Fabrication of Functional Materials for Dye-sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) have been developed as a promising photovoltaic cell type in recent decades because of their low cost, environmental friendliness, ease of fabrication, and suitability for a wide range of indoor and outdoor applications, especially under diverse shaded and low-light condition. They are typically composed of three main components: a transparent conducting oxide (TCO) substrate-based working electrode with wide-bandgap semiconductors and dye sensitizer molecules, an electrolytic mediator based on redox couple species, and a TCO-based counter electrode consisting of catalyst materials. The development of intrinsic and functional organic, inorganic, metal oxide, composite, and carbon-based materials has been intensively studied to enhance the efficiency of DSSCs. A simple and low-cost fabrication process that uses natural products is also considered essential for further large-scale production. In this article, we review the fabrication of various functional materials and their effects on DSSC performance.

Keywords: dye-sensitized solar cells, functional materials, carbon-based materials, composite materials, density functional theory

INTRODUCTION

Dye-sensitized solar cells (DSSCs) represent promising molecular architecture opportunities in the field of energy conversion. DSSCs consist of three crucial parts: a working electrode (WE) with a photosensitizer, an electrolytic mediator, and a counter electrode (CE).

The development of new photosensitizers for DSSCs is a challenge that is being pursued through investigations at the molecular level. Recently, dye molecules have been developed from natural and synthetic sources to allow practical implementation and have accordingly attracted the attention of numerous researchers seeking to develop materials with better photosensitizing properties. The sensitizer plays an essential role in light absorption and electron injection into the conduction band of a semiconductor.

In DSSCs, an electrolyte based on a tri-iodide/iodide (I$_3^-$/I$^-$) mediator provides the best electrochemical efficiency and is widely utilized with a metal catalyst. However, this electrolyte is extremely corrosive to the metal film catalyst of a CE (Olsen et al., 2000). Reducing the corrosive activity of iodide by using the highly stable catalyst materials is therefore a key to realizing the full potential of an I$_3^-$/I$^-$ electrolyte. The use of an organic disulfide/thiolate (T$_2^2$/T$^-$) electrolyte has also been investigated because of its high transmittance and low corrosivity; it exhibits higher efficiency and stability than the conventional I$_3^-$/I$^-$ electrolyte.
Since Pt-based CEs exhibit the best electrochemical efficiency, they are commonly used in high-performance DSSCs, but Pt is not the only catalyst that has been studied. Materials, such as conductive allotropes of carbon, graphite, graphene, and carbon nanotubes, as well as amorphous and diamond-like and graphite-like carbon composite films have also significantly advanced this field of research. Furthermore, high-performance catalysts using composite or functional materials have been developed to promote the greater surface area, low charge-transfer resistance, and cocatalytic activity.

To provide a clear picture of the progress of DSSC research, this review provides a summary of recent advances in the fabrication of DSSC components. Indeed, a great deal of research has been conducted to evaluate various WEs, photosensitizers, electrolytes, and CEs, as detailed in Figure 1 and Table 1, and discussed in the following sections.

**ADVANCED FUNCTIONAL MATERIALS FOR PHOTOELECTRODES**

**Metal Oxide and Nanocomposite Materials**

Nanocrystalline TiO$_2$-based mesoporous electrodes are frequently used in DSSCs because TiO$_2$ exhibits the highest efficiency among the investigated materials, which also include ZnO, SnO$_2$, Nb$_2$O$_5$, SrTiO$_3$, Zn$_2$SnO$_4$, and ZnO-coated SnO$_2$ (Hagfeldt et al., 2010). In an efficient DSSC, the photoelectrode should have the following characteristics (Hasan et al., 2020):

- High surface area and porosity.
- A conduction band level should be sufficiently lower than the lowest unoccupied molecular orbital of the dye molecule.
- High electrical conductivity.
- Good chemical stability avoid photo- or chemical corrosion.
- The ability to absorb or scatter the solar radiation effectively.

