RICE UNIVERSITY

[Nanomaterials Enabled Dye-sensitized Solar Cells]

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

[Doctor of Philosophy]

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HOUSTON, TEXAS
December 2013
ABSTRACT

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Dye sensitized solar cells (DSCs), as the third generation of solar cells, have attracted tremendous attention for their unique properties. The semi-transparent nature, low-cost, environmental friendliness, and convenient manufacturing conditions of this generation of solar cells are promising aspects of DSCs that make them competitive in their future applications. However, much improvement in many aspects of DSCs’ is required for the realization of its full potential. In this thesis, various nanomaterials, such as graphene, multi wall carbon nanotubes, vertically aligned single wall carbon nanotubes, hybrid structures and etc, have been used to improve the performance of DSCs.

First, the application of graphene covered metal grids as transparent conductive electrodes in DSCs is explored. It is demonstrated that the mechanical properties of these flexible hybrid transparent electrodes, in both bending and stretching tests, are better than their oxide-based counter parts.

Moreover, different kinds of carbon nanotubes, for instance vertically aligned single wall carbon nanotubes, have been used as a replacement for traditional platinum counter electrodes, in both iodine electrolyte, and sulfide-electrolyte. Further, a flexible, seamlessly connected, 3-dimensional vertically-aligned few wall
carbon nanotubes graphene hybrid structures on Ni foil as DSCs’ counter electrodes improve their efficiency significantly. All these nanomaterials enabled DSCs architectures achieve a comparable or better performance than standard brittle platinum/fluorine doped tin oxide combination. The large surface area of such nanomaterials in addition to the high electrical conductivity and their mechanical robustness provides a platform for significant enhancements in DSCs’ performance.
Acknowledgments

I am deeply grateful to my thesis advisor, Professor Jun Lou, for his mentoring throughout my PhD study at Rice University. Without his invaluable guidance, it is impossible for me to reach this point of my academic career. He has generously supported everything I could ever think and expect. Constantly, he shares his unusual wealth of knowledge, critical thinking and experience; moreover he highly encourages motivating. It is truly a fortune that I can have him as my advisor. His mentoring will be a lifelong treasure for me.

I would also like to thank the other members, Dr. Robert H. Hauge, Prof. Pulickel M. Ajayan, and Dr. Robert Vajtai, of my thesis committee. They not only reviewed this work, and more importantly, kindly supported me over various stages of my study and research at Rice University. They discussed with me and encouraged me a lot, which brought me incredible impetus and confidence to carry on this research.

During the five years at Rice, I have the opportunity to learn from many other distinguished scholars, including Prof. Xin Li, Prof. Cary Pint, Prof. James Tour, Prof. Yu Zhu, Dr. Feng Hao, Dr. Liang Gang and many more. I could not list them all, but I thank them all.

In addition, I feel very lucky to have the opportunity to collaborate with Prof. Hong Lin at Tsinghua University. Prof. Hong Lin generously provides access to her DSC works and keeps helping me throughout my whole projects. I benefit
tremendously from her rich experience and unique insight and her help on my research is sincerely appreciated.

During the past five years, I would like to thank my colleagues in Lou research group, Professor Yongjie Zhan, Professor Yang Lu, Professor Zheng Liu, Dr. Yogeeswaran Ganesan, Dr. Hao Lu, Dr. Jiangnan Zhang, Dr. Cheng Peng, Jing Zhang, Sina Najmaei, Phillip E. Loya, Peng Zhang, Bill Song, Linlin Cao, and more, for your generous help in many ways. They helped, assisted and collaborated with me in various aspects. It was so much fun to stay in the lab days and nights because of them. Especially, I would like to thank Emily Hacopian for editing suggestions.

Last but certainly not least, my family has always been there for me with unconditional love and support. This dissertation is dedicated to my parents, who I simply could not owe more. They bring me to the world, raised me and make me who I am. I am so proud of them.
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<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DSCs</td>
<td>Dye sensitized solar cells</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped tin oxide</td>
</tr>
<tr>
<td>GNCS</td>
<td>Guanidinium thiocyanate</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium doped tin oxide</td>
</tr>
<tr>
<td>MPN</td>
<td>2-methoxypropionitrile</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multi wall carbon nanotubes</td>
</tr>
<tr>
<td>NMBI</td>
<td>N-methylbenzimidazole</td>
</tr>
<tr>
<td>N719</td>
<td>[RuL₂(NCS)₂]: 2 TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetra-n-butylammonium)</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>PEN</td>
<td>Polyethylene naphthalate</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PMII</td>
<td>1-propyl-3-methyl-imidazolium iodide</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>RBM</td>
<td>Radial breathing modes</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Single wall carbon nanotubes</td>
</tr>
<tr>
<td>TBP</td>
<td>4-tert-butylpyridine</td>
</tr>
<tr>
<td>TCE</td>
<td>Transparent conductive electrodes</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TTIP</td>
<td>Titanium(IV) tetraisopropoxide</td>
</tr>
<tr>
<td>XRD</td>
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<tr>
<td>VAFWCNTs</td>
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<td>VAMWCNTs</td>
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<td>VASWCNTs</td>
<td>Vertically aligned single wall carbon nanotubes</td>
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Chapter 1

Chapter 1. Introduction of Dye-sensitized solar cells

One of the world’s greatest challenges is energy, which is also the key to maintaining the sustainable development of human society. Interests in solar energy conversion have been growing due to concerns over carbon dioxide emissions and increasing pressure on supply of fossil fuels.1,2,3,4 Meanwhile, the introduction of solar powered devices made from nanomaterials has the potential to impact global economic developments.5,6,7

The solar cell is one of the most important renewable energy sources in the world. Dye-sensitized solar cell (DSC), affiliated with the group of thin film solar cells8, is low-cost, easy to manufacture, and also able to utilize indoor light sources. DSC, also known as the Grätzel cell, was originally co-invented by Brian O’Regan and Michael Grätzel at UC Berkeley9 in 1988. Later, this work was developed by the aforementioned scientists at the École Polytechnique Fédérale de Lausanne (EPFL)
until the publication of the first high efficiency of 7.1%-7.9% in 1991\textsuperscript{10}. Michael Grätzel has been awarded the 2010 Millennium Technology Prize for this invention.\textsuperscript{11} Figure 1-1 shows some current DSC products from Dyesol\textsuperscript{12}, Oxfrod PV\textsuperscript{13} and Power Plastic\textsuperscript{14} on market.

A modern DSC utilizes two main components: a photo anode consisting of light-absorbing dye molecules adsorbed on a highly porous structure semiconductor material with an extremely high surface area, and an electrically conductive counter electrode that catalyzes an electrolyte redox reaction to regenerate electrons for the dye molecules.\textsuperscript{15, 16, 17, 18, 19}
The highest efficiency of the traditional DSC in our lab reaches 9.9%; while the world record is 15%\textsuperscript{20}. Although its current power conversion efficiency (PCE) is less than the best thin-film cells, in theory by achieving grid parity the price/performance ratio of DSC should be able to compete with fossil fuel electrical generation. Commercial applications were held up due to chemical stability problems.\textsuperscript{21} The European Union Photovoltaic Roadmap has forecasted a significant contribution to renewable electricity generation by 2020.\textsuperscript{22}

1.1. Current technology: semiconductor solar cells

Mesoscopic DSCs have recently emerged as a credible alternative to solid-state p-n junction photovoltaic devices in virtue of their great potential to enable more affordable solar-generated electricity using resource-abundant raw materials and energy-saving device processing techniques.\textsuperscript{10,23,24}

A traditional solid-state semiconducting solar cell is made from two doped crystals. One is doped with n-type impurities (n-type semiconductor) which adds additional free conduction band electrons. The other is doped with p-type impurities (p-type semiconductor) that add additional electron holes. When the two doped crystals are in contact, some of the electrons flow from the n-type portion into the p-type to "fill in" the electron holes. Eventually the Fermi levels of the two
materials will be equalized, since more and more electrons will flow across the boundary. The result is a p-n junction at the interface, on each side where charge carriers are accumulated and/or depleted. In silicon, a potential barrier of about 0.6 to 0.7 V is produced by this transfer of electrons.  

When the solar cell is under illumination, electrons on the p-type side of the semiconductor can be excited by the photons of the sunlight, which is also known as photoexcitation. In silicon, enough energy from sunlight can push an electron from the lower-energy valence band into the higher-energy conduction band. When a load is applied, these electrons will flow from the p-type materials into the n-type portion. There is some energy lost during the electrons moving through the external circuit. As soon as the electrons flow back into the p-type section, they will once again re-combine with the valence-band holes. In conclusion, this is how an electrical current can be created by sunlight in a semiconducting solar cell.  

In a semiconductor, the band gap means that only photons with a certain amount of energy, or more, can produce a current. In the case of silicon, there is always sufficient energy the majority of visible light from red to violet. Unfortunately, the higher energy photons, which are positioned at the blue and violet end of the spectrum, have more than enough energy to cross the band gap. The majority of this extra energy is wasted as heat, although some is transferred into the electrons. Another issue is that the n-type material has to be relatively thick in order to have a reasonable chance of capturing a photon. The thick n-type portion also increases the chance of recombination before reaching the p-n junction. Due to these effects, there is an upper limit on the efficiency of silicon solar cells. Currently,
for common modules it is around 12 to 15%, while the best laboratory cells have efficiencies up to 25%. Furthermore, as a result of Shockley–Queisser limit, 30% is the theoretical maximum efficiency for a single band gap solar cells.

The biggest problem with approaching conventional applications is cost: (1) To have reasonable photon capture rates, semiconducting solar cells require a fairly thick layer of doped silicon. (2) Silicon processing is also expensive. Over the last decade, there have been a lot of different efforts to reduce this cost, notably the thin-film approaches; however they also have other limited applications due to the practical problems.

Another aspect of research has been focused on improving efficiency dramatically through the multi-junction approach, however these very high cost cells are only suitable for large commercial deployments. Although the increase in supply has dropped the costs of solar cells suitable for rooftop deployment, the efficiency has not changed dramatically.

1.2. Introduction of Dye-sensitized solar cells

1.2.1. Construction

In the original design from Grätzel and O'Regan, the DSC consists 3 primary parts:

On top is a transparent photo electrode made of fluoride-doped tin dioxide (SnO$_2$:F, FTO) on the back of a substrate, typically glass. On the other side of this conductive plate is a highly porous structure of thin layer titanium dioxide (TiO$_2$)
with an extremely high surface area. TiO$_2$ can only absorb a small portion of the solar photons in the UV. The photo electrode is then immersed in solvent based molecular sensitizers, which is a mixture of a photosensitive ruthenium-polypyridine dye. After soaking, a thin layer of the dye molecules are covalently bonded to the surface of the semiconducting materials (TiO$_2$).

To prepare another plate, a thin layer of the iodide based electrolyte is spread over a platinum metal. To prevent the liquid electrolyte from leaking, the two plates are then packaged and sealed together. Notably Grätzel and O'Regan used several "advanced" materials, which are inexpensive compared to the silicon needed for normal solar cells, since they avoid the expensive manufacturing steps. For example, TiO$_2$ is already widely used as paints and varnishes as well as paper and plastics.

One of the efficient DSCs devices uses ruthenium-based molecular dye, e.g. cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) RuL$_2$(NCS)$_2$ : 2 TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetrabutylammonium) (N719) and cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) RuL$_2$(NCS)$_2$.2H$_2$O (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid) (N3). Dye molecules are bound to the surface of TiO$_2$ via carboxylate moieties.

After light absorption, the dye jumps from the ground state to the excited state. The electrons are rapidly injected into the TiO$_2$. After further diffusing through the sintered particle network, the electrons are collected by the transparent
conducting oxide (TCO) electrode. A redox shuttle, I-/I₃⁻, dissolved in a solution, will regenerate dye via reduction. Eventually the oxidized form diffuses to the counter electrode, which completes the circuit.²⁷

|Conductive Materials|

FTO has been widely used as the standard conductive layer in DSCs. FTO is nearly transparent (~ 80-85%) with low sheet resistance (~ 20-30 Ohm/sq). Additionally, FTO is resistive to most electrolyte systems used in DSCs, which makes it an ideal electrode material. Unfortunately, FTO, as with the related ITO, is very brittle. For flexible DSCs, the widely used transparent electrode ITO-polyethylene terephthalate (PET) can only survive a few bending cycles due to easy crack-propagation. As a result, although the remaining components in the DSCs are potentially fully flexible, present flexible DSCs work best under conditions in which they are not bent, or are only bent a few times.

A transparent electrode is therefore needed for flexible DSCs, which can be bent, folded and fitted to curved surfaces.

|Photo electrodes|

In DSC, the semiconducting material of photo electrodes is made of sintered nanoparticles, mainly TiO₂, ZnO or WO₃. Relying on trap-limited diffusion through the semiconductor, the electron transport is a slow mechanism, which limits the device efficiency. Longer wavelengths of radiation might help.
As the photo electrode, a ~12 \( \mu \text{m} \) thick film of transparent ~20 nm diameter \( \text{TiO}_2 \) nanoparticles (typically called transparent film) are covered with a ~4 \( \mu \text{m} \) thick film of ~400 nm diameter \( \text{TiO}_2 \) nanoparticles (typically called scattering film), which can scatter photons back into the transparent film. Moreover a high temperature sintering of nanoparticles (about 450 °C) restrict the fabrication to rigid solid and robust substrates.

**Counter electrodes**

In the DSC, the counter electrode material choice is one of the key factors in achieving a highly efficient DSC device. A Pt thin film deposited on the Fluorine doped tin oxide (FTO) substrate typically serves as the counter electrode in conventional DSCs.\(^{28,29,30}\) While offering excellent electrical conductivity, catalytic activity, and corrosion resistance, Pt is also an expensive and relatively rare element.

To lower materials cost and achieve feasible large-scale production, an alternative counter electrode material with excellent high conductivity as well as superior electrocatalytic activity is highly desirable. Due to the low cost, high durability, excellent catalytic activity and electrical conductivity, carbon based materials have been utilized as an effective alternative counter electrode for many years.\(^{18,31,32,33}\) Carbon nanotubes and nanohorns,\(^{18}\) carbon black\(^{32}\) and graphite,\(^{33}\) have all been tested as potential counter electrodes.
Therefore, the proper morphology of carbon materials can be an alternative material for counter electrode for DSC.

Dye

In DSCs, to pursue high PCE, the dye, which is usually nanometer sized, is one of the key components. In order to capture a reasonable amount of the photons from the incoming light, the layer of dye molecules needs to be relatively thick. To figure out this problem, a nanomaterial in a 3-D matrix is hired as a scaffold to hold enough dye molecules. Currently, this scaffolding is offered by the semiconducting material, which serves double-duty. Ruthenium Dyes are the most popular ones.

![Chemical structure of Black Dye](image)

Figure 1-2 "Black Dye", an anionic Ru-terpyridine complex. Reprinted with permission from reference 34. Copyright Dyesol.

In early experimental cells (circa 1995), the dyes used were only sensitive in the high-frequency portion of the solar spectrum, which is in the UV and blue. Newer versions of dye, which had much wider frequency response, were quickly introduced (circa 1999). It is notable that "triscarboxy-ruthenium terpyridine" \([\text{Ru}(4,4',4''-\text{COOH})_3\text{-terpy})(\text{NCS})_3]\) is efficient in the low-frequency range of red
and IR light. The dye with wide spectral response results has a deep brown-black color, and is named as "black dye", shown in Figure 1-2.\textsuperscript{35} The dyes show an excellent ability of converting a photon into an electron. Originally it can be around 80%, but almost perfect conversion can be achieved by further improvement in more recent dyes. Considering the "lost" 10% mostly coming from the optical losses in top electrodes, the overall efficiency is up to 90%.

In terms of stability, after subjected to 50 million cycles, no discernible performance degradation of "black dye" was observed. This means the "black dye" system was stable for ten years' worth of exposure under sun in Switzerland. Unfortunately, in high-light situations the dye is easy to breakdown. To address these concerns, some extensive research has been carried out over the last decade. For instance, copper-diselenium [Cu(In,Ga)Se\textsubscript{2}] offers higher conversion efficiencies; while 1-ethyl-3 methylimidazolium tetrocyanoborate [EMIB(CN)\textsubscript{4}] is extremely light- and temperature-stable.

In recent years, cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) [RuL\textsubscript{2}(NCS)\textsubscript{2}.2H\textsubscript{2}O (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid), (N3)], cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetraethylammonium) [RuL2(NCS)\textsubscript{2} : 2 TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetraethylammonium), (N719)], and cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-dinonyl-2'-bipyridyl)ruthenium(II), [RuLL'(NCS)\textsubscript{2} . 2 H\textsubscript{2}O (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid ;L' = 4,4'-dinonyl-2,2'-bipyridine), (Z907)] are the most popular ones. Figure 1-3 and Table 1-1 shows the details and description of these three dyes.
Figure 1-3. Ruthenium-based N-3, N-719 and Z-907 dyes. Reprinted with permission from reference 36. Copyright Dyesol.

<table>
<thead>
<tr>
<th>Synonym</th>
<th>Product</th>
<th>Description</th>
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| N-3     | cis-Bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium(II) | • Pioneering dye for use in DSSCs.  
• Sensitizes wide band gap semiconductors such as titanium oxide up to wavelengths of 700 nm. | 703206    |
| N-719   | Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)ruthenium(II) | • Modified dye to increase device voltage.  
• Highly studied, high performance dye. | 703214    |
| Z-907   | cis-Bis(isothiocyanato)(2,2’-bipyridyl-4,4’-dicarboxylato)(4,4’-di-nonyl-2’-bipyridyl)ruthenium(II) | • Hydrophobic dye.  
• Very efficiently sensitizes wide band-gap titanium oxide up to 750 nm. | 703168    |
Table 1-1  Dyesol dyes offered by Aldrich Materials Science. Reprinted with permission from reference 36. Copyright Dyesol.

|Electrolyte|

Currently, certified record PCE up to 11% has been achieved in conjunction with polypyridylruthenium complex sensitizers and an organic electrolyte containing ubiquitous I⁻/I₃⁻ redox couple. Nevertheless, there are several substantial drawbacks of this I⁻/I₃⁻ redox shuttle hindering its practical application and further efficiency enhancement, which mainly include (a) corrosiveness towards most metal substrates or metallic current-collectors in commercial modules, (b) large mismatch between its oxidation potential (0.35 V vs. the normal hydrogen electrode (NHE)) and the dye oxidation potential (~ 1.0 V vs. NHE), and therefore limitations on the achievable open-circuit voltage ($V_{oc}$) and (c) limitations on the short-circuit photocurrent density ($J_{sc}$) arising from competitive absorption of visible light by triiodide species, which will be more significant in back-illuminated devices based on metal substrates or devices with ionic liquid electrolytes containing a much higher iodide/iodine concentration.

