Yum, M. K. Nazeeruddin and M. Grätzel, *ACS Nano*, 2011, **5**, 9171.
- 131 D. W. Zhang, X. D. Li, H. B. Li, S. Chen, Z. Sun, X. J. Yin and S. M. Huang, *Carbon*, 2011, **49**, 5382.
- 132 M. Wu, X. Lin, A. Hagfeldt and T. Ma, *Chem. Commun.*, 2011, **47**, 4535.
- 133 M. Wu, X. Lin, A. Hagfeldt and T. Ma, *Angew. Chem., Int. Ed.*, 2011, **50**, 3520.
- 134 J. S. Jang, D. J. Ham, E. Ramasamy, J. W. Lee and J. S. Lee, *Chem. Commun.*, 2010, **46**, 8600.
- 135 M. Wu, X. Lin, Y. Wang, L. Wang, W. Guo, D. Qi, X. Peng, A. Hagfeldt, M. Grätzel and T. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 3419.
- 136 L. N. Ma, J. B. Ji, F. W. Yu, N. Ai and H. T. Jiang, *Microporous Mesoporous Mater.*, 2013, **165**, 6.
- 137 H. H. Choi, J. Park and R. K. Singh, *Appl. Surf. Sci.*, 2005, **240**, 7.
- 138 S. R. Kim, M. K. Parvez and M. Chhowalla, *Chem. Phys. Lett.*, 2009, **483**, 124.
- 139 T. Chen, W. Hu, G. Song, G. H. Guai and C. Li, *Adv. Funct. Mater.*, 2012, **22**, 5245.
- 140 R. Casillas, F. Lodermeier, R. D. Costa, M. Prato and D. M. Guldi, *Adv. Energy Mater.*, 2013, DOI: 10.1002/aenm.201301577.
- 141 J. Song, Z. Yin, Z. Yang, P. Amaladass, S. Wu, J. Ye, Y. Zhao, W.-Q. Deng, H. Zhang and X.-W. Liu, *Chem. – Eur. J.*, 2011, **17**, 10832.
- 142 J. Durantini, P. P. Boix, M. Gervaldó, G. M. Morales, L. Otero, J. Bisquert and E. M. Barea, *J. Electroanal. Chem.*, 2012, **683**, 43.

- 143 N. Yang, Y. Zhang, J. E. Halpert, J. Zhai, D. Wang and L. Jiang, *Small*, 2012, **8**, 1762.
- 144 Z. Peining, A. S. Nair, Y. Shengyuan, P. Shengjie, N. K. Elumalai and S. Ramakrishna, *J. Photochem. Photobiol., A*, 2012, **231**, 9.
- 145 W. Zhou, K. Pan, C. Tian, Y. Qu, L. Zhang, C.-C. Sun and H. Fu, *J. Photochem. Photobiol., A*, 2009, **207**, 306.
- 146 F. Xu, J. Chen, X. Wu, Y. Zhang, Y. Wang, J. Sun, H. Bi, W. Lei, Y. Ni and L. Sun, *J. Phys. Chem. C*, 2013, **117**, 8619.
- 147 W. Zhou, K. Pan, L. Zhang, C. Tian and H. Fu, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1713.
- 148 G. D. Sharma, D. Daphnomili, K. S. V. Gupta, T. Gayathri, S. P. Singh, P. A. Angaridis, T. N. Kitsopoulos, D. Tasis and A. G. Coutsolelos, *RSC Adv.*, 2013, **3**, 22412.
- 149 J. Fan, S. Liu and J. Yu, *J. Mater. Chem.*, 2012, **22**, 17027.
- 150 A. Kongkanand, R. M. Dominguez and P. V. Kamat, *Nano Lett.*, 2007, **7**, 676.
- 151 P. Brown, K. Takechi and P. V. Kamat, *J. Phys. Chem. C*, 2008, **112**, 4776.