The development of efficient WEs based on various types of materials is accordingly reviewed in this section. A modified photoelectrode was developed by adding nitrogen heterocycles as electron-donors, which produced a negative shift in the conduction band and reduced electron recombination (Lau and Soroush, 2019). Other additives in the semiconductor materials with a suitable cation/anion have also sufficient conduction band edge providing high electron injection rate (Hasan et al., 2020). A DSSC-based metal oxide semiconductor co-adsorbed with guanidinium [C(NH$_2$)$_2$]$^+$ cations achieved an efficiency of 11.04% (Grätzel, 2004). Furthermore, adding other cation dopants, such as Ni, W, Al, Nb, Sn, Li, Fe, Cu, Zn, Ce, La, and Eu, to semiconductor materials can change by the interfacial energy levels leading to faster electron hole separation from dye to mesoporous electrodes and also reduced the recombination of photoelectrons at the electrolyte–semiconductor interface (Watson and Meyer, 2004; Roose et al., 2015; Hasan et al., 2020). The anionic dopants, including N, B, C, S, P, F, I, and Br, have also been reported (Zhang et al., 2010; Cheng et al., 2015). In comparison to cationic dopants, anionic dopants have a greater electrical conductivity because of their superior thermal and photochemical stabilities (Hasan et al., 2020).

Besides cationic/anionic additives, Jarernboon et al. (2009a) studied the effects of multiwall carbon nanotubes (MWCNTs) on the reduction of the microcrack formation in metal oxide TiO$_2$ films. They successfully synthesized a nanocomposite TiO$_2$/MWCNT film using an electrochemical deposition technique, finding that a minimal addition of MWCNTs to the TiO$_2$ solution significantly reduced the degree of TiO$_2$ cracking. It was suggested that MWCNTs minimize cracking by bonding to TiO$_2$ particles through the interaction of their hydroxyl and carboxylic groups. The spectrophotometric measurements revealed that the MWCNTs were well dispersed on the film, and the amount of MWCNTs incorporated on the film increased with increasing MWCNT concentration in the solution.

Jarernboon et al. (2009b) reported the optimization of TiO$_2$ films for DSSC applications prepared via electrochemical deposition. It was found that the thickness of the TiO$_2$ films increased proportionally with the deposition time and voltage. However, as the deposition time or deposition voltage increased, the film surface became more discontinuous and microcracks became evident. The characteristics of these films as WEs were also analyzed. The energy conversion efficiency and photocurrent density were both dependent on TiO$_2$ thickness. The curve fitting of the relationship between energy conversion efficiency and TiO$_2$ thickness revealed an optimum solar cell efficiency of ~2.8% at a film thickness of ~14 µm.

Sae-kow et al. (2012) reported a huge increase in the photocurrent density and conversion efficiency of DSSCs manufactured using a high-intensity UV-O$_3$ treatment on TiO$_2$-layered WEs. This high-intensity UV-O$_3$ treatment reduces the charge-transfer resistance and increases the amount of dye adsorbed onto the TiO$_2$ surface. This appears to have the same effect as the sintering of electrical contacts through UV illumination during the manufacturing of the semiconductors.

**Photosensitizer and Molecular Development**

Photosensitizers are a critical component of DSSCs that play an essential role in light absorption and electron injection into the conduction band of a semiconductor. A dye sensitizer acts to absorb photons that contain energy equal to or higher than the energy gap of its molecules, improving the efficiency of DSSCs. Indeed, a sufficient driving force is required to convert light into electricity (Sang-aroon et al., 2019), providing an opportunity to design and develop molecular dyes for use as photosensitizers in DSSCs. Such dyes can either be derived from natural sources or be synthesized, and their molecular structures have been improved considerably by ongoing research. The molecular architecture of an effective photosensitizer has the following essential characteristics (Hagfeldt et al., 2010):

- The photosensitizer should have small molecules that are easily dispersed to cover the nanocluster surfaces of semiconductors and form many layers for adsorption.
- The absorption spectrum of the photosensitizer should cover the entire visible region and even part of the near-infrared (NIR) region.
- The photosensitizer should have many anchoring groups such as $-\text{OH}$, $-\text{COOH}$, $-\text{H}_2\text{PO}_3$, and $-\text{SO}_3\text{H}$, which can strongly bind to the semiconductor surface.
- The excited state of the photosensitizer should be higher in energy than the conduction band edge of the semiconductor, so that an efficient electron transfer process can occur between the excited dye and conduction band can occur. In contrast, the highest occupied molecular orbital of the photosensitizer should have a more positive potential than the valence band of the semiconductor.
- For dye regeneration, the oxidized state of the photosensitizer must be more positive than the redox potential of the electrolyte.
- Unfavorable dye aggregation on the semiconductor surface should be avoided by optimizing the molecular structure of the dye or by adding the co-adsorbers that prevent aggregation.
The photosensitizer should be photothermally and electrochemically stable.