Clearly, to overcome these disadvantages, development of non-corrosive redox mediators, with reduced mismatch between the oxidation potential of the dye and the redox couple is of vital importance not only to address the current PCE bottleneck but also to promote the commercialization of such promising photovoltaic devices. Wang et al. reported a promising organic disulfide/thiolate redox couple, 5,5′-dithiobis(1-methyltetrazole)/1-
methyltetrazole-5-thiolate ($\text{T}_2/\text{T}^-$). A PCE up to 6.4\% was achieved in conjunction with a Z907Na sensitizer under standard illumination conditions (AM 1.5G, 100 mW cm$^{-2}$).\textsuperscript{48} Following this pioneering work, this organic $\text{T}_2/\text{T}^-$ redox couple has attracted special interests due to its negligible corrosion properties in combination with weak visible light absorption and reasonable PCE.\textsuperscript{54, 55, 56, 57, 58} Meanwhile, by employing a bulky organic chromophore in conjunction with a ferrocene/ferrocenium redox couple, Udo and Spiccia et al. have demonstrated the feasibility of fabricating a 7.5\% efficiency DSC measured under standard testing conditions (STC).\textsuperscript{47} More importantly, studies on the replacement of $\text{I}_3^-/\text{I}^-$ redox system by cobalt polypyridine complexes have drawn much attention due to their lower visible light absorption, higher redox potential and the reduced corrosiveness towards metallic conductors.\textsuperscript{43, 59, 60, 61} However, the initial overall PCE obtained with these cobalt electrolytes was inferior compared with the $\text{I}_3^-/\text{I}^-$ couple, especially under higher incident light intensities. This has been attributed to the slower mass transport\textsuperscript{62, 63} and faster charge recombination of the injected electrons with the oxidized redox species.\textsuperscript{64, 65} The real boost in efficiency was achieved with the use of $\text{Co}^{2+}/3^+$ redox shuttles attaining a large open-circuit photovoltage in the order of 0.9 V by the groups of Dr L. Sun and A. Hagfeldt in 2010.\textsuperscript{45} In order to further increase the PCE, many efforts since then have been focused on the molecular structure of organic dyes,\textsuperscript{66, 67, 68, 69, 70, 71} TiO$_2$ film’s morphology, thickness and porosity,\textsuperscript{72, 73} cobalt mediator’s redox potential,\textsuperscript{74} and cathode composition,\textsuperscript{75, 76, 77} reaching efficiencies of more than 10\%.\textsuperscript{78, 79} For instance, recent evidence suggests that the introduction of long-chain alkyloxy groups in the dye structure or
incorporation of a blocking layer on the TiO$_2$ surface could efficiently retard the unwanted charge recombination process.$^{45, 65, 80}$ Donor-$\pi$-acceptor (D-$\pi$-A) sensitizers, endowed with such specific blocking groups, have recently shown to achieve $V_{oc}$ values exceeding 0.8V in conjunction with Co$^{(II/III)}$tris(bipyridyl) redox electrolytes.$^{42, 45, 66, 67, 68}$ Furthermore, meticulous device and sensitizer engineering have recently made it possible to reach a new PCE record up to 12.3% by Grätzel et. al.$^{79}$ The specific molecular design of [5,15-bis(2,6-dioctoxyphenyl)-10-(bis(4-hexylphenyl)amino)-20-(4-carboxyphenyl ethynyl)porphyrinato]Zinc(II) (YD2-o-C8) greatly retards the rate of interfacial back electron transfer from the conduction band of the nanocrystalline TiO$_2$ film to the oxidized cobalt mediator, which enables attainment of strikingly high open-circuit photovoltage approaching 1V. These reports explore new opportunities towards further optimization of the DSCs performance, especially by modifying the optoelectronic properties of the organic dyes to reduce the effective optical gap, fine tuning the novel redox shuttle structures to control their redox potential, using alternative solvents to better dissolve the redox couple and facilitate diffusivity, and importantly developing alternative cathode materials for those novel iodine-free redox shuttles (Error! Reference source not found.).
As a popular choice in high-efficiency DSCs, Pt has been recognized as a benchmark material in the field of cathodic catalyst owing to its excellent conductivity and high catalytic activity.\cite{81, 82, 83, 84} Nevertheless, Pt has obvious drawbacks, particularly, the high costs and limited availability,\cite{85} which restricts its application to the mass production of DSCs. In addition, recent studies have shown that Pt might be dissolved in electrolytes containing the iodide/iodine redox couple, forming PtI\(_4\) compound and consequently leading to a 40% increment in the activation energy and a drop in the current density for the triiodide reduction.\cite{33, 86, 87, 88} Moreover, it has been identified that the contribution of a cathode to the total series resistance occurs in two ways: a) by a charge transfer resistance at the cathode surface, \(R_{ct}\), and b) by an ohmic layer resistance, \(R_s\). Conventional Pt
cathodes show poor catalytic activity toward the aforementioned promising iodine-free redox couples and a high $R_{ct}$, which results in a poor fill factor (FF) and relatively moderate PCE.\textsuperscript{59, 68} It has been pointed out that a low FF with sulfur-functionalized redox mediators most likely resulted from the adsorption of the sulfur atoms on the cathode surface and thus slowed the catalytic reduction of the oxidized species at the Pt cathode.\textsuperscript{48, 56, 57}

Therefore, it is imperative to seek suitable Pt-free catalysts for these promising redox shuttles. During the last decade, with the introduction of a series of low-cost, high-efficiency cathode catalysts, such as CoS,\textsuperscript{89} TiN,\textsuperscript{90} carbon materials,\textsuperscript{91} and some organic polymers (poly(3,4-alkylenedioxythiophene, PEDOT),\textsuperscript{92, 93} and polyaniline\textsuperscript{94}), the research interests on alternative Pt-free catalysts has increased drastically. It is believed that the breakthrough in cathode catalysts could promote progress towards reducing material costs of DSCs, thus rendering them more competitive among various photovoltaic devices.

Apparently, most of the recent advances in these efficient catalysts have been realized by judiciously controlling the morphology of nanomaterials or by utilizing the collective properties of nano-assembly systems.

Finally, our previous review work\textsuperscript{95} also highlights the importance of matchup between redox couples and suitable catalysts, as well as the crucial issues that should be addressed in the pursuit of developing low-cost and high-catalytic cathodes for DSCs.
1.2.2. Mechanism

The two functions provided by silicon have been separated in a traditional DSC’s design. Normally the silicon provides both the photoelectrons and the electric field, which can separate the charges and then generate a current. In the DSC, the semiconductor material is solely used for charge transport; while a separate photosensitive dye provides photoelectrons. At the surfaces between the dye, semiconducting materials and electrolyte, the charge separation happens.

The main steps in a DSC go as follows:

Step 1: Photons are converted to the current.

1. The Ru complex photosensitizers on the TiO2 surface absorb the incident photon.

2. The dye molecules are excited from the ground state (S) to the excited state (S*), shown in Equation 1-1. This can be understood as electron-hole pair. The excited electrons are then injected into the conduction band of the semiconducting material, i.e. TiO2 electrode. This finally oxidizes the photosensitizer (S+), shown in Equation 1-2.

\[
S + h\nu \rightarrow S^*
\]

Equation 1-1 The dye molecules are excited from the ground state (S) to the excited state (S*)

\[
S^* \rightarrow S^+ + e^- (TiO_2)
\]

Equation 1-2 The excited electrons (S*) oxidizes the photosensitizer (S+).
3. The injected electrons are in the conduction band of TiO$_2$. These electrons diffused between TiO$_2$ nanoparticles toward the back contact, and finally reach the counter electrode through the circuit.

4. Electrons from the I$^-$ ion redox mediator will be accepted by the oxidized photosensitizer (S$^+$), which leads to regeneration of the ground state (S). At the same time, the I$^-$ is oxidized to I$_3^-$, shown in Equation 1-3.

\[
S^+ + e^- \rightarrow S
\]

**Equation 1-3 Regeneration of the ground state.**

5. I$_3^-$, which plays as the oxidized redox mediator, transports toward the counter electrode with diffusion, and then is reduced to I$^-$ ions, shown in Equation 1-4.

\[
I_3^- + 2e^- \rightarrow 3I^-
\]

**Equation 1-4 I$_3^-$ is reduced to I$^-$ ions.**

A diagram illustrating the key kinetic processes occurring in a working DSC is given in Figure 1-5. $^{95}$ Mimicking the natural photosynthesis process, light is first absorbed by an organic chromophore adsorbed to the surface of TiO$_2$ nanoparticles ($k_1$). The excited dye molecule rapidly injects an electron into the TiO$_2$ conduction band ($k_2$), which is ultimately the source of the photocurrent. A redox shuttle in the organic solution is employed to regenerate the dye ($k_3$), while diffusion of the oxidized form of the redox shuttle ($D_o$) to be reduced at the cathode completes the circuit. Concurrently, these processes compete with several back reactions which inhibit the efficient operation of a DSC including the decay (either radiative or
nonradiative) of the chromophore’s excited state \((k_1)\) prior to injection as well as back-electron transfer from the TiO\(_2\) nanoparticle to the oxidized dye \((k_4)\) or the oxidized form of the redox shuttle \((k_5)\).

Figure 1-5 Schematic energy diagram displaying the major kinetic processes in the operation of DSCs. The relevant processes of the redox shuttle described in the text: dye regeneration \((k_3)\), diffusion \((D_0)\), and charge recombination with the injected electron in TiO\(_2\) electrode \((k_5)\). Inset shows the energy levels of various redox couple electrolytes.  

1.2.3. Fabrication

DSC fabrication using rigid substrate-compatible procedure. The Fluorine doped tin oxide (FTO) glasses (Pilkington FTO glass Tec 8 &15 Glass, 2.2 mm of thickness) were cleaned using an ultrasonic bath in a detergent solution, consisting of DI water and 200 proof alcohol, and repeated twice. The clean FTO glasses were screen-printed with TiO\(_2\) paste. The paste for the transparent TiO\(_2\)
layer (DSL 18NR-T, Dyesol) was printed four times on the FTO glass plate. A diffusing layer (WER4-O, Dyesol) was then formed once. The printed thickness was controlled to 12.5 μm by successive printing. After each printing, each layer was dried at 125 °C for 6 minutes and then sintered at 500 °C for 60 min in air. Anatase structure was confirmed from the X-ray diffraction (XRD) result. The sintered photo electrode was immersed in the N719, [RuL₂(NCS)₂]: 2 TBA (L = 2,2’-bipyridyl-4,4’-dicarboxylic acid; TBA = tetra-n-butylammonium); PMII, 1-propyl-3-methylimidazolium iodide, B2 N719, Dyesol) solution (3 x10⁻⁴ mol/L) for 24 h at room temperature. The photo electrode and counter electrode were stacked and sealed with a sealant (1170 Series, 25 and 60μm, Solaronix) at 125 °C for 20 s twice. The electrolyte solution, with a composition of 50 mM I₂, 500 mM LiI, 500 mM 4-tert-butylpyridine (TBP), and 2-methoxypropionitrile (MPN) as the solvent, was injected into the cell and sealed using additional sealant.

DSCs fabricated using a flexible substrate compatible procedure. 8μm TiO₂ (Titanium (IV) oxide, ~21 nm particle size, Sigma-Aldrich) was screen printed on clean Indium doped tin oxide (ITO)- Polyethylene naphthalate (PEN). The photo electrodes were sintered at 150 °C for 30 min in air. Other procedures are similar as that for DSC with half rigid substrate. The photo electrode and counter electrode were stacked and sealed with a sealant (1170 Series, 25 and 60μm, Solaronix) at 125 °C for 20 s twice. The electrolyte solution, with a composition of 50 mM I₂, 500 mM LiI, 500 mM 4-tert-butylpyridine (TBP), and 2-methoxypropionitrile (MPN) as the solvent, was injected into the cell and sealed using additional sealant.
To characterize the performance of DSC, we performed testing under standard conditions (AM 1.5, 100 mW/cm\textsuperscript{2}) at 25 °C using a solar simulator (Solar simulator, 94041A, Oriel) calibrated using a reference silicon cell (calibrated at NREL, Oriel). Electrical impedance measurements were tested using a 608C electrochemical analyzer workstation (CH Instruments, Austin, Texas).

The frequency range is from 0.05 Hz to 100,000 Hz, while the magnitude of the modulation signal is 5 mV. Z-View software (v2.9c, Scribner Associates Inc.) was utilized to fit the experimentally measured spectra with the appropriate equivalent circuit.

1.2.4. Measurement

The PCE of a DSC depends on four energy levels of the component: the Fermi level of the photo electrode, the ground state (highest occupied molecular orbital (HOMO)) and the excited state (approximately lowest unoccupied molecular orbital (LUMO)) of the photosensitizer, and the redox potential of the mediator of the in the electrolyte, for instance I\textsuperscript{−}/I\textsubscript{3}\textsuperscript{−}. \textsuperscript{96}

Several important measurements are used to characterize DSCs. The most important is PCE which represents the total amount of electrical power produced for the solar power. Electrical power is the product of current and voltage, so the maximum values for these measurements are important as well, short circuit current densities ($J_{sc}$) and open circuit voltage ($V_{oc}$), respectively.
A solar cell’s quantum efficiency (QE), applying to incident photon to converted electron (IPCE) ratio, indicates the amount of current produced when illuminated by photons of a particular wavelength. QE states a device’s electrical sensitivity to light. To characterize the efficiency at each photon energy level, QE is always measured over a range of different wavelengths, since the photon energy is inversely proportional to its wavelength. When the photon energy is below the band gap, QE is zero. DSCs are extremely efficient in QE terms: (1) The photon is very likely to be absorbed, according to the "depth" in the nanostructure. (2) The dyes are very good at converting the photons to electrons. Most of the energy losses in DSC’s are from the conduction losses in the TiO₂, or optical losses in the photo electrode. For instance, the overall QE of green light is about 90%; while the "lost" 10% mainly comes from the optical losses in photo electrode.

In theory, the $V_{oc}$ of DSCs is simply the difference between the redox potential of the electrolyte and the (quasi-)Fermi level of the TiO₂, about 0.7 V under 1 sun illumination. In terms of $V_{oc}$, value of DSCs is slightly higher than that of silicon solar cells, about 0.7 V compared to 0.6 V. The value of $V_{oc}$ varies in a slightly small range; as a result $J_{sc}$ dominates the real-world differences.

The current world record for prototypes lies at 15%.\textsuperscript{20}
1.3. Advantages and Disadvantages

1.3.1. Advantages

The DSC has a number of attractive features: (1) It is simple to make using conventional roll-printing techniques. (2) It is semi-transparent. (3) Most of the materials used are low-cost. In practice it is hard to eliminate a number of expensive materials, notably platinum and ruthenium.

Currently DSCs are very efficient third-generation solar cells. Compared to the traditional low-cost commercial silicon panels operate between 14% and 17%, other thin-film solar technologies belonged to the new generation of solar cell are typically between 5% and 13%. In "low density" applications like rooftop solar collectors, the DSC attracted a lot of attentions as a replacement for existing technologies, due to its the mechanical robustness and light weight.

Moreover, the process of injecting an electron directly into the TiO₂ is another advantage, compared with a traditional cell, where the electron is "promoted" within the original crystal. Given low rates of production, in theory, the there is a recombination between the high-energy electrons and its own hole by giving off a photon generally without no current generated. Even if this is not a universal case, for an electron, it is still fairly easy to hit a hole left.

Talking about the injection process in the DSC, there is only an extra electron, instead of an implanting hole in the TiO₂. It is energetically possible that the electron will recombine back into the dye. Fortunately, compared to the rate that the dye
regains the electrons from the electrolyte, the recombination rate is quite slow. It is also possible to have the recombination from the species in the electrolyte to TiO$_2$. Considering for optimized devices, this reaction in the photo electrode portion is still rather slow. On the contrary, it is extremely fast for electron transfer between counter electrodes to the species in the electrolyte.

As a result of the pre-discussed favorable "differential kinetics", DSCs can work even in dim conditions. For example, DSC are able to work under cloudy skies indoor light, and non-direct sunlight, whereas traditional solar cells would suffer a "cutout" at some lower limit of illumination. Especially when charge carrier mobility is very low which leads to a huge recombination happened, the cutoff is so low. At this time DSCs are even being proposed for indoor use, for example small devices using the lights in the house.

Similar to most thin-film technologies, a practical advantage is that mechanical robustness of DSC do not directly leads to higher PCE in higher temperatures. In the semiconductor, increasing temperature will "mechanically" promote more electrons into the conduction band. Traditional silicon cells are very fragile, and then require protection cautions, typically by encasing solar cell in a glass box with a metal backing for strength. The protection systems suffer noticeable decreases in PCE as the cells heat up internally. In contrast, built with only a thin layer of conductive plastic, DSCs normally allow radiating away heat much easier, and therefore work at lower internal temperatures.
1.3.2. Disadvantages

Though the dye molecules are highly efficient at converting the absorbed photons into the electrons in the semiconducting material ($\text{TiO}_2$), only photons ultimately produce the current. The photon absorption rate depends upon the solar flux spectrum and upon the absorption spectrum range of photo electrodes. Therefore the maximum possible photocurrent is determined by the overlap between these two spectra. Compared to silicon, in general the current used dyes have poor performance in the red part of the spectrum. These factors is the limitation of the current about 20 mA/cm$^2$, in contrast, a traditional silicon-based solar cell could go up to about 35 mA/cm$^2$. When exposed to ultra violet radiation, the performance of the DSC degrades. In the future, including UV stabilizers, UV absorbing luminescent chromophores and antioxidants may help protect and improve PCE.

The major disadvantage to the DSC design is the liquid electrolyte, which has temperature stability and sealing problems. The liquid electrolyte can freeze at low temperatures, which further lead to power production and potentially ending physical damage. The liquid might expand at higher temperatures, and then result in a series sealing problem. Therefore replacing the liquid electrolyte with a solid state material attracts a lot of attentions. In 2012 an all-solid-state DSC have been reported with 10.2%.\textsuperscript{99}

A third major drawback is volatile organic compounds in the electrolyte solution, which must be sealed carefully. Otherwise these hazardous elements will
harm the environment and human health. For the flexible DSC, the solvents might permeate plastics substrate. This will preclude large-scale outdoor application and further integration into flexible surface or structure.\textsuperscript{100}

Another disadvantage is the cost. Though the DSC is designed for low cost, however several parts, i.e. platinum (catalyst), the ruthenium (dye), and conducting glass or plastic (contact), are still kind of pricy.