- 152 T. Sawatsuk, A. Chindaduang, C. Sae-kung, S. Pratontep and T. Gamolwan, *Diamond Relat. Mater.*, 2009, **18**, 524.
- 153 J. Yu, J. Fan and B. Cheng, *J. Power Sources*, 2011, **196**, 7891.
- 154 W. J. Lin, C. T. Hsu and Y. C. Tsai, *J. Colloid Interface Sci.*, 2011, **358**, 562.
- 155 C. Y. Yen, Y. F. Lin, S. H. Liao, C. C. Weng, C. C. Huang, Y. H. Hsiao, C. C. M. Ma, M. C. Chang, H. Shao, M. C. Tsai, C. K. Hsieh, C. H. Tsai and F. B. Weng, *Nanotechnology*, 2008, **19**, 045604.
- 156 W.-C. Chang, Y.-Y. Cheng, W.-C. Yu, Y.-C. Yao, C.-H. Lee and H.-H. Ko, *Nanoscale Res. Lett.*, 2012, **7**, 166.
- 157 L. Yang and W. W.-F. Leung, *Adv. Mater.*, 2013, **25**, 1792.
- 158 H.-I. Kim, G.-H. Moon, D. Monllor-Satoca, Y. Park and W. Choi, *J. Phys. Chem. C*, 2012, **116**, 1535.
- 159 G. Williams, B. Seger and P. V. Kamat, *ACS Nano*, 2008, **2**, 1487.
- 160 N. Yang, J. Zhai, D. Wang, Y. Chen and L. Jiang, *ACS Nano*, 2010, **4**, 887.
- 161 Y. B. Tang, C. S. Lee, J. Xu, Z. T. Liu, Z. H. Chen, Z. He, Y. L. Cao, G. Yuan, H. Song, L. Chen, L. Luo, H. M. Cheng, W. J. Zhang, I. Bello and S. T. Lee, *ACS Nano*, 2010, **4**, 3482.
- 162 S. Sun, L. Gao and Y. Liu, *Appl. Phys. Lett.*, 2010, **96**, 083113.
- 163 A. Du, Y. H. Ng, N. J. Bell, Z. Zhu, R. Amal and S. C. Smith, *J. Phys. Chem. Lett.*, 2011, **2**, 894.
- 164 A. A. Madhavan, S. Kalluri, D. K. Chacko, T. A. Arun, S. Nagarajan, K. R. V. Subramanian, A. S. Nair, S. V. Nair and M. S. Balakrishna, *RSC Adv.*, 2012, **2**, 13032.
- 165 H. Yang, G. H. Guai, C. Guo, Q. Song, S. P. Jiang, Y. Wang, W. Zhang and C. M. Li, *J. Phys. Chem. C*, 2011, **115**, 12209.
- 166 R. D. Costa, S. Feihl, A. Kahnt, S. Gambhir, D. L. Officer, M. I. Lucio, M. A. Herrero, E. Vázquez, Z. Syrgiannis, M. Prato and D. M. Guldi, *Adv. Mater.*, 2013, **25**, 6513.
- 167 F. Xu, J. Chen, X. Wu, Y. Zhang, Y. Wang, J. Sun, H. Bi, W. Lei, Y. Ni and L. Sun, *J. Phys. Chem. C*, 2013, **117**, 8619.
- 168 G. Katsukis, C. Romero-Nieto, J. Malig, C. Ehli and D. M. Guldi, *Langmuir*, 2012, **28**, 11662.
- 169 H. Wedemeyer, J. Michels, R. Chmielowski, S. Bourdais, T. Muto, M. Sugiura, G. Dennler and J. Bachmann, *Energy Environ. Sci.*, 2013, **6**, 67.
- 170 K. Tennakone, V. P. S. Perera, I. R. M. Kottegoda and G. Kumura, *J. Phys. D: Appl. Phys.*, 1999, **32**, 374.
- 171 J. Xia, N. Masaki, M. Lira-Cantu, Y. Kim, K. Jiang and S. Yanagida, *J. Am. Chem. Soc.*, 2008, **130**, 1258.