Many different sensitizing dyes, including synthetic dyes (i.e., metal complexes and metal-free organic dyes) and natural dye pigments, have been evaluated for the application as photosensitizers in DSSCs according to the requirements in the studies by Sang-aroon et al. (2012, 2013, 2014), Chaiamornnugool et al. (2017), Tontapha et al. (2017), and Phinjaturus et al. (2016). The theoretical calculations are an important tool that can be used to understand, express, predict, and optimize the properties of the photochemical mechanism of sensitizing dyes during the intramolecular transition. In particular, a fundamental understanding of density functional theory (DFT) is helpful for designing and developing molecular structures to achieve better photosensitizer efficiency. Therefore, the DFT and time-dependent DFT (TD-DFT) methods have been used to calculate and predict the geometric structures of different dyes and explain their interactions within DSSC cells at an electron scale (Sang-aroon et al., 2012, 2013, 2014; Chaiamornnugool et al., 2017; Tontapha et al., 2017).

Among the natural sensitizing dyes, monosaccharides (Sang-aroon et al., 2012), cochineal and lac dyes (Sang-aroon et al., 2013), orcein dyes (Sang-aroon et al., 2014), anthocyanins (Maiaugree et al., 2015a; Phinjaturus et al., 2016; Chaiamornnugool et al., 2017; Tontapha et al., 2017), mangosteen dyes (Maiaugree et al., 2015a; Tontapha et al., 2017), and others (Sang-aroon et al., 2019) have shown good photosensitizing properties in both theoretical and experimental procedures. The main properties of DSSCs with various dye sensitizers are summarized in Table 1. However, the conversion efficiency of natural dyes when used as molecular sensitizers is still lower than that of synthetic dyes. Thus, it is necessary to search for new and highly effective synthetic dyes for the development of more effective photosensitive materials. Alternatively, the dye adsorption patterns can be designed with double- or triple-layered architectures to provide high-efficiency DSSCs. However, this is currently a challenge, as molecular engineering must be used to modify the electronic and molecular structures of the dyes to shift their absorption into the visible light region. Additionally, the adsorption kinetics of sensitizing dyes should be experimentally determined to develop an understanding of the adsorption rate of individual dyes.

**ELECTROLYTES**

Electrolytes are an important part of dye charge regeneration from its oxidized state to neutral state form by receiving electrons from redox mediators. The electrolyte-based redox couple system provides several benefits when applying an electrolyte to a device, such as (Krishna et al., 2019; Sang-aroon et al., 2019; Hasan et al., 2020):

- **Substantial ion mobility and low viscosity to support the fast transfer of electrons.**
- **A high diffusion coefficient.**
- **Long-term stability.**

The development of catalyst materials with properties comparable with those of Pt is a crucial challenge in which the following characteristics must be attained:

- **Use of low-cost materials, such as carbon-based materials, metal oxides, metal carbides, metal sulfides, conductive polymers, and natural products.**
- **Use of low-cost, facile synthesis, and fabrication processes based on screen printing, doctor-blade application, hydrothermal deposition, and annealing processes.**
- **Use of cocatalyst materials as well as more active catalytic sites; that is, incorporating composites and dopants.**

Generally, carbon-based, metal-based, and composite-based CE materials have been investigated to achieve these characteristics.