Any product is not designed for all the applications. Consider the pre-discussed advantages and disadvantages, any improvement in the DSC, especially PCE, might make a huge difference.

\section*{1.4. Development and Milestones}

It was discovered that organic dyes under illumination can generate electricity at oxide electrodes in the late 1960s.\textsuperscript{101} The phenomenon with chlorophyll extracted from spinach (bio-mimetic or bionic approach) was studied at the University of California at Berkeley, in order to understand and simulate photosynthesis process.\textsuperscript{102} Based on this, electric power generation through the DSC principle was demonstrated and discussed in 1972.\textsuperscript{103} The main challenge was identified as the instability of the dye solar cell. During The following two decades, by optimizing the porosity of the electrode, the efficiency of dye solar cell has been improved, unfortunately the instability was always a problem.\textsuperscript{104}
1.4.1 Year 2003

At the Swiss Federal Institute of Technology, by using amphiphilic ruthenium sensitizer in conjunction, a group of researchers has announced increased the thermo stability of DSC with quasi-solid-state gel electrolyte. The stability of their DSCs matches that of a conventional silicon based solar cell. The cell is stable at 80 °C for 1,000 h.

Previously, this group has prepared a ruthenium amphiphilic dye Z-907 (cis-Ru(H₂dcbp))(dnbpy)(NCS)₂ and a quasi-solid-state gel electrolye with a 3-methoxypropionitrile (MPN)-based liquid electrolyte.

The DSC with the amphiphilic Z-907 dye achieved an PCE of 6.1%. More importantly, this novel device was very stable under soaking with light and thermal stress. The good performance was sustained at 80 °C for 1,000 h, which maintain 94% of its initial value. Under accelerated illumination in a solar simulator for 1,000 h at 55 °C, the efficiency only decreased by less than 5% for cells.

This enhanced performance may come from a decrease in solvent permeation across the sealant. Under both soaking with light and thermal stress, this much improved stabilities of the DSCs has never before reported before. This wok matches the durability criteria applied to solar cells for much more practical outdoor applications.¹⁰⁵ ¹⁰⁶

1.4.2 Year 2006

The first successful solid-hybrid DSCs were reported in 2006. ¹⁰⁷
To get the best trade of between maintaining the high surface area needed for dye adsorption and improving electron transport, an alternate semiconductor morphologies have been designed. They are arrays of nanowires and a combination of nanowires and nanoparticles, which can offer a direct path to the electrode from the semiconductor conduction band. These structures may provide a alternative way to improve the quantum efficiency (QE) of DSCs in the red region of the spectrum. This is also addresses the current limitation discussed before.

To prove the thermal and chemical robustness of the 1-ethyl-3 methylimidazolium tetracyanoborate solar cell, on August in 2006, the novel DSCs were subjected at 80 °C in the dark for 1000 hours, followed by at 60 °C for 1000 hours under light soaking. Getting through the whole procedures, 90% of the initial PCE was maintained. This is the first time that such excellent thermal stability has been reported for a liquid electrolyte with such a high PCE. In contrary, the performance of silicon solar cells declines with increasing temperature. Meanwhile, when increasing the operating temperature up to 60 °C, the DSCs were only negligibly influenced.

1.4.3 Year 2007

At Massey University in New Zealand, Wayne Campbell has explored a wide variety of organic dyes based on porphyrin.\textsuperscript{108} Porphyrin in nature, is the basic building block of the hemoproteins. By using these low-cost dyes, he reports PCE of 5.6%.\textsuperscript{109}
1.4.4 Year 2008

The DSCs with 8.2% PCE using a new solvent-free liquid redox electrolyte has been reported. The electrolyte consists of a melt of three salts. 110

1.4.5 Year 2009

At Georgia Tech, by wrapping around a quartz optical fiber, a group of scientists made DSCs with a higher effective surface area. 111, 112 By removing the cladding from optical fibers, zinc oxide nanowires were able to grow along the surface. With the same surface area, this DSCs are six times more efficient than a zinc oxide (ZnO) cell with the same surface area.[34]. These DSCs only collect light at the tips, but future fiber DSCs could be made to absorb sunlight along the entire length of the fiber.111 Max Shtein in the University of Michigan said “a sun-tracking system would not be necessary for such cells, and would work on cloudy days when light is diffuse”.111

1.4.6. Year 2010

At EPFL and the Université du Québec à Montréalclaim, researchers had overcome two of the DSC’s major issues:113

To get a non-corrosive and transparent electrolyte, "New molecules" have been created, which increase the photo voltage and further improve the output and stability of the DSCs.

Cobalt sulfide, which is far less expensive, more stable, more efficient, and easier to produce in the laboratory, became an alternative counter electrode.114
1.4.7. Year 2011

Tata Steel Europe and Dyesol announced in June 2011 that the development of the world’s largest DSC module can be printed onto steel in a continuous production line. 115

In October, CSIRO and Dyesol announced a “Successful Completion of Second Milestone in Joint Dyesol / CSIRO Project”. Gordon Thompson, Dyesol Director. said, "The materials developed during this joint collaboration have the potential to significantly advance the commercialisation of DSC in a range of applications where performance and stability are essential requirements. Dyesol is extremely encouraged by the breakthroughs in the chemistry allowing the production of the target molecules. This creates a path to the immediate commercial utilisation of these new materials." 39

In November, Tata Steel Europe and Dyesol released the targeted development of “Grid Parity Competitive BIPV solar steel”. This new device does not require government subsidised feed in tariffs. TATA-Dyesol "Solar Steel" Roofing now has been installed on the Sustainable Building Envelope Centre (SBEC) in Shotton, Wales. 116, 117

1.4.8 Year 2012

By using nanotechnology and the conversion of the liquid electrolyte to a solid, the researchers in Northwestern University announced a solution to a primary problem of DSCs, which address the difficulties in using and containing the liquid electrolyte.117.
1.4.9 Year 2013

The fabrication of DSCs with 15.0% PCE has been announced by Michael Gratzel. This new DSCs have been reached by the means of hybrid perovskite CH3NH3PbI3 dye.20

As the young member of solar cell family, DSCs are still at the start of the development cycle. More and more studies have been focused on improving the performance of the DSCs, by using quantum dots, solid-state, and changing the doping of the TiO₂, etc.

1.5. Current Marketing

Though the DSCs are very young in the solar cell families, there are already several series commercial providers now. These companies make a promising availability of DSCs in the near future:118

On 7 October 2008, Dyesol’s new manufacturing facilities have been officially launched in Queanbeyan, Austrila. For the development and large scale manufacture of DSC BIPV, subsequently Dyesol has announced partnerships with Pilkington Glass (Dyetec-Solar) and Tata Steel (TATA-Dyesol. Meanwhile, Singapore Aerospace Manufacturing and a joint Venture with TIMO Korea (Dyesol-TIMO) and Merck, Umicore, CSIRO, Japanese Ministry of Economy and Trade, also join Dyesol as the working relationships.119 120 A three metres long module, which represents a major BIPV breakthrough is shown in Figure 1-6.
Figure 1-6 The module is three metres long and represents a major BIPV breakthrough. 119, 120 Reprinted with permission from reference 119, 120. Copyright Dyesol.

Being a company specialized DSC materials since 1993, Solaronix in Swiss has extended their premises in 2010. Later, Solaronix also host a manufacturing pilot line of DSC modules.121

Founded in 2006, G24 innovations is based in Cardiff, South Wales, UK. G24i claimed the production of the first commercial grade DSCs on 17 October 2007. 122, 123

DSCs with a PCE of 10%, have been developed by Sony Corporation as a level seen as necessary for commercial use. The dedicated DSCs from Sony have been shown in Figure 1-7.
Figure 1-7 Images of DSCs in Sony Corporation

Logitech DSC

Logitech begin to apply the DSCs’ technology into their product, shown in Figure 1-8. ⁵²⁴
Chapter 1 provides the background information of DSC in the last 20 years and the standard assembling technology of the traditional DSCs.

In Chapter 2, the metal grids covered by graphene were used as transparent conductive electrodes in dye sensitized solar cells. The efficiency of dye sensitized solar cells with graphene-on-Pt grids were 0.4%. Compared to the control group, in which the platinum grids were used as a transparent conductive layer, the efficiency of dye sensitized solar cells with graphene was more than two times better. To our knowledge it is the most efficient dye sensitized solar cell to use a graphene-based transparent conductive electrode without a conductive oxide support such as fluorine doped tin oxide or indium doped tin oxide. The dye sensitized solar cell prepared by 150°C as the low temperature processes, which are essential for fabricating flexible dye sensitized solar cells, was fabricated using a hybrid graphene on Ni grids transparent conductive electrode and it exhibited an efficiency of 0.25%. The mechanical properties of the flexible hybrid transparent electrode are better than the oxide-based transparent conductive electrode in both bending and stretching tests. Therefore, the long-term stability of the flexible dye sensitized solar cells could be enhanced by using this new transparent conductive layer.
In Chapter 3, 4 and 5, different kinds of carbon nanotubes, for instance vertically aligned single wall carbon nanotubes, have been used as a replacement for traditional platinum counter electrodes, in both iodine electrolyte, and sulfide-electrolyte. Further, a flexible, seamlessly connected, 3-dimensional vertically-aligned few wall carbon nanotubes graphene hybrid structures on Ni foil as DSCs’ counter electrodes improve their efficiency significantly. All these nanomaterials enabled DSCs architectures achieve a comparable or better performance than standard brittle platinum/FTO combination. The large surface area of such nanomaterials in addition to the high electrical conductivity and their mechanical robustness provides a platform for significant enhancements in DSCs’ performance.

Conclusion and future work were discussed in the Chapter 6.
Chapter 2

Chapter 2. Graphene on Metal Grids as the Transparent Conductive Material for Dye-sensitized Solar Cell

2.1. Traditional conductive materials for Dye-sensitized solar cells

FTO has been widely used as the standard conductive layer in DSCs. FTO is nearly transparent (~ 80-85%) with low sheet resistance (~ 20-30 Ohm/sq). Additionally, FTO is resistive to most electrolyte systems used in DSCs, which makes it an ideal electrode material. Unfortunately, FTO, as with the related ITO, is very brittle. For flexible DSCs, the widely used transparent electrode ITO-polyethylene terephthalate (PET) can only survive a few bending cycles due to easy crack-propagation. As a
result, although the remaining components in the DSCs are potentially fully flexible, present flexible DSCs work best under conditions in which they are not bent, or are only bent a few times. A transparent electrode is therefore needed for flexible DSCs, which can be bent, folded and fitted to curved surfaces.

A number of flexible transparent electrodes have been proposed using materials such as silver nanowires, carbon nanotubes and graphene. Unfortunately, most research is concentrated on the characterization of the transparent electrodes, with less research regarding the application of those materials to DSCs. This is partially due to the corrosive nature of iodine-based electrolyte of DSCs and relative high sheet resistance of most potential FTO substitution materials. For example, silver nanowires are not compatible with the electrolyte system in DSCs cells. Among those materials, graphene has been proven to be a promising material for the transparent electrode. Considering its stability and conductivity, graphene could be the best transparent electrode candidate for flexible DSCs. However, the conductivity of graphene strongly depends on its method of production. The wet chemistry-based graphene exfoliation techniques produce graphene oxide (GO) that is an oxidized form of graphene. GO has low conductance and needs to be reduced chemically and/or thermally to partially restore its conductivity. In addition, the thermal annealing of GO requires treatment at temperatures that are often destructive to polymer-based flexible substrates. Therefore, the best performing reduced graphene oxide (rGO) electrode-based DSC, to the best of our knowledge,
has a PCE of only 0.26% (with an active area of ~0.11 cm²). One of the reasons could be the poor quality of the rGO, showing relatively high sheet resistance. In comparison to the rGO, graphene produced by chemical vapor deposition (CVD) exhibits higher quality and conductivity. Unfortunately, although conductive CVD graphene-based transparent electrodes have been reported, there has been no demonstration of the use of CVD graphene as the transparent electrode in DSCs. The reason for this could be that CVD graphene requires doping to reach similar sheet resistance as conductive oxide, and such doping is generally incompatible with the electrolyte system in DSCs.

2.2. Novel conductive material as the replacement of Fluorine doped tin oxide or Indium doped tin oxide

Recently, a new hybrid graphene on metal grids (graphene/metal grids) transparent electrode was fabricated and the performance of the electrode was comparable with ITO. Additionally, this new hybrid transparent electrode exhibits high bending test flexibility. The hybrid electrode was bent to a cylinder 1 cm in diameter. The sheet resistance was low and stable up to 500 bending cycles. It was conjectured that this new transparent electrode hybrid would provide arate to make flexible DSCs with enhanced stability and flexibility.
Figure 2-1 Schematic illustrations of transparent electrode and a DSC. Left: The graphene on Pt grids (graphene/Pt grids) hybrid transparent electrode. The grids size and grids line width in the figure are only illustrative and are not scaled with the graphene molecular structure. Right: A DSC atop the hybrid graphene electrode.

In this work a CVD-derived graphene/metal grids was used as the transparent conductive layer while adopting both standard and low temperature processing techniques for rigid (Figure 2-1) and flexible DSC fabrications, respectively. The high performance graphene based flexible transparent electrodes were used to fabricate DSCs and the PCE was improved compared to those fabricated using rGO transparent electrodes.
2.3. Preparation and characterization

TCE fabrication: the transparent electrodes were fabricated based on a modified literature procedure. The glass substrates (Premiere® brand 9101 microscope slides) were cut into 1 inch × 1 inch square samples. The square samples were cleaned in a fresh piranha solution (7:3 mixture of 98% H₂SO₄ / 30% H₂O₂. Caution: The mixture is strongly oxidizing and may detonate upon contact with organic material. The substrates were then rinsed with deionized water. Photoresist (Shipley 1813) was spun onto the substrate (4000 rpm, 60 s). The samples were baked for 60 s at 90 °C and then exposed using the prepared grids mask. After being soaked in chlorobenzene for 60 s, the samples were blown dry with N₂ and baked again for 60 s at 90 °C. The chlorobenzene soak treatment helped to form an undercut in the following development step. Then the samples were developed by MICROPOSIT MF-319 developer (45 s). The samples were sputtered with 5 nm Ti and 100 nm Pt or Ni using a CrC-150 sputter coater (for the metal grids fabrication on flexible substrates, e-beam evaporation was used instead of sputtering). In the final step, the photoresist was lifted off by acetone and metal grids were formed. Graphene growth and transferring procedures are the same as previously disclosed. Briefly, the graphene was grown on the copper foil by using chemical vapor deposition method. A thin layer of PMMA (Poly(methyl methacrylate)) was spun coated on the surface of graphene. The PMMA coated sample was transferred to the etching solution and the copper was removed. The PMMA coated graphene
was then transferred onto the metal grids substrate. Finally, the PMMA was removed by acetone. \(^{133}\)

**Novel DSC preparation**

**DSC fabrication using rigid substrate-compatible procedure.** A 12 \(\mu\)m diffusion TiO\(_2\) layer (DSL 18NR-T, Dyesol) and 8 \(\mu\)m scattering layer (WER4-O, Dyesol) were screen-printed onto the hybrid TCE glass as prepared above. Other procedures are the same to DSC fabrication using rigid substrate-compatible procedure under Chapter 1.2.

**DSCs fabricated using a flexible substrate compatible procedure.** 8 \(\mu\)m TiO\(_2\) (\(~\)21 nm particle size, Sigma-Aldrich) was screen printed on clean TCE. Other procedures are the same to the normal preparation mentioned in DSCs fabricated using a flexible substrate compatible procedure under Chapter 1.2.

**Characterization.** The transmittance spectrum was obtained by a UV-vis-NIR spectrometer (Shimadzu). The efficiency of the DSC was tested under standard conditions (AM 1.5, 100 mW/cm\(^2\)) at 25 \(^\circ\)C using a solar simulator (94041A, Oriel) calibrated using a reference silicon cell (calibrated at NREL, Oriel), as stated under Chapter 1.2. The active area of the DSC was 16 mm\(^2\) (Table 1). EIS tests were carried out on an electrochemical workstation (CHI 650C) in the frequency range of 0.1 Hz to 100 kHz.

**DSC using graphene/ Pt grids as TCE**
A modified procedure based on the literature\textsuperscript{133} was used to fabricate the graphene/metal grids transparent electrodes for this work. In the original procedure, the metal film was deposited and then the photolithography and wet-etching procedure were used to generate the grids patterns. However, this method is limited by the compatibility of the etchant and photoresist. Metals such as Pt cannot be used due to lack of a suitable etchant. Here we used a lift-off procedure to prepare the metal grids. The key step in this modified procedure was to soak the exposed photoresist in chlorobenzene. This additional step enables the formation of undercut features that are crucial for successful patterning of large areas. Figure 2-2a,b shows the graphene/Pt grids on glass substrates, while Figure 2-2c,d are graphene on nickel grids (Graphene/Ni grids) fabricated on flexible transparent substrates. In Figure 2-2e, the transmittance of the Ni grids and the hybrid film is above 80\% through the visible region, which proves that the electrode is highly transparent. The new procedure is applicable to many metals and substrates, providing better opportunities to design a superior DSC.
Figure 2-2 Images and characterization of the graphene/metal grids hybrid photo electrodes. (a) The graphene/Pt grids hybrid photo electrode on glass. The orange area is comprised of TiO$_2$ nanomaterials with dye particles (100 × 100 × 10 µm; the metal grids size is 100 µm × 100 µm and metal grids line width is 10 µm). (b) Optical image of the graphene/Pt hybrid film structure (100 × 100 × 10 µm). (c) A bent graphene/Ni grids hybrid electrode (100 × 100 × 10 µm) on polyethylene terephthalate (PET). (d) Optical image of the graphene/Ni hybrid film structure (100 × 100 × 10 µm). (e) Transmittance of the graphene/Ni grids hybrid film (100 × 100 × 10 µm). (f) Scanning electron microscope (SEM) image of the crack that is highlighted by arrow, along the Pt metal grids after coating the TiO$_2$ protection layer.
Many metals can be used to fabricate the graphene/hybrid transparent electrode, however, only few of them can survive in the iodine based electrolyte. Metal grids made of gold, silver and copper, although highly conductive, were found to quickly degrade in contact with the electrolyte. In this work, Pt and Ni were used to make the metal grids due to their high stability in the electrolyte solution and relatively high conductivity. However, Pt is highly catalytic in the iodide/triiodide redox couple reaction. Electrons collected by the Pt grids will be lost due to fast combination with triiodide triggered by the catalytic property of Pt.\textsuperscript{28,29,30} To avoid contact between Pt and the electrolyte, the grids were covered by a thin layer of compact TiO\textsubscript{2} as a protective layer. The TiO\textsubscript{2} protective layer was prepared using three different procedures: (1) 5 nm, 10 nm, 30 nm or 50 nm of Ti was sputtered or e-beam evaporated and then oxidized by O\textsubscript{2} plasma or heated at 100 °C in air to form TiO\textsubscript{2}. (2) 110 nm of TiO\textsubscript{2} was e-beam evaporated. (3) A precursor TiO\textsubscript{2} sol solution was prepared by mixing 5 mL acetic acid and 6.3 mL titanium(IV) tetraisopropoxide (TTIP) in 50 mL ethanol. The precursor solution was left at room temperature for 2 d without stirring to form the sol solution. The sol solution was then diluted to 5%, 10%, 15%, and 50% (v/v) in ethanol, and each concentration was spin-coated separately on top of the graphene covered metal grids. For methods (1) and (2), cracks close to the edge of the metal grids were always present (Figure 2-2f). The presence of the cracks might be due to the surface contractions while cooling after the sputtering or evaporation steps. The electrolyte can easily contact the metal grids through these cracks, and consume the electrons from the Pt grids.
Hence, there is no clear photovoltaic effect observed for the DSC cells fabricated using methods 1 and 2. When the TiO$_2$ protective layer was prepared by using method 3, a better photovoltaic performance was observed.