- 172 J. K. Koh, J. Kim, B. Kim, J. H. Kim and E. Kim, *Adv. Mater.*, 2011, **23**, 1641.
- 173 K.-S. Jung, S.-B. Lee, Y.-K. Kim, M.-H. Seo, W.-P. Hwang, Y.-W. Jang, H.-W. Park, B.-R. Jin, M.-R. Kim and J.-K. Lee, *J. Photochem. Photobiol., A*, 2012, **231**, 64.
- 174 P. V. Kamat, M. Haria and S. Hotchandani, *J. Phys. Chem. B*, 2004, **108**, 5166.
- 175 H. Usui, H. Matsui, N. Tanabe and S. Yanagida, *J. Photochem. Photobiol., A*, 2004, **164**, 97.
- 176 N. Ikeda and T. Miyasaka, *Chem. Lett.*, 2007, **3**, 466.
- 177 M. S. Akhtar, J. G. Park, H. C. Lee, S. K. Lee and O. B. Yang, *Electrochim. Acta*, 2010, **55**, 2418.
- 178 Y. C. Wang, K. C. Huang, R. X. Dong, C. T. Liu, C. C. Wang, K. C. Ho and J. J. Lin, *J. Mater. Chem.*, 2012, **22**, 6982.
- 179 Y. H. Chang, P. Y. Lin, S. R. Huang, K. Y. Liu and K. F. Lin, *J. Mater. Chem.*, 2012, **22**, 15592.
- 180 Y. Zhang, J. Zhao, B. Sun, X. Chen, Q. Li, L. Qiu and F. Yan, *Electrochim. Acta*, 2012, **61**, 185.
- 181 K. C. Huang, Y. H. Chang, C. Y. Chen, C. Y. Liu, L. Y. Lin, R. Vittal, C. G. Wu, K. F. Lin and K. C. Ho, *J. Mater. Chem.*, 2011, **21**, 18467.
- 182 C. P. Lee, L. Y. Lin, P. Y. Chen, R. Vittal and K. C. Ho, *J. Mater. Chem.*, 2010, **20**, 3619.
- 183 C. P. Lee, M. H. Yeh, R. Vittal and K. C. Ho, *J. Mater. Chem.*, 2011, **21**, 15471.
- 184 I. Ahmad, U. Khan and Y. K. Gun'ko, *J. Mater. Chem.*, 2011, **21**, 16990.
- 185 M. H. Jung, M. G. Kang and M. J. Chu, *J. Mater. Chem.*, 2012, **22**, 16477.
- 186 S. S. Babu, H. Möhwald and T. Nakanishi, *Chem. Soc. Rev.*, 2010, **39**, 4021.
- 187 M. K. Lim, S. R. Jang, R. Vittal, J. Lee and K. J. Kim, *J. Photochem. Photobiol., A*, 2007, **190**, 128.
- 188 T. Shiga and T. Motohiro, *Thin Solid Films*, 2008, **516**, 1204.
- 189 L. L. Pleux, A. L. Smeigh, E. Gibson, Y. Pellegrin, E. Blart, G. Boschloo, A. Hagfeldt, L. Hammarstrom and F. Odobel, *Energy Environ. Sci.*, 2011, **4**, 2075.
- 190 X. Yan, X. Cui, B. Li and L.-S. Li, *Nano Lett.*, 2010, **10**, 1869.
- 191 D. Kiessling, R. D. Costa, G. Katsukis, J. Malig, F. Lodermeier, S. Feihl, A. Roth, L. Wibmer, M. Kehrner, M. Volland, P. Wagner, G. G. Wallace, D. L. Officer and D. M. Guldi, *Chem. Sci.*, 2013, **4**, 3085.
- 192 R. D. Costa, J. Malig, W. Brenner, N. Jux and D. M. Guldi, *Adv. Mater.*, 2013, **25**, 2600.