2.4. Performance of the new transparent conductive electrode in Dye sensitized solar cells

![Figure 2-3 J-V curves of the DSCs with the graphene/metal grids hybrid structures. The black line represents the J-V curve of the DSC with Pt grids only, the red line shows the J-V curve of the DSC with graphene on the Pt grids, and the blue line illustrates the J-V curve of the DSC with graphene/Ni grids.](image)

As shown in Figure 2-3, with a protection layer made from 10% (v/v) TiO$_2$ sol solution in ethanol, the efficiency of DSC with Pt grids as the conductive layer was
0.17% (Table 2-1). The efficiency of DSC with the graphene/Pt grids as the conductive layer of the DSC was 0.4%; 1.4 times more than that without graphene. The graphene/Pt grids hybrid electrode also has a larger short circuit current, which indicates that graphene helps to collect electrons from the anode of the DSC. Compared to the grids-only electrode, the short circuit current ($J_{sc}$) increased up to 254%. Although the open circuit voltage ($V_{oc}$) of the DSC with graphene/metal grids decreased, which is mainly due to the change of work function of the anode materials, the combined effects lead to an increase of the PCE. Future studies on modulating the working function of graphene-based hybrid electrodes might further improve the efficiency of the solar cells.\textsuperscript{146}

<table>
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<tr>
<th>Dye-Sensitized Solar Cell Performance $^{[a]}$</th>
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<td><strong>Entry</strong></td>
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$^{[a]} V_{oc}$=open-circuit voltage; $J_{sc}$=short-circuit photocurrent density; FF=fill factor

Table 2-1 Dye-Sensitized Solar Cell Performance under 1 sun Illumination (AM 1.5G, 100 mW cm$^{-2}$)
The grids size of the Pt grids and Ni grids are both 100 µm × 100 µm and the grids line width is grids 10 µm grids. Only entry 2 had the protective TiO₂ layer, which was prepared by spin-coating 10% TiO₂ sol solution in ethanol. All three entries used glass substrates. Only entry 3 was prepared under 150°C procedures for the anode of flexible DSCs; while the first two entries were following the traditional 500°C procedures for the photo electrode of rigid DSCs.

Figure 2-4 shows the results from the electrical impedance spectroscopy (EIS) measurement under -0.7 V bias voltage. Our simulation model (Figure 2-4b) is different from the traditional equivalent circuit (Figure 2-4c). In most cases the interface between the FTO/electrolyte is negligible, due to the slow recombination at the interface. In this DSC system with Pt grids, the electrolyte could leak through the grids’ edge (Figure 2-4f). As a result, one more interface between the Pt grids/electrolyte is necessary in the EIS analysis. At the same time, in Figure 2-4 (a), the radius of the second semicircle of the DSCs with Pt grids only (~44 Ω) is smaller than that of the DSCs with graphene/Pt girds (~56 Ω). This comparison indicates the graphene and TiO₂ protection layer reduces the recombination reaction between the Pt grids and the electrolyte, which results in an increase in $J_{sc}$. Bolotin’s recent work also established that the thin layer graphene could inhibit the corrosion of underlying metals. Since the $J_{sc}$ of our device is still quite low, we think the recombination reaction still exists. In the future, better quality graphene without tares could improve the performance of this novel DSC by further blocking the
recombination between the liquid iodide based electrolyte and the underlying Pt grids.

Figure 2-4 EIS results of the DSCs with and without graphene. (a) Nyquist plots of the DSCs with and without graphene. (b) The equivalent circuit used in the fitting process of the DSCs in this work. (c) The equivalent circuit used in the fitting process of the traditional DSCs with FTO conductive material as reference.

Low temperature processed DSC using graphene/Ni grids as the TCE

Using a modified fabrication procedure, a different TCE can be used in flexible DSCs. It is noted that even traditional Pt counter electrodes currently used in flexible DSCs develop cracks after several bending cycles, degrading the performances of such cells. The low temperature processing technique developed in this work is fully compatible with polymer-based flexible substrates, making a fully flexible and durable DSC technologically viable.
Considering the 500°C annealing for the TiO₂ protection layer, the protection layer cannot be used to improve the performance of DSC with graphene/Pt grids. Therefore, Ni metal (Figure 2-2c,d) was used to replace Pt, since it is fairly stable in iodine-based electrolyte and has no catalytic effect like Pt. Moreover, from Figure 2-2e, the graphene/Ni grids electrode is highly transparent, with a transmittance of higher than 80% from 300 nm to 1200 nm. In addition, the graphene/Ni grids hybrid electrodes do not need the TiO₂ coating to form a workable solar cell, although the sheet resistance of the Ni grids is \( \sim 40 \pm 10 \, \Omega/\square \), which is higher than that of Pt grids, at \( \sim 15 \pm 5 \, \Omega/\square \). Adopting the fabrication procedures compatible with flexible DSCs, the efficiency of the DSCs with graphene/Ni grids is 0.25%. The open voltage is 0.33 V while the short circuit current is 1.33 mAcm\(^{-2}\). For a control group, the efficiency of DSCs with only the Ni grids without graphene as conductive layer was close to 0%.
Figure 2-5 Normalized change in electrical resistance as the function of strain in PET/ITO and PET/Ni grids/graphene electrodes. The black line shows the electrical resistance as a function of the strain in PET/ITO while the red line represents the electrical resistance as a function of the strain in PET/Ni grids/graphene electrodes.

To further verify the mechanical durability of such TCE, the graphene/Ni grids electrode was tested for the samples fabricated on PET substrates. The electrical resistance was measured during uni-axial tensile loading.\textsuperscript{149,150} Figure 2-5 shows the normalized change in electrical resistance as a function of the applied tensile strain. The thickness of all the samples was 175 m. The strain rate was $\sim 3 \times 10^{-4}$/s, which is slow enough for the quasi-static loading condition. Critical strain, defined as the strain when the normalized change in electrical resistance starts to increase dramatically, is used to evaluate the electro-mechanical properties of electrodes. For the Ni grids with the graphene electrode, the critical strain of 6% is higher than the critical strain of 3% in the ITO-PET electrode. In other words, the metal grids electrode covered with graphene remains electrically conductive when subject to a
modest elongation (<6%). As the applied tensile strain further increases, the electrical resistance first rises gradually, and then increases dramatically, leading to electrical failure. It is noted that bending strain would be the most common form of strain that flexible DSCs would encounter in real applications, and 6% of tensile strain usually corresponds to a very high level of bending strain depending on the thickness of the flexible substrates used. Therefore, the electromechanical performance demonstrated by graphene/metal grids electrodes is considered quite good.

In summary, for the first time, graphene/metal grids hybrid structure was used as the TCE for DSCs. The efficiency of the DSC with graphene/Pt grids was 0.4%, which is the highest efficiency so far seen for DSCs with graphene as the transparent conductive layer (without ITO or FTO supports). The sheet resistance of this TCE is low (up to 3 Ω/□ at 80% transmittance); while its mechanical properties are stable under strain. The efficiency of DSCs with graphene/Ni grids fabricated using 150°C processing techniques was 0.25%. It may be possible to achieve further improvements, and thus different strategies to improve the cell efficiency will be explored. With a good combination of mechanical and electrical properties, graphene/metal grids could contribute to the development of next generation flexible DSCs on arbitrarily surfaces, while maintaining their performance and long term durability upon strain.
Chapter 3. Multi-Walled Carbon Nanotubes with graphene-like film hybrid structure as Counter Electrodes for Dye-Sensitized Solar Cells

3.1. Introduction of carbon nanotubes as the replacement of traditional Pt counter electrodes for Dye-sensitized solar cell

In DSCs, the counter electrode material choice is one of the key factors in achieving a highly efficient DSC device. A Pt thin film deposited on a FTO substrate typically serves as the counter electrode in conventional DSCs. Indeed Pt can provide excellent electrical conductivity, catalytic activity, and corrosion resistance; however it is also an expensive and relatively rare element. To decrease materials
cost and achieve feasible large-scale production, an alternative counter electrode material with excellent high conductivity as well as superior electrocatalytic activity is highly desirable. Due to the low cost, high durability, excellent catalytic activity and electrical conductivity, carbon based materials have been utilized as effective alternative counter electrode for many years.\textsuperscript{18, 31, 32, 33} Carbon nanotubes and nanohorns\textsuperscript{18}, carbon black \textsuperscript{32} and graphite\textsuperscript{33} have all been tested as potential counter electrodes. Traditionally, these structures have been applied as 2D films. Therefore, proper 2D carbon materials can be alternative material for counter electrode for DSCs. Here, the novel hybrid carbon materials has been approved to be an alternative counter electrodes for DSCs.

Due to special 2-dimensional structure, the excellent electronic, optical and mechanical properties of graphene have drawn much attention in recent years.\textsuperscript{138, 151,152,136,153,154} Various methods have been introduced to prepare graphene samples of different sizes, from nanoribbons to large-area films of centimeters widths. Mainly these methods include: mechanical exfoliating (repeated peeling) of highly oriented pyrolytic graphite (HOPG),\textsuperscript{138, 155} liquid phase exfoliating of HOPG,\textsuperscript{156} vacuum graphitization of SiC crystals,\textsuperscript{157,158} chemical de-oxidation of exfoliated graphite oxide (GO)\textsuperscript{159,160} and chemical vapor deposition (CVD).\textsuperscript{161,162} Comparatively the CVD method has predominance, since large area graphene samples can be prepared easily through this method, such potency can be found in two typical works using copper foil and sputtering nickel films (on silicon substrate) as growing substrates respectively to prepare graphene.\textsuperscript{163, 164}
It’s well known that the CVD method is also one of standard routes to prepare carbon nanotubes (CNTs). Typical carbon resources in which are also hydrocarbons such as methane and ethyne; while catalysts used are metal nanoparticles, such as iron nanoparticles by pyrolyzing ferrocene at high temperatures. One major difference between these two fabrications is: the catalysts selected in syntheses of graphene samples are 2-dimensional metal foils and films; while the carbonic products are graphene and graphene-like 2-dimensional marerials. Whereas in syntheses of CNTs samples, the selected catalysts are isolated metal nanoparticles, and the products are quasi 1-dimensional CNTs, diameters of these CNTs are restricted by the sizes of catalytic metal nanoparticles. The obvious common ground of these two routes hints the possibility of verified CVD methods to prepare more complicated structures composing of graphene and CNTs. The procedure that sputtering metal nanoparticles (as catalyst) on CVD-induced graphene and then growing CNTs on this graphene substrate is a natural conceive. However here we suggest another simpler “one-pot” synthesis, in which CNTs/graphene-like hybrid structure can be prepared in a more compact method. To the best of our knowledge, such a synthesis route has not been discussed yet.

In this improved CVD method the copper substrates with pre-sputtered thin film of carbon nanoparticles were able to result in a hybrid structure that composing bamboo-like carbon nanotubes and graphene-like film.

In this chapter, we introduced the copper substrates with thin surface coating of pre-sputtering carbon nanoparticles. After studying the effect of such substrate on
CVD products, it is found that in some occasions such a compound substrate can result in a hybrid structure that composing bamboo-like carbon nanotubes and graphene-like film. After exploring the procedure further, the novel carbon carpet can be self-peeling from the copper substrate, and then attached to the FTO-glass as the counter electrode of DSC.

3.2. Preparation and characterization

**Hybrid structure on copper substrate:** Copper foil of 0.025mm thickness (Aldrich, 349208-5G, 99.98% trace metals basis) was selected as growing substrate, on one side of which 35nm carbon nanoparticles were pre-sputtered with CRC-150 Sputter Coater and there the hybrid carbon nanostructure grew in following CVD process.

One typical growth process in a tubular furnace with an inner diameter of 22 mm goes as follows: pre-sputtered copper foil (~1 ×0.5 cm) was placed in silica boat, and then the silica boat was placed in the middle of the sealed silica tube. Nitrogen and hydrogen were used as carrier and protective gases respectively in experiments, and ethyne was used as gaseous carbon resource. Normally the flowing ratios of these gases were: $F_{N_2} : F_{H_2} : F_{C_2H_2} = 100:10:5$ (sccm). Typical reaction temperature is between 850-950 °C. The copper foils were firstly heated in the mixed flow composing of $N_2$ and $H_2$, when the temperature has been reached at 920°C, ethyne (5-20 sccm) was introduced and kept for 20 minutes. Then the ethyne
was cut off. Later, the power of furnace was turned off to cool the samples to room temperature; meanwhile the nitrogen and hydrogen were still flowing.

One typical sample grows on copper foil (with a pre-sputtered carbon coating) is a black film with rough surface, which can be removed from copper substrates by immersing the sample in FeCl$_3$ solution of suitable density. And then one smooth bottom of the black film appears. Since another side of copper foil without carbon coating can also act as growth substrate in graphene synthesis, one should be careful to distinguish these different carbon products. Generally it's easy to identify them by their different colors and transparencies. One can paste the back of the copper foil on glass with tape before etching process and therefore the graphene-like sample exfoliated from the back of the foil will adhere to the glass substrate. It turned out to be that only the hybrid films from the front side is released. The removed hybrid films can be transferred on Si substrate, conductive carbon tape and copper grid for further scanning electron microscope (SEM) and transmission electron microscope (TEM) observation in Figure 3-1 and Figure 3-2. The SEM images were taken on a FEI Quanta 400 SEM and the TEM images were taken on a JEOL 1230 high contrast TEM.
Figure 3-1- SEM images of one as-prepared sample. (a) the front surface with dense nanowires; (b) the nanowires with lengths of several microns, (c) smooth backside of the sample; (d)-(e) section of broken films, showing the connection of films and nanowires and (f) one broken but still continuous section of sample.

The black irreflexive surface (top) and shining back (bottom) of the sample can be directly distinguished through visual observation, implyies the different morphologies of these two sides, which can be verified by SEM images shown in Figure 3-1. Figure 3-1 a and b reveal that top of the sample is composed of nanowires of high density and large aspect-ratios, the lengths of these nanowires are several microns. Figure 3-1c-f show the morphologies of backside substrate, a continuous subtransparent film. Compared with the lengths of those nanowires, the bottom film is rather thin, as a resultits thickness is almost negligible. One bend-
induced dislocation is shown in Figure 3-1 f reveals the flexibility of such a bottom film.

**Figure 3-2 TEM images of the sample.** (a) Tubular nanotubes and the back film, the arrow shows the connection of nanotubes to film; (b)-(c) Nanotubes with zigzag inner surfaces, shown a bamboo-like structures and (d) A nanosheet bridges two neighboring nanotubes.

TEM images in Figure 3-2 show further details of the aforementioned “nanowires”. Actually they have tubular nanostructure, external diameters of which are normally from 60nm to 100nm. The inner surfaces of these nanotubes are not
smooth. Zigzag longitudinal sections can be easily identified almost everywhere. As a result, we named is “bamboo-like” carbon nanotubes. The connection style of the bamboo-like nanotubes to the bottom film is an interesting question, careful observation revealed that the roots of (some) nanotubes lie on the carbon film as shown in Figure 2a, pointed by the arrow). This connection style will provide more contact areas for these nanotubes and carbon film and therefore is in favor of their tight connection with chemical bonding. The succeeding upward growth of these thicker nanotubes is a natural result of their reciprocal support. In Figure 2d one short section of carbon nanosheet was shown to bridge neighboring nanotubes. Detailed observation also shows that the film is not always smooth, on which there are many local granular structural scatterings on it.
Figure 3-3 Characterization: HRTEM images of (a) section of one nanotube, shown clearly the multi-walls and interface layers; (b) one edge film section, shown layers of carbon sheets; Raman spectra of (c) the front side of the sample and (d) the backside of the sample.

High resolution transmission electron microscope (HRTEM) images shown in Figure 3-3 reveal more information of the hybrid structure. Figure 3-3a shows the splitting of surrounding carbon walls of bamboo-like nanotubes, parts of inner walls compose of the interface layers of “bamboo”, typical thickness of these interface layers is several nanometers. The sections of bottom film are shown in Figure 3-3b,
layered structure can be found in these sections, the numbers of layers are more than 10 and normally around 20. Compared with those multi-walls nanotubes as shown in Figure 3-3a, these layers are obvious less flat or uniform. The HRTEM images reveal that the bottom of the hybrid product mainly is layered crystalline structure, a graphene-like layered structure.

Raman spectra has also been used to characterize the properties of such hybrid sample. Figure 3-3c and d show the Raman patterns of front and back of the sample respectively. They have little difference: Both Figure 3-3c and d have the characteristic D peak, G peak and 2D peak of carbon nanostructures, however the properties of typical graphene materials are not clear at back. The D peak that reflect the defect proportion in sample is obvious, which is in accordance with the HRTEM results. As a result, in this specific route, the quality of graphene-like film in this hybrid structure is not high enough. In occasions copper foils were selected to synthesize graphene, the CVD growth circumstance normally were of low gas pressure\textsuperscript{163,165}. Unfortunately experiments show that low gas pressure will decrease the density of CNTs and then will not be in a favor of the formation of hybrid structure. There is a contradict here, some subtle compromise is needed in further research to balance the synthesize of CNTs and graphene-like film with higher quality.

Thin carbon nanoparticles coating on copper foil is the key factor to form such composite structure. Our initial purpose to introduce such a coating is to precisely control the thickness of fabricated few-layers graphene (FLG) or graphite-like films,
since we can easily measure and control the deposition thickness of carbon coatings. The carbon coatings act as carbon resource to replace the normal gaseous resources such as CH\(_4\) and C\(_2\)H\(_2\). Another similar method has been proved to be practicable\(^{166}\). We believed that only such a replacement in carbon resource still has not shown sufficient benefits when compared with typical gaseous carbon-resource CVD routes. In further experiments when this solar carbon resource was combined with typical gaseous carbon resource (C\(_2\)H\(_2\)), complicated hybrid nanostucture was synthesized through traditional CVD process.

The selection of substrate is another decisive factor in this method. In check experiments we also replaced copper foil with nickel foil (0.025mm thickness, 99.5%), and then sputtered carbon coating of same thickness on it. Through the same reaction process, only smooth graphene-like film without CNTs was fabricated on nickel substrate. The different results might attribute to the different carbon solubilities in nickel (~0.1 at.%, 900 °C) and in copper (~0.001 at.%, 900 °C).\(^{165}\) At high temperature, the pre-coated carbon nanoparticles can be fully dissolved in nickel foil, along with the carbon from the gaseous precursor. Therefore as the growth substrates, the pre-coated nickel foil and pure nickel foil gave similar product, which same case didn’t happen on the copper substrates, due to its poor carbon solubility. Since we suppose the pre-sputtered carbon nanoparticles cannot be fully dissolved in the copper foil, both the continuous carbon supporting from the C\(_2\)H\(_2\), and those redundant carbon nanoparticles can act as the “seeds” for the further growth of the bamboo-like nanotubes. To some extent, the excess supply of
carbon element that beyond the solution ability of copper substrates is important to form the composite nanostructure.

Using copper foil without carbon coating as growth substrate and simply increasing the flowing ratio of \( \text{C}_2\text{H}_2 \) in reaction system cannot easily give the same result. In check experiments, we adjusted the flowing ratios of three gases to \( \text{F}_2\text{H}_2: \text{F}_2\text{H}_2: \text{F}_2\text{C}_2\text{H}_2 = 100:10:30 \) (sccm), the ratio of \( \text{C}_2\text{H}_2 \) in which is 6 times of former value, through the same reaction process the obtained sample (on copper foil) was a silvery non-transparent brittle film, a typical glassy phase carbon material, which is mainly the direct pyrolysis product and actually can exist on non-metal substrates, they can be found easily on the surface of quartz boat. Therefore both pre-sputtered carbon film and suitable amount of \( \text{C}_2\text{H}_2 \) are also necessary in this method. We suppose that those sputtered carbon nanoparticles act as “seeds” and carbon resource is for the early growth of nanotubes. At high temperature, part of these nanoparticles, along with carbon from \( \text{C}_2\text{H}_2 \), are dissolved in copper foil. Because the carbon solubility in copper is rather low, redundant carbon will come out from the copper foil, and then the residual carbon nanoparticles scattering on copper foil now will act as nucleus for growth of nanotubes. In this growth process copper clusters or nanoparticles given off from the foil can act as catalyst. The distribution of carbon nanoparticles has local fluctuation, which will also affect the growth continuity of nanotubes, so the final products have zigzag inner walls and bamboo-like structure, unlike typical nanotubes with smooth inner sides. As the growth goes on, solid carbon are gradually depleted and turned into nanotubes. As a uniform 2-
dimensional catalyst substrate, the copper foil will help to grow graphene-like film at the latter stage. One scheme of the growth mechanism is shown in Figure 3-4.

Figure 3-4. The scheme of the possible growth mechanism of as-prepared hybrid structure

CH$_4$ is a more frequently used gaseous carbon resource to prepare carbon nanotubes, graphene and few-layers graphene (FLG) material. Unfortunatley in this method its effect is not obvious, because of its slow thermolysis ratio. The product is mainly graphene-like film, the density of bamboo-like nanotubes on which is rather low.

This primary work still has deficiencies: (1) the quality of back film is not very satisfying, which means more precise adjustments in the concentration of carbon resources, gas pressure in CVD process are needed in further research. (2) The diameters of upside nanotubes are relative large and its bamboo structure might be easily broken and not suitable for some mechanical applications. Besides these deficiencies, this work shows that complicated structure can be prepared in a rather compact process. A suitable combination of C$_2$H$_2$, pre-sputtered carbon nanoparticles and copper foil substrate in this route, is active and fruitful. The nucleation effect of carbon nanoparticles, the lower carbon solubility of copper foil and the higher
themolysis ratio of $C_2H_2$, are in favor of the formation of the hybrid structure; while further improvement in synthesis might be based on better adjustment of such combination.

### 3.3. Performance of novel Dye-sensitized Solar Cells

Furthermore, to expand the application of this hybrid material as the counter electrode of DSCs, the thickness of carbon coating on copper substrate was increased up to 120nm. All the other procedures were similar to the previous steps. The newly carbon carpet shows self-peeling properties. 0.5wt% Polyvinylidene fluoride (PVDF) in N,N-dimethylacetamide were used as binder to attach the hybrid carbon material to FTO-glass at 95°C for 30 minutes. The novel counter electrodes were shown in the inset images in Figure 3-5 (a).
Figure 3-5 Performance of DSCs (a) $J$-$V$ curves of the reference and the MWCNTs-DSCs; Inset image represents the counter electrodes for DSCs. (b) Nyquist plots of the DSCs with MWCNT/Graphene

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>$R_s$ ($\Omega$)</th>
<th>$R_{pt}$ ($\Omega$)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs/Graphene</td>
<td>44</td>
<td>11</td>
<td>0.73</td>
<td>14.83</td>
<td>55%</td>
<td>5.9%</td>
</tr>
<tr>
<td>Pt</td>
<td>32</td>
<td>25</td>
<td>0.72</td>
<td>15.14</td>
<td>52%</td>
<td>5.6%</td>
</tr>
</tbody>
</table>

[a] $R_s$=series resistance; $R_{pt}$=charge-transfer resistance; $V_{oc}$=open-circuit voltage; $J_{sc}$=short-circuit photocurrent density; FF=fill factor; PCE=power conversion efficiency.

Table 3-1 $J$-$V$ parameters of MWCNT-DSC

We tested one group of reference DSCs with Pt counter electrode and DSCs with MWCNTs/Graphene. The characteristic $J$-$V$ plots of the devices were shown in Figure 3-5, the detailed photovoltaic parameters are summarized in Table 3-1. For the DSCs with MWCNTs/Graphene, the short-circuit current densities ($J_{sc}$) are measured to be 14.8 mA/cm$^2$ yielding a total conversion efficiency of 5.9%, with an open-circuit
voltage \( (V_{oc}) \) and FF of 0.73 V and 55%, respectively. An efficiency of 5.9% is also higher to 5.6% as the efficiency of the reference DSC with evaporated Pt as counter electrode. The value of \( V_{oc} \) and FF of DSCs with hybrid structure is slightly higher than that of DSCs with Pt.

To further understand the important parameters in the operation of the DSCs, electrochemical impedance spectroscopy (EIS) analysis employing the ZView software were carefully conducted. As clearly shown in Figure 4b, there are two semi-circles in the Nyquist plots. After the plots have been fitted with the equivalent circuit, the charge transfer resistance (\( R_{pt} \)) of MWCNTs was found to be from 11Ω; while the \( R_{pt} \) of the reference DSC was around 25Ω. This proves that the MWCNTs offer lower interface resistance between the electrolyte and counter electrode, compared to the reference DSCs.

At the same time, the series resistance (\( R_s \)) of DSC with MWCNTs/graphene is 44Ω, while \( R_s \) of the reference DSC is 32 Ω. The intrinsic resistance of the MWCNTs is a significantly lower than 44Ω. Since the resistance of FTO is 15 Ω/□ in both DSCs with MWCNTs/graphene and the reference DSCs with Pt, it can be assumed that the high resistance is directly related to the poor contact from PVDF binder between the hybrid carbon structure and FTO glass. However, it is notable that even with this non-ideal condition, the DSC devices fabricated in this way still achieved 5.9% conversion efficiency, which is higher than 5.6% in the reference DSC.

In conclusion, we introduced copper foils with thin pre-sputtering carbon nanoparticles coating as substrate to synthesize a hybrid structure that composing
bamboo-like carbon nanotubes and graphene-like film. In further research, the as-prepared carbon materials were attached to the FTO-glass as the counter electrode of DSC. Our experiments determine that the DSCs with MWCNTs/graphene achieves an efficiency of 5.9%, comparable to 5.6% obtained with a reference DSCs with Pt. EIS results determine that the resistance of electrolyte-MWCNTs in this architecture is lowered than that of Pt, whereas the MWCNT-FTO interface has a higher resistance due to the PVDF binder.
Chapter 4. Vertically Aligned Single-Walled Carbon Nanotubes as Low-cost and High Electrocatalytic Counter Electrode for Dye-Sensitized Solar Cells

To improve the electrical interface between CNTs arrays and the back-contact could yield DSC device performance exceeding that which can be obtained with a traditional counter electrode design, while also providing a lower cost alternative to Pt.

The Vertically aligned single wall carbon nanotubes (VASWCNTs) morphology attracts tremendous attentions, due to their higher surface area and strong van Der Waals interfacial adhesion with a surface that it is placed in contact with compared
to the interaction with the growth substrate (where this interface has been etched). This allows simple contact transfer in the framework of the “gecko effect” that is performed in a fully dry state, and allows the MWCNTs material to be transferred to nearly any surface. As a result of its simplicity, this technique is highly scalable and could be envisioned to take place in a roll-to-roll, or large-scale industrial process.

In this Chapter, VASWCNTs were tested in both iodine and sulfide electrolyte.

4.1. Introduction of counter electrodes for Dye-sensitized solar cells

Due to the low cost, high durability, excellent catalytic activity and electrical conductivity, carbon based materials have been utilized as effective alternative counter electrode for many years.\textsuperscript{18, 31, 32, 33} Carbon nanotubes and nanohorns,\textsuperscript{18} carbon black\textsuperscript{32} and graphite,\textsuperscript{33} have all been tested as potential counter electrodes. Traditionally, these structures have been applied as 2D films, but this approach suffers several drawbacks. The 2D structure limits the available catalytic surface area of the carbon material, and electron transfer is less efficient because the electrons must hop between the different carbon structures within the film during transport. Vertically-aligned carbon nanotubes (VACNTs) present a solution to both of these problems. Stemming from the high surface to volume ratio of VACNTs’, this 3D structure has much higher available catalytic surface area than any 2D film, and its vertical alignment allows direct electron transport to occur through individual tubes, which will eliminate the contact resistance encountered in 2D counter
electrodes. Proving the validity of this approach, a DSC utilizing vertically-aligned multi-walled carbon nanotubes (VAMWCNTs) counter electrode was fabricated by J. G. Nam et al. and it was found that the vertical alignment realized by low temperature CVD growth of vertically-aligned MWNTs directly on FTO glass clearly improved the fill factor (FF) thus corresponding cell efficiency as compared to the deposited 2D MWNT films. Lee et. al. and Ramasamy et al further proved the efficiency was related to the thickness of MWCNT, as a result of variations in the charge transfer resistance between the electrolyte and CNT interface.


Single-walled carbon nanotubes (SWCNTs) have smaller diameters than multi-walled nanotubes while offering comparable or better electrical and catalytic properties. Vertically aligned SWCNTs (VASWCNTs) therefore could provide even
higher catalytic surface areas than VAMWCNT arrays, and have the potential to offer superior catalytic performance.

4.2. Vertically aligned single-walled carbon nanotubes as counter electrodes for Dye-sensitized Solar Cells with iodine electrolyte

4.2.1 Literature review of the counter electrodes for Dye-sensitized solar cells with iodine electrolyte

In this spirit, in iodine electrolyte dense VASWCNTs is an ideal material to be utilized as a counter electrode due to their attractive features – combining a high surface area counter electrode that is chemically stable, with excellent electrical transport properties due to the one-dimensional nature of the SWCNTs. Due to these reasons, there have been a few reports of using SWCNTs as counter electrodes in DSC devices. Suzuki et al. reported on the casting of SWCNTs films on FTO-glass and Teflon membranes to make counter-electrodes for DSCs, demonstrating conversion efficiencies of 3.5% and 4.5% respectively,\(^\text{168}\) which was still appreciably lower than that of traditional Pt based DSC (5.4%). In 2009, Lee et al. achieved 4.03% conversion efficiency from adding SWCNTs to Pt as the counter anode.\(^\text{169}\) In 2010, an efficiency of around 8% by using gel-coated binder-free SWCNTs were reported.\(^\text{170}\) In the same year, C. Wang’s group achieved 1.3037% by employing
SWCNTs with functional group deposition.\textsuperscript{171} SWCNTs had also been applied on different substrates in DSC, i.e. stainless steel\textsuperscript{172} and flexible PET substrates.\textsuperscript{173} All of the above had used wet processing methods which involve dispersing SWCNTs in solvents then spraying or spin coating the solution onto substrates to prepare the SWCNTs counter electrode. Nonetheless, there remains significant variation between the conversion efficiencies reported using different counter electrode preparation approaches, making it difficult to assess the promise of SWCNTs as a counter electrode material for DSCs.

In this study\textsuperscript{174}, we employed high quality VASWCNTs arrays as counter electrodes for DSC device design, demonstrating the use of a dry-transfer of the SWCNT arrays to produce robust counter electrodes on FTO-glass substrates (Figure 4-1). Compared with wet processing methods, the dry method is simple, repeatable and easy to control, offering high density of SWCNT arrays. Using this scalable counter electrode fabrication approach, the conversion efficiencies of 5.5\% were obtained, yielding a competitive counter electrode design to the expensive Pt electrode. Also we studied the DSC with various lengths of VASWCNTs as counter electrode. It turned out that VASWCNTs with \~34\,\mu m original length produced the best result. Based upon this study, we expect an optimized SWCNT material to be an ideal candidate for low-cost, scalable, and highly efficient DSC device design in the future.
4.2.2 Preparation and characterization

Figure 4-2a is a picture showing the original growth substrate being held by a tweezers to demonstrate the clean transfer from one surface to the next that was consistently observed in this study. Inset in Figure 4-2a is an image of SWCNTs arrays transferred to FTO-glass substrates prior to fabricating DSC devices. Detailed, systematic studies of the effect of SWCNTs array length suggested optimal device performance at lengths of ~ 34 µm, prior to transfer of the VASWCNTs. The characteristics of a representative SWCNT array, including SEM (FEI Quanta 400 ESEM, FEI, USA) imaging before (Figure 4-2b, 2c and 2e) and after (Figure 4-2d) contact transfer to FTO are shown. High-resolution transmission electron microscopy (TEM, JEOL 2010, JEOL, Japan) characterization and Raman spectra are shown in Figure 4-2f and Figure 4-3. From the Raman characterization (633 nm excitation), it is evident that the SWCNTs are of high quality, with a G/D ratio ~ 10 suggesting a very low amount of defects of amorphous carbon in the material. Also observable are some radial breathing modes from the SWCNTs, depicting the wide range of diameters present in the SWCNTs arrays. In order to characterize the SWCNT material, we imaged as-grown and transferred SWCNT arrays (Table 3.1). For example, prior to transfer of one of the VASWCNT arrays, the original lengths (controllably tuned utilizing the known relation between the growth time and the carpet height\textsuperscript{175}) were ~ 34 µm. Following the transfer, the lengths of the SWCNTs array were observed to be ~ 6 µm due to some compression by an applied shear-
force that is placed on the SWCNTs array to facilitate transfer. This compaction
effect, although in a varying degree, was consistently observed in all VASWCNT
array transfer processes with different original lengths (Table 3.1). Typical
measured carbon densities of this material are $\sim 60$ mg/cm$^2$ with measured
average SWCNTs diameters near 2.5 nm. These are determined utilizing a
combination of mass measurements, optical measurements, and electron
microscopy. This yields a $\sim 7\%$ dense material following growth. This means that
following transfer the structure is, on average, $\sim 40\%$ dense, leading to better
conduction properties while still maintaining a high exposed surface area.
Figure 4-2- Characteristics of a representative VASWCNT array (a) transfer VASWCNTs from silicon substrate to FTO (inserted picture: three VASWCNTs counter electrode); (b) & (c) & (e) SEM images of VASWCNTs before transfer; (d) SEM image of VASWCNTs after transfer; (f) TEM image of VASWCNTs. Reprinted with permission from {Dong P, et al. Vertically Aligned Single-Walled Carbon Nanotubes as Low-cost and High Electrocatalytic Counter Electrode for Dye-Sensitized Solar Cells. ACS Applied Materials & Interfaces 3, 3157-3161 (2011)}. Copyright {2011} American Chemical Society.

Figure 4-2e depicts a high magnification image of the SWCNT array, showing the bundle structure (average bundle diameter of ~ 20 nm) and the good alignment in the as-grown SWCNTs array. Figure 2f shows TEM characterization of the SWCNT material, after sonication in ethanol and drop casting onto a TEM grid. Evident from
these images are SWCNTs that have a diameter range (2-4 nm) consistent with previous detailed imaging and characterization reported elsewhere.\textsuperscript{175, 177}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{raman_spectra.png}
\end{figure}

In order to fabricate VASWCNTs-DSC devices, the VASWCNTs were grown in a water-assisted thermal chemical vapor deposition system at 750 °C utilizing atomic hydrogen catalyst reduction prior to growth.\textsuperscript{168} The catalyst substrates consisted of 0.5 nm thick Fe films and subsequent 10 nm thick Al\textsubscript{2}O\textsubscript{3} films deposited onto Si. Following growth, the carbonaceous interface between the catalyst and the SWCNTs was etched using a 3-5 minute H\textsubscript{2}/H\textsubscript{2}O treatment at 750 °C, and the SWCNTs arrays
were transferred by simple contact printing in a manner described in detail elsewhere.\textsuperscript{177,178} In brief, the VASWCNTs morphology enables strong van Der Waals interfacial adhesion with a surface that it is placed in contact with compared to the interaction with the growth substrate (where this interface has been etched). This allows simple contact transfer in the framework of the “gecko effect” that is performed in a fully dry state, and allows the VASWCNTs material to be transferred to nearly any surface. As a result of its simplicity, this technique is highly scalable and could be envisioned to take place in a roll-to-roll, or large-scale industrial process. Following transfer, this counter electrode is assembled into a modified DSC architecture, as illustrated in Figure 4-1.

The procedures of assembling the DSC are the same to the normal preparation mentioned in DSCs fabricated using a flexible substrate compatible procedure under Chapter 1.2.

To characterize the performance of DSC devices with VASWCNTs as the counter-electrode material, we performed testing under standard conditions (AM 1.5, 100 mW/cm\textsuperscript{2}) at 25 °C using a solar simulator (Oriel) calibrated using a reference Silicon cell (calibrated at NREL, Oriel). Electrical impedance measurements were tested using a 608C electrochemical analyzer workstation (CH Instruments, Austin, Texas). The frequency range is from 0.05Hz to 100,000 Hz, while the magnitude of the modulation signal is 5mV. Z-View software (v2.9c, Scribner Associates Inc.) was utilized to fit the experimentally measured spectra with the appropriate equivalent circuit.
4.2.3 Performance of the novel Dye-sensitized solar cells

To evaluate the DSC performance, we tested one group of reference DSC with Pt used as counter electrode and four groups of VASWCNTs-DSC with different SWCNT lengths. The characteristic J-V plots of the devices are shown in Fig. 4 and the detailed photovoltaic parameters are summarized in Table 3.1. For the DSCs made from VASWCNTs with 34μm original length, the short-circuit current densities (J_{sc}) are measured to be 13.80 mA/cm^2 yielding a total conversion efficiency of 5.5% (SWCNT area of 0.11 cm^2), with an open-circuit voltage (V_{oc}) and FF of 0.66 V and 61%, respectively. Based on Table 1, the efficiency of the DSC made from VASWCNTs with 34μm original length achieved the highest value, compared with other VASWCNTs-DSCs. An efficiency of 5.5% is also very close to the efficiency of the reference DSC fabricated following the same procedure as described earlier but employed evaporated Pt as counter electrode, which is 5.6%. The difference between 5.5% and 5.6% is negligible, due to the margin of error of estimates that go into the efficiency, such as measuring dimensions of the DSC device and reasonable offset of the solar simulator. In other words, these two values are the same within the accuracy of the measurement technique.

To further understand the important parameters in the operation of the DSCs, EIS analysis employing the ZView software were carefully conducted. As clearly shown in Figure 4-5, there are two semi-circles in the Nyquist plots. After we fit the plots with the equivalent circuit (insert in Fig 4-5, where CPE 1 = Constant Phase Element #1; DX 1= Extended Distributed Elements #1), the charge transfer resistance (R_{pt}) of
VASWCNTs was found to be from 5Ω to 10Ω, depends on their different lengths; while the $R_{pt}$ of the reference DSC was around 30Ω. This proves that the VASWCNTs offer lower interface resistance between the electrolyte and counter electrode, compared to the reference DSC.

![I-V Curve](image)  

**Figure 4-4- $J$-$V$ curves of the reference and the VASWCNTs-DSCs.** Reprinted with permission from (Dong P, et al. Vertically Aligned Single-Walled Carbon Nanotubes as Low-cost and High Electrocatalytic Counter Electrode for Dye-Sensitized Solar Cells. ACS Applied Materials & Interfaces 3, 3157-3161 (2011)). Copyright {2011} American Chemical Society.

<table>
<thead>
<tr>
<th>As-grown lengths</th>
<th>After-transfer lengths (μm)</th>
<th>$V_{oc}$ (V)</th>
<th>Current density (mA.cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>N/A</td>
<td>0.70</td>
<td>13.67</td>
<td>59%</td>
<td>5.6%</td>
</tr>
</tbody>
</table>
At the same time, the series resistance ($R_s$) of VASWCNTs-DSC is from 18Ω to 49Ω depends on different lengths, while $R_s$ of the reference DSC is around 16 Ω. The intrinsic resistance of the VASWCNTs have been measured (along their length) to be near $\sim 3 \times 10^{-6}$ Ωm,\textsuperscript{177,179} which should yield a significantly lower resistance than 18Ω to 49Ω. Since the resistance of FTO is the same in both VASWCNTs-DSCs and the reference DSC, it can be assumed that the high resistance is directly related to the mechanical contact between the VASWCNTs and FTO glass which could be further improved. However, it is notable that even with this non-ideal condition, the DSC devices fabricated in this way still achieved 5.5% conversion efficiency, which is almost the same to 5.6% in the reference DSC, within the margin of error.

| ~15μm VASWCNTs | ~1 | 0.73 | 12.90 | 51% | 4.8% |
| ~22μm VASWCNTs | ~3 | 0.73 | 14.88 | 49% | 5.3% |
| ~34μm VASWCNTs | ~6 | 0.65 | 13.80 | 61% | 5.5% |
| ~53μm VASWCNTs | ~7 | 0.68 | 14.73 | 52% | 5.1% |


Meanwhile, important parameters including recombination impedance and chemical capacitance were also analyzed for both VASWCNTs-DSCs and the reference DSC, demonstrating a non-negligible effect of VASWCNT electrodes on photo anode performances. Furthermore, measurement of monochromatic incident photon-to-electron conversion efficiency (IPCE) of VASWCNTs-DSCs confirmed the sub-optimal performances of photo anodes, suggesting the possibilities of increasing the total conversion efficiency by improving the quality of photo electrodes.
Finally, it should be noted that a key advance in this study is the integration of high quality VASWCNTs into the DSC device design. In this architecture, the ultra-long VASWCNTs arrays (as shown in Figure 4-2c) allows direct contacts between electrolyte and the FTO surfaces that is mediated by individual SWCNT assembled in parallel. This allows charge transport processes to be determined by intra-tube transport, as opposed to inefficient electron hopping processes that occur between nanotubes and are likely to limit the performance of CNT electrodes prepared utilizing other techniques.

Therefore, the scheme developed in the current study made it possible for the electrical resistance of the high surface area electrode material to be significantly reduced, while also providing a technique promising for scalable and cost-effective counter electrode fabrication for DSC devices. These results suggest that VASWCNTs could eventually yield better performance compared to Pt as a counter electrode material in DSC device design.

In conclusion, we explored the performance of VASWCNT-DSC with various SWCNT lengths. This DSC architecture with ~34μm VASWCNT length was found to yield the optimal counter electrode in our systematic study. Our experiments determine that the VASWCNT-DSC has an efficiency of 5.5%, comparable to 5.6% obtained with a reference Pt-DSC. Electrical impedance measurements determine that the electrolyte-VASWCNT resistance in this architecture is lowered by up to ~6× compared to Pt, whereas the VASWCNT-FTO interface has a higher resistance due to the contact transfer process utilized here. Nonetheless, our studies
emphasize that future work focus on improving the electrical interface between VASWCNT arrays and the back-contact could yield DSC device performance exceeding that which can be obtained with a traditional counter electrode design, while also providing a lower cost alternative to Pt.

4.3. Vertically aligned single-walled carbon nanotubes as counter electrode for Dye-sensitized solar cells with sulfide electrolyte

Mesoscopic DSCs have recently emerged as a credible alternative to solid-state p-n junction photovoltaic devices, primarily due to its potential to generate electricity on resource-abundant raw materials and energy-saving device processing. Currently, certified PCE up to 11% has been achieved in conjunction with a polypyridyl ruthenium complexes based sensitizer and an organic solvent containing I\(^{-}/I_3^{-}\) redox couple. Nevertheless, there are substantial drawbacks of this benchmark I\(^{-}/I_3^{-}\) redox shuttle hindering its practical applications, such as large energy loss of dye regeneration process, visible light absorption and corrosiveness towards most current-collecting metal grids. Clearly, it would be highly desirable to identify alternative, noncorrosive and weakly absorbing redox couples. This will not only further boost up the PCE but also promote the practical implementation of this promising low-cost photovoltaic technology.
4.3.1 Literature review of the counter electrodes for Dye-sensitized solar cells with sulfide electrolyte

Recently, Wang et al. reported a promising disulfide/thiolate ($T^-/T_2$) redox couple that has negligible absorption in the visible spectral range. Using this novel noncorrosive redox electrolyte in conjunction with a Z-907Na sensitized heterojunction, a PCE up to 6.4% was achieved under standard illumination conditions.\textsuperscript{48} However, conventional planar platinum counter electrode showed poor catalytic activity towards this iodine-free redox couple, thus resulting in a poor fill factor (FF) and relatively moderate PCE. The phenomenon of a low FF with sulfur-functionalized redox mediators most likely results from the slow catalytic reduction of the oxidized species at the platinum counter electrode.\textsuperscript{48,56,57} The slow electron transfer thus leads to a high interfacial charge transfer resistance limiting the FF of the device.\textsuperscript{181} Therefore, it is imperative to seek suitable platinum-free catalysts that exhibit fast electron transfer kinetics for the disulfide-to-thiolate reduction, especially taking into account the low abundance (0.0037 ppm) and high cost (US$50/gram) of the platinum resources.\textsuperscript{85}

Additionally, semiconductor quantum dots (QDs) such as CdS, CdSe, PbS, InAs and InP constitute reliable alternative light absorbers\textsuperscript{182,183} due to their intrinsic properties (i.e., size-dependent band gap,\textsuperscript{184} high extinction coefficients,\textsuperscript{185} and large intrinsic dipole moment\textsuperscript{186}). More importantly, demonstration of the multiple exciton generation by impact ionization in colloidal QDs\textsuperscript{187} could push the
thermodynamic efficiency limit of these devices up to 44\%^{188} instead of the current 31\% of the Shockley-Queisser detailed balance limit.\(^\text{189}\) However, most QDs suffer from photodegradation when used in conjunction with the I\(^{-}/I_3\(^{-}\) redox couple.\(^\text{190}\) Consequently, quantum dot-sensitized solar cells (QDSCs) are often based on aqueous polysulfide electrolyte with minor use of the Fe(CN)\(_{6}^{3-}/Fe(CN)_{6}^{4-}\) couple\(^\text{191}\) and various cobalt-based electrolytes\(^\text{192}\) featuring notable attenuated corrosiveness, as well as, adjustable redox potential. Normally, in conjunction with such polysulfide electrolytes, Pt and other noble metals like Au are poor catalysts, and generate considerable overpotentials for the electrolyte regeneration. This is reflected in a reduction of the fill factors and thus PCE of the solar cell.\(^\text{193}\) Therefore, alternative catalytic materials for polysulfide solution have been investigated such as CoS, Cu\(_2\)S, NiS, and carbon materials.\(^\text{194, 195, 196}\) However, low electrocatalytic activities were observed for carbon, Au, and Pt, followed by NiS, while the best results were obtained for CoS and Cu\(_2\)S recently. Nevertheless, stability measurements in the presence of a photoanode indicated that CoS and Cu\(_2\)S electrodes may contaminate the electrolyte and subsequently the photoanode.\(^\text{194}\) Therefore, it would be of high importance to identify alternative highly-active catalytic counter electrode materials for further progress of this polysulfide electrolytes widely utilized in QDSCs.

To this end, efforts have been made to replace Pt with abundant low-cost alternatives in these iodine-free electrolyte systems, including tungsten carbide embedded into the ordered mesoporous carbon,\(^\text{56}\) mesoporous carbon
nanofibers,\textsuperscript{197} niobium oxide,\textsuperscript{198} Cu2S reduced graphene oxide composite,\textsuperscript{199} and PbS.\textsuperscript{193} It is worth mentioning that carbon nanotube (CNT) has recently attracted numerous attentions as practical Pt-free counter electrodes material in iodine electrolyte based DSCs and exhibited reasonable performance.\textsuperscript{18, 91, 200, 201} Specifically, aligned multi-walled carbon nanotube (MWCNT) arrays have been widely used to replace the platinum counter electrodes to catalyze the reduction of triiodide in DSCs with the target of better performance and lower material cost.\textsuperscript{88, 202, 203, 204, 205, 206} In 2011, Peng’s group developed a new fabrication method for aligned CNTs/polymer film as the electrode material\textsuperscript{203} and reported an efficiency of 6.6%.\textsuperscript{207} It is noted that Cheng’s team successfully obtained a PCE of 6.05% in the iodine electrolyte system by utilizing a hybrid carbon structure, VACNTs grown on graphene paper.\textsuperscript{205} 

SWCNTs can provide much higher surface area than MWCNTs due to their single graphitic layer structure and small diameter. Most recently, the efficiency of gel-coated SWCNTs-DSC reached 8% in conjunction with iodine electrolyte.\textsuperscript{88} According to the high surface area to volume ratio in the vertically aligned 3D structure, even higher available catalytic surface area can be achieved in the VASWCNTs. Moreover, electrons can directly transfer through individual tubes, instead of hopping between the different carbon structures within this film. As the result, VASWCNTs have been applied as low-cost counter electrode material for DSCs in our recent work\textsuperscript{201} and demonstrated comparable PCE with iodine electrolyte to the conventional Pt analogue. However, to the best of our knowledge, these promising three-
dimensional electrocatalysts have not been employed in the iodine-free electrolyte up to date. Such results motivated us to explore the implementation of VASWCNTs as potential electrocatalyst for the aforementioned sulfide-mediated electrolytes.

Herein, we present for the first time, VASWCNTs that have been successfully transferred onto TCO glass and implemented as efficient low-cost, platinum-free counter electrode in iodine-free DSCs, featuring notably improved electrocatalytic activity toward thiolate/disulfide redox shuttle and aqueous polysulfide electrolyte over that of conventional planar Pt counter electrode. Impressively, The charge-transfer resistance ($R_{ct}$) of VASWCNTs-counter electrode is only 21.22 $\Omega$ towards aqueous polysulfide electrolyte commonly applied in QDSCs. This value is several orders of magnitude lower than that of a Pt electrode. DSCs devices incorporating VASWCNTs counter electrodes and thiolate/disulfide redox electrolytes also show a significant gain in FF and short-circuit photocurrent density with respect to that of Pt electrodes.

### 4.3.2 Preparation and characterization

As depicted in Figure 4-6, high quality VASWCNTs arrays were firstly grown in a water-assisted thermal CVD system at 750 $^\circ$C (Process 1 in Figure 4-6), and then dry-transferred onto FTO glass substrates to produce robust counter electrodes (Process 2 and 3 in Figure 4-6). When compared with wet processing methods, the dry-transfer method is simple, reproducible and easy to control,
offering high packing density of the obtained VASWCNTs arrays. Such VASWCNTs offer strong van Der Waals interfacial adhesion with a contacting surface, compared to the interaction with the growth substrate. According to this, a simple dry contact transfer can be achieved following the principle of the “gecko-effect” in a fully dry state. Figure 4-7a presents a representative cross-sectional SEM image of the as-grown VASWCNTs arrays with a length around 30 μm, demonstrating the vertical alignment of these SWCNTs. As depicted in Figure 4-7b, following the dry-transfer process, the lengths of the SWCNTs arrays are observed to be approximately 6 μm due to the compression by an applied shear-force placed on the SWCNTs arrays, which is in line with our previous study of the compression effect on the VASWCNTs arrays’ lengths. Top surface morphology from Figure 4-7c clearly demonstrates the large interstices around the CNTs bundles. Such a geometrical structure of the VASWCNTs possesses double-functional merits of direct electron transport through individual vertically aligned tubes as well as rapid redox diffusion in the open structure around tubes. Figure 4-7d shows a typical TEM image of the SWCNTs material, after sonication in ethanol and drop casting onto a TEM grid. It is evident from these images that SWCNTs have a diameter range of 2~4 nm, giving rise to a significant high surface area of the CNTs arrays. Due to its repeatability and simplicity, the dry contact transfer printing is highly scalable. This technique can be applied in a roll-to-roll, or large-scale industrial manufacturing settings.
Figure 4-6 Process flow of preparing the VASWCNTs-DSCs: Pre-etched VASWCNTs on silicon substrate (Process 1) were flipped on top of the FTO-glass, and then a force was loaded onside the silicon top (Process 2). After simply removing the silicon wafer (Process 3), the VASWCNTs were transferred onto the FTO-glass substrate. Finally, the VASWCNTs-DSC (Process 4) was successfully assembled by utilizing this new counter electrode.
Figure 4-7- Representative cross-sectional SEM images of as-grown (a), transferred (b), top morphological (c) and TEM (d) images of VASWCNTs. Insets of (c) and (d) show the magnified topomorphology and panoramic TEM image.

Raman spectroscopy was further applied to characterize the quality of the VASWCNTs arrays. From the Raman characterization (633 nm excitation) of Figure 4-8, it is obvious that the VASWCNTs are of high quality with a G/D ratio around 9. This suggests a very low amount of defects, such as amorphous carbon in the nanotubes. At the same time, radial breathing modes (RBM) can be observed from the Raman spectra of the materials.

Figure 4-8- Raman spectra of VASWCNTs electrodes (633 nm excitation)

Similar to our previous work,201 10 nm thick Al₂O₃ film and subsequent 1 nm thick Fe film are deposited onto Si substrate. VASWCNTs growth was carried out in a water-assisted thermal CVD system at 750 °C. After a quick cooling treatment, the
post-growth $\text{H}_2/\text{H}_2\text{O}$ vapor etch took 3~5 min at 750 °C. This etch would release the chemical bonds between the nanotubes and the catalyst particles. And then the VASWCNTs were transferred onto FTO substrate by simple dry contact transfer printing.\textsuperscript{180}

Conventional sputtered Pt counter electrode was prepared by an ion sputtering coater (SBC-12, KYKY Technology Development Ltd., China) for comparison. The thickness of the obtained Pt film was approximately 50 nm. DSCs devices were fabricated according to our previous reports.\textsuperscript{210} Briefly, TiO$_2$ paste composed of 18% commercial P25 nanoparticles and 9% ethyl cellulose in terpineol was used to screen printing porous TiO$_2$ films (approximately 14 μm thick) on FTO substrate (sheet resistance: 12 Ω/square, Nippon Sheet Glass, Co., Ltd.). The obtained TiO$_2$ electrodes were dipped into dry ethanol solution containing $5 \times 10^{-4}$ M cis-bis(isothiocyanato) bis(2',2'-bipyridyl-4,4'-dicarboxylato) ruthenium( II ) bistetrabuyl-ammonium (N719, ruthenium TBA535, Solaronix, Switzerland) for 20 h. The dye-sensitized TiO$_2$ electrodes, VASWCNTs and Pt counter electrodes were assembled to form DSCs by sandwiching a redox couple (T$^-$/T$_2$) electrolyte solution composed of 0.4 M T$^-$, 0.4 M T$_2$, 0.5 M 4-tertbutylpyridine, and 0.05 M LiOCl$_4$ in acetonitrile:ethylene carbonate=6:4, V:V). The organic redox couple (T$^-$/T$_2$) was synthesized by the literature method.\textsuperscript{48} Aqueous polysulfide electrolyte was composed of 1 M sulfur, 1 M Na$_2$S·9H$_2$O, and 0.1 M NaOH in deionized water.
The morphologies of the obtained VASWCNTs were characterized by field emission scanning electron microscopy (FEI Quanta 400 ESEM, FEI, USA) and TEM (JEOL 2010, JEOL, Japan). Raman characterization (633 nm excitation) was performed by a Renishaw inVia Raman Microscope. To assess the corresponding catalytic performance of different counter electrodes, the $R_{ct}$ across the counter electrode/electrolyte interface was investigated by means of EIS with the symmetrical thin-layer cells method. The frequency range was set from 100 mHz to 1 MHz, and the amplitude of the alternating current was set to 10 mV. Tafel measurements were performed with a scanning rate of 10 mV s$^{-1}$ in the potential range of 0.5 V to -0.5 V. The photocurrent-voltage ($J$-$V$) characteristics of DSCs were measured with a digital source meter (2400, Keithley Instruments, USA) under AM 1.5G illumination (100 mW cm$^{-2}$), which was realized by a solar simulator (91192, Oriel, USA, calibrated with a standard crystalline silicon solar cell).

### 4.3.3 Performance of the novel Dye-sensitized solar cells

To assess the potential applications of the VASWCNTs counter electrodes in DSCs, devices were assembled with N719 sensitized TiO$_2$ electrodes with a thickness of 14 μm and an active area of 0.16 cm$^2$ in conjunction with the VASWCNTs electrodes (Process 4 in Figure 4-6) or conventional sputtered Pt counter electrodes. Figure 4-9 demonstrates the characteristic $J$-$V$ performance for devices with VASWCNTs and reference Pt counter electrodes measured under Air Mass 1.5G illumination and the detailed photovoltaic parameters are tabulated in Table 3.2. Device A with Pt
electrode in conjunction with $\text{T}^-/\text{T}_2$ electrolyte exhibits an open-circuit voltage ($V_{oc}$) of 612 mV, a short-circuit photocurrent density ($J_{sc}$) of 10.26 mA cm$^{-2}$, an FF of 0.56, yielding an overall PCE of 3.49%. It is remarkable that device B with VASWCNTs displays a $J_{sc}$ enhancement up to 12.66 mA cm$^{-2}$, a considerable increase in FF up to 0.68, and produces a PCE of 5.25%. Apparently, the enhancement of the PCE is directly originated from the $J_{sc}$ and FF increase.

It is important to note that the FF of a DSC device is attenuated by the total series resistance of the cell, including the sheet resistances of the substrate and counter electrode, electron transport resistance through the photoanode, ion transport resistance, and Rct at the counter electrode. Therefore, the FF enrichment in the current work is mainly a result of the superior electrocatalytic activity of the VASWCNTs and consequent significantly reduced charge-transfer resistance across the counter electrode/electrolyte interface. Significant improvement in charge transfer at the counter electrode/electrolyte interface not only reduces internal resistances, but also attenuates the recombination rates and concentration gradients in the electrolyte, which have been proved to affect $J_{sc}$ strongly. The obtained FF and PCE is of great advantage when compared to that with other catalyst materials, such as tungsten carbide embedded ordered mesoporous carbon, as well as graphite. Efforts to further enhance the PCE are currently in progress in our laboratory, which include optimizing the photoanode structure and employment of other sensitizers with strong hydrophobicity to inhibit charge recombination between the photoelectrode and electrolyte.
Figure 4-9- Photocurrent–voltage characteristics of DSCs using VASWCNTs or Pt counter electrodes under 1 sun illumination (AM 1.5G, 100 mW cm$^{-2}$). The electrolyte was comprised of 0.4 M T$_7$, 0.4 M T$_2$, 0.5 M 4-tertbutylpyridine, and 0.05 M LiClO$_4$ in acetonitrile: ethylene carbonate (6:4, V:V).

The electrocatalytic activity of the as-fabricated VASWCNTs counter electrodes towards thiolate/disulfide redox shuttle$^{48}$ was first investigated by EIS.$^{211,212}$ Figure 4-10a presents the corresponding Nyquist spectra of symmetrical dummy cells with VASWCNTs counter electrodes and conventional sputtered Pt counter electrodes as the reference. It is generally recognized that in the order of increasing frequency, the response can be attributed to the Warburg diffusion processes in the electrolyte and charge transfer at the counter electrode/electrolyte interface.$^{212}$ Apparently, incorporation of the VASWCNTs promotes a significantly reduced diameter of the high-frequency semicircles. By fitting with the Randles equivalent circuit, the R$_{ct}$ of the VASWCNTs as shown in Table 3.2 is only 12.66 Ω, a value almost six-fold lower than that of conventional Pt counter electrode (76.28 Ω) under similar measurement conditions, highlighting the superior electrocatalytic activity of the
VASWCNTs towards thiolate/disulfide redox couples. Furthermore, obvious high-frequency shift of the characteristic response peaks in the high-frequency regime of Bode plot shown in Figure 4-10b demonstrates a faster electron transfer at the interface between VASWCNTs and electrolyte with respect to conventional Pt counter electrode. In addition, it is also observed that the VASWCNTs electrodes exhibit a notably larger double-layer capacitance ($C_{dl}$) than the planar Pt electrodes do, suggesting a higher specific surface area in the former counter electrodes. This is in agreement with the results from other nanostructured counter electrodes with a high porosity.\textsuperscript{213,214} Noteworthy is that our VASWCNTs do not increase the redox diffusion resistance in the electrolyte, probably arising from the relative open structure as characterized by the SEM image in Figure 4-7c.
Figure 4-10- Corresponding Nyquist plots (a) and Bode plots (b) of the symmetrical dummy cell towards thiolate/disulfide electrolyte with a recipe of 0.4 M T⁻, 0.4 M T₂, 0.5 M 4-tertbutylpyridine, and 0.05 M LiOCl₄ in acetonitrile: ethylene carbonate (6:4, V:V). The frequency range was set from 100 mHz to 1 MHz, and the amplitude of the alternating current was set to 10 mV in impedance measurements. Tafel measurements were performed with a scanning rate of 10 mV s⁻¹.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>R_s (Ω)</th>
<th>R_{ct} (Ω)</th>
<th>C_{dl} (F)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm⁻²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>26.08</td>
<td>76.28</td>
<td>4.93E-8</td>
<td>0.61</td>
<td>10.26</td>
<td>0.56</td>
<td>3.49</td>
</tr>
<tr>
<td>VASWCN Tₛ</td>
<td>25.67</td>
<td>12.66</td>
<td>4.60E-6</td>
<td>0.61</td>
<td>12.66</td>
<td>0.68</td>
<td>5.25</td>
</tr>
</tbody>
</table>

[a] R_s=series resistance; R_{ct}=charge-transfer resistance; C_{dl} = double-layer capacitance; V_{oc}=open-circuit voltage; J_{sc}=short-circuit photocurrent density; FF=fill factor; PCE=power conversion efficiency. Values presented here are the average of at least three samples.
Table 4-2 EIS parameters fitted from the equivalent circuit and corresponding photovoltaic performance of DSCs with different counter electrodes in conjunction with $T^-/T_2$ electrolyte under 1 sun illumination (AM 1.5G, 100 mW cm$^{-2}$).[a]

The superior electrocatalytic activity of VASWCNTs electrodes towards $T^-/T_2$ electrolyte inspired us to the implementation of this encouraging counter electrode in other electrolyte systems, such as the aqueous polysulfide electrolyte commonly applied in QDSCs. Similar to the aforementioned experimental conditions, symmetrical dummy cells were fabricated in combination with the aqueous polysulfide electrolyte with a recipe of 1 M sulfur, 1 M Na$_2$S·9H$_2$O, and 0.1 M NaOH in deionized water. Figure 4-11 displays the corresponding Nyquist plots (a), Bode plots (b) and Tafel curves (c) of the symmetrical dummy cells measured under the similar conditions. Dramatic reduction in the Rct of VASWCNTs electrode is observed in comparison with that of Pt electrode as summarized in Table 3.3. In parallel with previous studies on the catalytic activity for polysulfide solutions,[194, 195, 215, 216, 217] planar Pt electrode exhibits a huge Rct in the order of 105 Ω, mainly due to the poor catalytic activity. Encouragingly, utilization of the VASWCNTs greatly enhances the electrocatalytic activity, yielding a small Rct value of only 21.22 Ω, as seen from the inset of Figure 4-11a. To the best of our knowledge, such an Rct value is the lowest ever seen in the polysulfide electrolyte, even compared with recently reported PbS$^{193}$ and Cu$_2$S$^{189}$ counter electrodes. Complementally, significant high-frequency shift of the characteristic response peaks in the Bode plot
shown in Figure 4-11b, further confirms the superior catalytic activity of the VASWCNTs electrodes to polysulfide electrolytes.

<table>
<thead>
<tr>
<th>Counter electrodes</th>
<th>$R_s$ [Ω]</th>
<th>$R_{ct}$ [Ω]</th>
<th>$C_{dl}$ [F]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>21.41</td>
<td>20339</td>
<td>1.33E-7</td>
</tr>
<tr>
<td>VASWCNTs</td>
<td>14.23</td>
<td>21.22</td>
<td>5.80E-6</td>
</tr>
</tbody>
</table>

[a] $R_s$=series resistance, $R_{ct}$=charge transfer resistance, $C_{dl}$=double-layer capacitance. Values presented here are the average of three samples.

**Table 4-3 EIS parameters** fitted from the equivalent circuit of symmetrical dummy cell towards aqueous polysulfide electrolyte with a recipe of 1 M sulfur, 1 M Na$_2$S·9H$_2$O, and 0.1 M NaOH in deionized water with different counter electrodes.[a]
Figure 4-11- Corresponding Nyquist plots (a), Bode plots (b) and Tafel curves (c) of the symmetrical dummy cell towards aqueous polysulfide electrolyte with a recipe of 1 M sulfur, 1 M Na₂S·9H₂O, and 0.1 M NaOH in deionized water. The frequency range was set from 100 mHz to 1 MHz, and the amplitude of the alternating current was set to 10 mV in the impedance measurements. Tafel measurements were performed with a scanning rate of 10 mV s⁻¹.
Tafel polarization measurement was further employed to study the interfacial charge-transfer properties of the polysulfide redox couples on the counter electrode surface. Figure 4-11c shows the logarithmic current density as a function of applied voltage of the symmetrical dummy cells. The exchange current density ($J$) is obtained as the intercept of the extrapolated linear region of the curve when the overpotential is zero. In the curve at high potential (horizontal part), the limiting diffusion current density ($J_{\text{lim}}$) can be derived. These two parameters are closely related with the electrochemical activity of the catalysts.\textsuperscript{218} Evidently, the anodic and cathodic branches of the VASWCNTs electrodes exhibit an obvious larger slope than the conventional Pt counter electrodes do, indicating the presence of a large exchange current density ($J_0$) on the electrode surfaces. Moreover, a higher $J_{\text{lim}}$ is noted in conjunction with VASWCNTs counter electrode, which suggests a higher diffusion coefficient of the polysulfide redox couple in the electrolyte compared to that of Pt electrode according to Equation 3-1:

$$D = \frac{l}{2nFC} J_{\text{lim}}$$

Equation 3-1 Diffusion coefficient

Where $D$ is the diffusion coefficient of the polysulfide, $l$ is the electrolyte thickness, $n$ is the number of electrons involved in the reduction of disulphide at the counter electrode, $F$ is the Faraday constant, and $C$ is the polysulfide concentration.\textsuperscript{219} These results confirm that the catalytic activity towards
polysulfide redox shuttle of VASWCNTs is superior to that of conventional Pt counter electrodes. Furthermore, studies on the photovoltaic implementation of VASWCNTs counter electrodes in QDSCs are in progress in our laboratory.

In summary, we have developed VASWCNTs as efficient low-cost counter electrode material in iodine-free DSCs, featuring notably improved electrocatalytic activity towards thiolate/disulfide redox shuttle. Spectacularly, device in conjunction with VASWCNTs counter electrode demonstrates a high FF of 0.68 and PCE up to 5.25%, which is significant higher than 0.56 and 3.49% for that with a conventional Pt counter electrode. Moreover, in QDSCs system, the $R_{ct}$ of VASWCNTs counter electrode is as low as 21.22 $\Omega$ towards aqueous polysulfide electrolyte. This is several orders of magnitude lower than that for Pt electrode. In comparison with alternative counter electrode materials previous reported such as Au, CoS, Cu$_2$S or PbS, to the best of our knowledge, such a $R_{ct}$ value is the lowest ever seen in the polysulfide electrolyte system. Therefore, the highly catalytic VASWCNTs counter electrodes are believed to be a versatile candidate for further improvement of the PCE of other iodine-free redox couple based DSCs and polysulfide electrolyte based QDSCs.
4.4. Conclusions

VASWCNTs enabled DSCs architectures achieve a comparable or better performance than standard brittle platinum/FTO combination. The large surface area of such nanomaterials in addition to the high electrical conductivity and their mechanical robustness provides a platform for significant enhancements in DSCs’ performance.
Chapter 5. Few-Walled Carbon Nanotubes/Graphene Counter Electrode for Efficient Dye-Sensitized Solar Cells

According to the high $R_{pt}$ of DSC from EIS results in chapter 3 and 4, both MWCNTs/Graphene and VASWCNTs didn’t have a good contact with the FTO-glass. Combing the hybrid structure from the chapter 3, and the higher surface area of VASWCNTs in chapter 4, vertically aligned few wall carbon nanotubes (VAFWCNTs)/graphene directly grown on Ni foil were utilized as the counter electrodes for DSC to further improve the performance of DSC.
5.1. Introduction of vertically aligned few-walled carbon nanotubes

Based on the work in Chapter 3, VACNTs are typically prepared on silicon substrate. In order to be integrated into the DSC device, the VACNTs need to be transferred to the suitable conductive substrates like FTO glass or ITO-PEN substrates. Both wet transfer process\textsuperscript{168, 169, 170, 171} and dry transfer process\textsuperscript{180} have been reported. However, the wet process couldn’t preserve the vertically aligned morphology of CNTs, reducing their surface area and conductivity, and the dry transfer technique suffered the contact problem between the carbon carpet and the conductive substrate. In both cases, the catalytic effectiveness of the carbon electrode is still lower than Pt based electrode.

Here in this work, a seamless 3-dimensional VAFWCNTs/graphene hybrid material\textsuperscript{220} was used as the counter electrode in DSCs. This hybrid material satisfied all the requirements above: it provides over 2000 m\textsuperscript{2}/g specific surface area and ohmic contact between the graphene and the vertically aligned carbon nanotubes, and the metal base.\textsuperscript{220} The entire hybrid material can be prepared on thin nickel (Ni) foil substrate, which is directly used for the DSC electrode without any transfer steps. As a result, the electron transfer at the counter electrode/electrolyte interface is an order of magnitude faster than that of the reference and the fabricated DSCs out-perform the reference Pt based cells. More importantly, the present configuration eliminates the need to employ a brittle FTO or ITO-PEN for the
electrode substrate. This work provides a low-cost, highly efficient counter electrode for future DSCs.

5.2. Preparation and characterization

Preparation of counter electrode: The preparation of the counter electrode materials are based on a modified procedure in literature\textsuperscript{220}. In brief, the Ni foil (0.025 mm, annealed, 99.5\%, Alfa Aesar) is cut into 1”x1” square. Graphene is grown on the Ni surface by chemical vapor deposition method.\textsuperscript{220} A shadow mask (with circles of 1 cm in diameter) is used to evaporate 1 nm iron and 3 nm alumina oxide on the graphene covered Ni substrate. The iron is evaporated first and then the aluminum oxide is evaporated. The sample is charged in a low-pressure chemical vapor deposition system and vertically aligned carbon nanotubes are grown from graphene surface. The obtained sample is directly used for device fabrication without further treatment.

For the semi-rigid DSC preparation: The FTO glasses (Pilkington FTO glass Tec 15 Glass, 2.2 mm of thickness) were first cleaned using an ultrasonic bath in DI water and 200 proof alcohol sequentially. 12 µm diffusion TiO\textsubscript{2} layer (DSL 18NR-T, Dyesol) and 8 µm scattering layer (WER4-O, Dyesol) were screen-printed onto the FTO glass. Each layer was dried at 125 °C for 6 minutes after printing. The photo electrode was sintered at 500 °C for 30 mins in air. The sintered photo electrode was immersed in the N719 ([RuL\textsubscript{2}(NCS)\textsubscript{2}]:2 TBA (L = 2,2’-bipyridyl-4,4’-dicarboxylic acid; TBA = tetra-n-butylammonium), B2 N719, Dyesol) solution (3 × 10\textsuperscript{-4} mol/L)
for 24 h at room temperature. The photo electrode and counter electrode were packaged with the sealant (1170 Series, 60 µm, Solaronix) at 125°C for 7 s twice. The electrolyte solution, with a composition of 0.05M I₂, 1.0M 1-propyl-3-methylimidazolium iodide (PMII), 0.5 M N-methylbenzimidazole (NMBI), 0.1 M Guanidinium thiocyanate (GNCS) in 2-methoxypropionitrile (MPN) as the solvent, was injected into the cell and sealed using additional sealant.

**For the flexible DSC preparation:**

8um TiO₂ (Titanium (IV) oxide, ~21 nm particle size, Sigma-Aldrich) was screen printed on clean ITO-PEN. The photo electrodes were sintered at 150°C for 30 mins in air. Other procedures are similar as that for DSC with semi-rigid substrate.

The efficiency of the DSCs were tested by the solar simulator (Solar simulator, 94041A, Oriel) calibrated using a reference silicon cell (calibrated at NREL, Oriel) under standard test conditions (AM 1.5, 100 mW/cm²) at 25°C. The active area of the DSC is from 14mm² to 16mm² (Table 1).

EIS measurements were carried out on an electrochemical workstation (CHI 650C) in the frequency range of 0.1 Hz to 100 kHz. Fig. 4 presents the corresponding Nyquist spectra of DSCs with VAFWCNTs/graphene on Ni foil and conventional sputtered Pt as the reference.

Characterization of the counter electrode
Figure 5-1a is a schematic image of the VAFWCNTs/graphene electrode, and the actual electrode with VAFWCNTs/graphene atop the Ni substrate. The CNTs grown in this work are few-walled, (typically, the number of wall is 1 to 3). The graphene film on Ni is usually less than three layers. The schematic image of the DSC is shown in Fig. 1b. The left part of Figure 5-1b is VAFWCNTs/graphene based counter electrode; while the right part is the photo-electrode with TiO$_2$ and dye molecules.

![Scheme of the DSC fabricated in this work](image)

**Figure 5-1- Scheme of the DSC fabricated in this work** (a) Schematic structure of the VAFWCNTs/graphene. The rings highlighted in red represent the seven member rings that seamlessly fuse planar graphene and tubular CNTs. However, the CNTs are tens of microns long while the graphene is < 1 nm thick. Inset is the image of the VAFWCNTs/graphene (black circle) on Ni foil counter electrode. The diameter of the black circle is 6 mm. (b) Schematic image of DSC with the VAFWCNTs/graphene on Ni foil as the counter electrode.

The VAFWCNTs/graphene counter electrode was synthesized based on the previous report.$^{220}$ Figure 5-2a is the top view of the edge of the CNTs forest standing on a graphene-covered Ni substrate. The SEM image of the section of the VAFWCNTs (Figure 5-2b) indicates the tip growth mechanism.$^{221}$ Instead of forming
aligned structure on the entire surface, the CNTs only aligned within every section, which can benefit the electrolyte wetting in the solar cell devices. The graphene layer has been shown to be crucial for preventing catalyst aggregation during the growth, leading to the higher growth rate of VAFWCNTs on the metal substrate. As shown in Figure 5-2c and Figure 5-2d, the graphene and CNTs form a fused structure after growth. The Raman spectra of the counter electrode are shown in Figure 5-3. Typical CNT Raman spectra based on different CNT growth times are plotted in Figure 5-3. The G/D ratios vary in the range from 4.3 to 8.0 where the tubes are less defective or have less amorphous carbon with increased growth time. The strong radial breathing mode signals between 100 and 300 cm\(^{-1}\) indicate that the diameters of the tubes are all small. The graphene grown on Ni foil in this work was evaluated by Raman spectroscopy mapping. A typical graphene spectrum was plotted in Fig. 3b and the G/D ration of a 25 × 25 \(\mu\)m sample was plotted in Figure 5-3b. The high G/D ratio implies a reasonable quality of graphene film synthesized in this work.
Figure 5-2 SEM and TEM characterization of counter electrode materials used in this work. (a) Top-view SEM image of the VAFWCNTs/graphene on Ni foil; scale bar: 50 µm. (b) Side view SEM image of the VAFWCNTs/graphene on Ni foil with high magnification; scale bar: 2 µm. (c) TEM image indicates that CNTs forest is connected to the graphene film. (The metal substrate was removed by etching and the CNTs/graphene material was transferred onto the TEM grid.) Aberration-corrected TEM images showing the CNT-graphene seamless junction have been shown previously. Scale bar: 100 nm. (d) High resolution TEM image indicates the graphene is few-layered and the CNTs material are 1-3-walled. Scale bar: 10 nm.
Figure 5-3- Raman Spectra of counter electrode materials. (a) Typical Raman spectra of VAFWCNTs synthesized in this work. The min indicated in the legend is the CNT CVD growth time of different samples. (Raman laser wavelength: 633 nm). (b) A typical Raman spectrum of graphene in this work. (Raman laser wavelength: 514 nm) (c) The G/D ratio map from Raman spectroscopy mapping on graphene covered nickel foil (mapping area: 25 × 25 μm, Raman laser wavelength: 514 nm).

The semi-rigid DSCs utilizing flexible VAFWCNT/graphene counter electrodes and standard FTO glass based photoanodes were fabricated as shown in the Methods. Iodine salt-based electrolytes were used. For comparison, the standard Pt counter electrode, with 20 nm Pt sputtered on a FTO-glass substrate, was used to fabricate the control group DSCs. As the photoanode used here was based on rigid FTO glass, the samples in the control group are fully rigid and the DSCs with the carbon hybrid materials are semi-rigid. We systematically investigated the performance of novel DSCs made from VAFWCNTs/graphene of various CNTs lengths. As shown in Table 1, the thickness of the VAFWCNTs layer was 20 to 25 μm, 75 to 92 μm, and 100 to
150 μm, under 4 min, 30 min, or 60 min CNT growth, respectively. The G/D ratio increased slightly from 4.3 to 6.2 then 8.0, with the increase in growth time. For longer exposures, the top of the forest is experiencing etching of defective carbon nanotubes selectively, as is evidenced by the increasing G/D ratio with growth time. The longer carbon nanotubes can provide higher surface area, and this eventually resulted in a better catalytic function in the following tests.

5.3. Performance of the novel Dye sensitized solar cells

Figure 5-4a shows the characteristic $J-V$ performance for DSCs with the carbon hybrid materials counter electrode. Based on the results in Table 1 and Fig. 4, the open-circuit voltage ($V_{oc}$) of the DSCs with VAFWCNTs/graphene varied in the small range from 0.69 to 0.73 V, similar to the value of Pt control group cells (0.71 V). The values of $V_{oc}$ do not follow a clear trend due to the increased lengths of VAFWCNTs. The FF of the carbon DSCs is between 65% and 68%, which is slightly higher than that of the traditional DSC (64%). From Table 1 and Fig. 4a, it is clear that the major improvement provided by the new counter electrode is the increased short-circuit photocurrent density ($J_{sc}$). Compared to 13.86 mA/cm$^2$ in the traditional Pt based DSC, the $J_{sc}$ of the new cells reached 14.33 mA/cm$^2$, 16.02 mA/cm$^2$, and 17.83 mA/cm$^2$ with the different VAFWCNTs lengths. This increase leads to up to 20% enhancement of the power conversion efficiencies, which are 7.1% to 8.2% for the new VAFWCNTs/graphene cells and only 6.8% for the standard Pt control group. The DSCs with the highest efficiency are those fabricated with
VAFWCNTs/graphene having the longest growth time (corresponding length of the nanotubes was 100 to 150 μm). Such a phenomenon indicated that the higher surface area of the cathode is preferred during the cathode redox reactions of novel electrode.

EIS was conducted in order to further investigate the electron transport at the counter electrode surface. The results are shown in Figure 5-4b. By fitting with the transmission line equivalent circuit shown in bottom right of Fig. 4b, the series resistance ($R_s$) and the charger transfer resistance ($R_{pt}$) of the counter electrode can be estimated. The $R_s$ of the VAFWCNTs/graphene on the Ni foil counter electrode was 23 Ω and the $R_s$ of the Pt counter electrode was 24.5 Ω. However, $R_{pt}$ of the new counter electrode was 0.91 Ω for the semi-rigid DSC. These values are more than ten times lower compared to that of the DSC having a Pt counter electrode, which is ~19.6 Ω. This result indicates the superior electrocatalytic activity of the hybrid carbon system; the low interfacial $R_{pt}$ may lead to a faster electron transfer, thus further increasing the $J_{sc}$ and the performance of the DSC device.\textsuperscript{181}
Figure 5-4 Characterization of semi-rigid DSCs using flexible VAFWCNTs/graphene on nickel foil (CNTs/G/Ni) as the counter electrodes and standard FTO glass based photoanodes (a) Photocurrent–voltage characteristics of DSCs using CNTs/G/Ni or Pt counter electrodes under 1 sun illumination (AM 1.5G, 100 mW cm\(^{-2}\)). The electrolyte was comprised of 0.05 M I\(_2\), 1.0 M 1-propyl-3-methyl-imidazolium iodide (PMII), 0.5 M N-methylbenzimidazole (NMBI), 0.1 M guanidinium thiocyanate (GNCS) in 2-methoxypropionitrile (MPN) as the solvent. The time in the legend is the growth time of VAFWCNT and they correspond to the length of 20 to 25 µm (4 min), 75 to 92 µm (30 min) and 100 to 150 µm (60 min). (b) Nyquist plots of DSCs. The frequency range was set from 100 mHz to 1 MHz, and the amplitude of the alternating current was set to 10 mV in impedance measurements. The upper inset represents the enlarged EIS result from 22 Ω to 32 Ω, which also clearly reflects the first semi-circle of the DSC with CNTs/G/Ni. The lower inset shows the equivalent circuit used in the fitting process of the CNTs/G/Ni in this work.
### Table 5-1 J-V Parameters of Semi-Rigid DSCs with VAFWCNTs/Graphene on Ni Foil under 1 Sun Illumination (AM 1.5G, 100 mW cm⁻²) and the G/D Ratio of the VAFWCNTs/Graphene on Ni Foil

<table>
<thead>
<tr>
<th>Counter electrode</th>
<th>Growth time (min)</th>
<th>As Growth Length (μm)</th>
<th>G/D</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm⁻²)</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAFWCNTs/Graphene on Ni foil</td>
<td>4</td>
<td>20-25</td>
<td>4.3</td>
<td>0.73</td>
<td>14.33</td>
<td>68%</td>
<td>7.1%</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>75-92</td>
<td>6.2</td>
<td>0.69</td>
<td>16.02</td>
<td>66%</td>
<td>7.3%</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>100-150</td>
<td>8.0</td>
<td>0.71</td>
<td>17.83</td>
<td>65%</td>
<td>8.2%</td>
</tr>
<tr>
<td>Pt</td>
<td>NA</td>
<td>20 nm</td>
<td>NA</td>
<td>0.72</td>
<td>13.86</td>
<td>64%</td>
<td>6.4%</td>
</tr>
</tbody>
</table>

[a] $V_{oc}$ = open-circuit voltage; $J_{sc}$ = short-circuit photocurrent density; FF = fill factor; PCE = power conversion efficiency.

Another obvious advantage of the CNTs/G/Ni counter electrode is flexibility. Flexible DSCs on a conducting plastic substrate attract considerable attention due to their unique characteristics such as portability and low weight. The standard flexible counter electrode is prepared by sputtering Pt on ITO-PEN. However, the most widely used conductive layer in DSCs, ITO, is very brittle. Due to easy crack-propagation, ITO-PEN in flexible DSCs can only survive a few bending cycles. As a result, present ITO-based flexible DSCs cannot be bent even a few times. 222 The CNTs/G/Ni electrode is therefore preferred for flexible DSCs, which can be bent,
folded and fitted to curved surfaces. The flexible DSCs are fabricated by using an ITO-PEN anode and the CNTs/G/Ni counter electrode. For comparison, the control group DSCs were fabricated with a 20 nm Pt coated ITO-PEN substrate as the counter electrode. As shown in Fig. 5 and Table 2, the PCE of the flexible DSC with CNTs/G/Ni as the counter electrode achieves 3.9% with an FF of 0.60, which again rivaled the standard flexible DSC (PCE 3.4% and FF 0.59). The $J_{sc}$ of the flexible DSC with CNTs/G/Ni was found to be 9.23 mA/cm$^2$ with a $V_{oc}$ of 0.71 V; meanwhile, the $J_{sc}$ of DSC with Pt was 7.94 mA/cm$^2$ with a $V_{oc}$ of 0.72 V. The FF of the DSC with CNTs/G/Ni is slightly higher than that of the traditional DSC with Pt as the counter electrode. The better performance of the flexible DSCs with CNTs/G/Ni is attributed to the lower $R_{pt}$ properties provided by the novel materials, which leads to a higher $J_{sc}$. All these trends show the same consistency as the ones we discussed in semi-rigid DSCs. The bendability of this new counter electrode could contribute to the development of next generation flexible DSCs on arbitrary surfaces, while maintaining their performance and long term durability.
Figure 5-5 Photocurrent–voltage characteristics of flexible dye-sensitized solar cells (DSCs) using CNTs/G/Ni or Pt as counter electrodes under 1 sun illumination (AM 1.5 G, 100 mW cm\(^{-2}\)). The inset represents the schematic of the flexible DSC. The electrolyte is described in the main text. The blue line and green line represent the \( J-V \) curves of tradition and the CNTs/G/Ni rigid DSCs, separately.

<table>
<thead>
<tr>
<th>Counter Electrodes</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt on ITO-PEN</td>
<td>0.72</td>
<td>7.94</td>
<td>0.59</td>
<td>3.4</td>
</tr>
<tr>
<td>VAFWCNTs/graphene on Ni foil</td>
<td>0.70</td>
<td>9.26</td>
<td>0.60</td>
<td>3.9</td>
</tr>
</tbody>
</table>

[a] \( V_{oc} \)=open-circuit voltage; \( J_{sc} \)=short-circuit photocurrent density; FF=fill factor; PCE=power conversion efficiency.
Table 5-2 The corresponding photovoltaic performance of flexible DSCs with VAFWCNTs/graphene on Ni counter electrodes under 1 sun illumination (AM 1.5G, 100 mW cm$^{-2}$)

In conclusion, a novel seamless 3-dimensional CNTs/G/Ni scaffold was implemented as the transparent conducting oxide and Pt-free counter electrodes for DSCs. The graphene and VAFWCNTs layers were grown in situ on the Ni foil, avoiding any transfer process that is recognized to be detrimental to interfacial electron transfer$^{174}$. DSC devices with VAFWCNTs of 100 to 150 μm length achieved the highest PCE at 8.2%, which is significantly higher than that of the rigid reference with sputtered a Pt counter electrode (ca. 6.4%). The EIS analysis results show that the $R_{pt}$ of the new counter electrode was only 0.91 Ω for the semi-rigid DSC, ten times lower than that of the DSC with Pt (19.6 Ω), which leads to a ten times faster electron transfer rate at the counter electrode/electrolyte interface. In addition, the flexibility of this new CNTs/G/Ni electrode enables the fabrication of truly flexible DSC devices. The flexible DSC with the new counter electrode exhibits a PCE over 3.9%, outperforming that of 3.4% from the DSC with a Pt counter electrode. This superior electrocatalytic activity of the VAFWCNTs/graphene may originate from the combination of high specific surface area of the hybrid electrode and seamless electrical connection between the VAFWCNTs and graphene layer. The experimental results demonstrate that the CNTs/G/Ni electrode can be an ideal cost-effective, high-performance and flexible, alternative counter electrode for DSC.
Chapter 6

Chapter 6. Conclusion Remarks

Dye sensitized solar cells (DSCs), as the third generation of solar cells, have attracted tremendous attention for their unique properties. The semi-transparent nature, low-cost, environmental friendliness, and convenient manufacturing conditions of this generation of solar cells are all promising characteristics of DSCs that make them competitive in their future applications. However, much improvement in many aspects of DSCs' is required for the realization of its full potential. In this thesis, various nanomaterials, such as graphene, multi wall carbon nanotubes, vertically aligned single wall carbon nanotubes, hybrid structures and etc, have been used to improve the performance of DSCs.

In Chapter 2, for the first time, a graphene/metal grids hybrid structure was used as the TCE for DSCs. The efficiency of the DSC with graphene/Pt grids was
0.4%, which is the highest efficiency seen for DSCs with graphene as the transparent conductive layer (without ITO or FTO supports). The sheet resistance of this TCE is low (up to 3 Ω/□ at 80% transmittance); while its mechanical properties are stable under strain. The efficiency of DSCs with graphene/Ni grids fabricated using 150°C processing techniques was 0.25%. It may be possible to achieve further improvements, thus different strategies to improve the cell efficiency will be explored. With a good combination of mechanical and electrical properties, graphene/metal grids could contribute to the development of the next generation of flexible DSCs on arbitrary surfaces, while maintaining their performance and long term durability upon strain.

From Chapter 3 to 5, several different kinds of carbon nanotubes have been used as a replacement for traditional platinum counter electrodes:

In Chapter 3, a hybrid structure that is composed of bamboo-like carbon nanotubes and graphene-like film can be self-peeled from the copper substrate, and then attached to the FTO-glass as the counter electrode of DSC. Our experiments determine that the MWCNT-DSC has an efficiency of 5.9%, comparable to 5.6% obtained with a reference Pt-DSC. EIS determine that the electrolyte-MWCNT resistance in this architecture is lowered than that of Pt, whereas the MWCNT-FTO interface has a higher resistance due to the PVDF binder.

In Chapter 4, we explored the performance of VASWCNT-DSC with various SWCNT lengths. This DSC architecture with ∼34μm VASWCNT length was found to
yield the optimal counter electrode in our systematic study. Our experiments
determine that the VASWCNT-DSC has an efficiency of 5.5%, comparable to 5.6%
obtained with a reference Pt-DSC. Electrical impedance measurements determine
that the electrolyte-VASWCNT resistance in this architecture is lowered by up to ~
6× compared to Pt, whereas the VASWCNT-FTO interface has a higher resistance
due to the contact transfer process utilized here.

Later, VASWCNTs have been used as efficient low-cost counter electrode material
in iodine-free DSCs, featuring notably improved electrocatalytic activity towards
thiolate/disulfide redox shuttle. Interestingly, device in conjunction with
VASWCNTs counter electrode demonstrates a high FF of 0.68 and PCE up to 5.25%,
which is significant higher than 0.56 and 3.49% for that with a conventional Pt
counter electrode. Moreover, in QDSCs system, the $R_{ct}$ of VASWCNTs counter
electrode is as low as 21.22 Ω towards aqueous polysulfide electrolyte. This is
several orders of magnitude lower than that of Pt electrode. In comparison with
alternative counter electrode materials previously reported such as Au, CoS, Cu$_2$S or
PbS, to the best of our knowledge, such an $R_{ct}$ value is the lowest ever seen in the
polysulfide electrolyte system.

Therefore, the highly catalytic VASWCNTs counter electrodes are believed to be a
versatile candidate for further improvement of the PCE of both iodine and iodine-
free redox couple based DSCs and polysulfide electrolyte based QDSCs. Nonetheless,
our studies still emphasize that future work needs to focus on improving the
electrical interface between VASWCNT arrays and the back-contact could yield DSC device performance exceeding that which can be obtained with a traditional counter electrode design, while also providing a lower cost alternative to Pt.

In Chapter 5, to avoid the contact problem, the seamless 3-dimensional SWCNTs/graphene on Ni foil scaffold was used as the counter electrodes for TCO and Pt-free dye-sensitized solar cells. The 8.2% efficiency of the DSC made from FWCNTs with 100-150μm original length achieved the highest value, compared with other FWCNTs-DSCs. All the PCEs of the DSCs with novel hybrid counter electrode materials are higher than 6.4% as the PCE of the rigid reference DSC with Pt counter electrode. In all flexible substrates, the PCE of DSC with the new counter electrode reached 3.9%, higher than 3.4% from the DSC with Pt as the control group. According to the EIS results, electrons transferred a magnitude faster at the counter electrode/electrolyte interface for VACNTs/graphene samples than that for Pt, The results show that the VACNTs/graphene on Ni foil provides an ideal low-cost, flexible alternative counter electrode for DSC.

In conclusion, based on the systematic research in this thesis, the large surface area of the previously discussed nanomaterials in addition to the high electrical conductivity and their mechanical robustness provides a platform for significant enhancements in DSCs’ performance.
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