**Carbon and Carbon-based Materials**

Allotropes of carbon have previously been reported as excellent catalysts because of their low cost, large surface area, high...
| Counter electrode | Dye-sensitizer | Electrolyte | J<sub>SC</sub> (mA/cm<sup>2</sup>) | V<sub>OC</sub> (V) | FF | PCE (%) | PCE/Pt (%) | References |
|-------------------|----------------|-------------|-------------------------------|----------------|----|---------|-------------|-------------|
| **Photosensitizer and molecular development** | | | | | | | | |
| Pt | Anthocyanins | I<sub>r</sub>/I<sub>s</sub> | 2.91 | 0.46 | 0.53 | n/a | 0.71 | Chiamornnugool et al., 2017 |
| Pt | α-mangostin | I<sub>r</sub>/I<sub>s</sub> | 5.199 | 0.55 | 0.62 | n/a | 1.78 | Tangtrakarn et al., 2019 |
| Pt | Anthocyanins | I<sub>r</sub>/I<sub>s</sub> | 3.57 | 0.46 | 0.64 | n/a | 1.06 | Phinjaturus et al., 2016 |
| **Carbon and carbon based materials** | | | | | | | | |
| Carbon black mixed graphite | N719 | I<sub>r</sub>/I<sub>s</sub> | 11.34 | 0.83 | 0.71 | 6.70 | n/a | Bak and Grätzel, 1996 |
| Carbon black | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.80 | 0.79 | 0.69 | 9.10 | n/a | Murakami et al., 2006 |
| Electrospun carbon nanofibers | N719 | I<sub>r</sub>/I<sub>s</sub> | 12.60 | 0.76 | 0.57 | 5.50 | 6.97 | Joshi et al., 2010 |
| Sub-micrometer-sized graphite (CG-c) | N719 | I<sub>r</sub>/I<sub>s</sub> | 12.70 | 0.79 | 0.62 | 6.20 | 8.80 | Veerappan et al., 2011 |
| Graphene | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.99 | 0.75 | 0.54 | 6.81 | 8.49 | Zhang et al., 2011 |
| SWCNT | N719 | I<sub>r</sub>/I<sub>s</sub> | 14.94 | 0.80 | 0.64 | 7.61 | 8.49 | Zhang et al., 2011 |
| DWCNT | N719 | I<sub>r</sub>/I<sub>s</sub> | 15.43 | 0.80 | 0.65 | 8.30 | 8.49 | Zhang et al., 2011 |
| MWCNT | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.20 | 0.74 | 0.64 | 7.67 | 7.83 | Lee et al., 2009 |
| MWCNT | N719 | I<sub>r</sub>/I<sub>s</sub> | 15.25 | 0.80 | 0.56 | 7.06 | 8.49 | Zhang et al., 2011 |
| Mg incorporated MWCNT (W-Mg-0.04-g-CNT-1-min) | N719 | I<sub>r</sub>/I<sub>s</sub> | 3.71 | 0.67 | 0.43 | 1.08 | n/a | Pimapanp et al., 2009 |
| rGO | N719 | I<sub>r</sub>/I<sub>s</sub> | 12.58 | 0.70 | 0.58 | 5.11 | 7.89 | Rakspun et al., 2020 |
| AN-rGO (1:10) | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.34 | 0.78 | 0.54 | 6.88 | 7.89 | Rakspun et al., 2020 |
| NB-rGO (1:10) | N719 | I<sub>r</sub>/I<sub>s</sub> | 15.92 | 0.72 | 0.62 | 7.11 | 7.89 | Rakspun et al., 2020 |
| rGO | N719 | [Co(bpy)3]<sup>3+/2+</sup> | 6.82 | 0.69 | 0.71 | 3.34 | 4.57 | Rakspun et al., 2020 |
| AN-rGO (1:10) | N719 | [Co(bpy)3]<sup>3+/2+</sup> | 10.20 | 0.67 | 0.65 | 4.44 | 4.57 | Rakspun et al., 2020 |
| NB-rGO (1:10) | N719 | [Co(bpy)3]<sup>3+/2+</sup> | 10.36 | 0.67 | 0.65 | 4.51 | 4.57 | Rakspun et al., 2020 |
| Cement/CNTs (29:71) | N719 | I<sub>r</sub>/I<sub>s</sub> | 18.66 | 0.80 | 0.64 | 9.60 | 11.22 | Chindapaksit et al., 2019 |
| Annealed-hydrothermal (AHT)-MWCNT | N719 | I<sub>r</sub>/I<sub>s</sub> | 14.27 | 0.78 | 0.68 | 7.66 | 8.01 | Siriroj et al., 2012 |
| ITO/Pr/10 sccm N2 doped DLC | N719 | I<sub>r</sub>/I<sub>s</sub> | 2.33 | 0.58 | 0.34 | 1.85 | 3.20/3.53 | Wang et al., 2011 |
| 600°C annealed DLC | N719 | I<sub>r</sub>/I<sub>s</sub> | 10.57 | 0.73 | 0.65 | 5.00 | n/a | Park and Kim, 2011 |
| 500°C-DLC | N719 | I<sub>r</sub>/I<sub>s</sub> | 15.70 | 0.74 | 0.66 | 7.61 | 7.74 | Uppachai, 2015 |
| Annealed-nanoporous carbon microspheres (A-CMS) | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.82 | 0.80 | 0.57 | 7.71 | 8.05 | Lowpa et al., 2015 |
| Manganese peel carbon (MPC) | | | | | | | | |
| Manganese peel carbon (MPC) | | | | | | | | |
| Annealed-carbon | N719 | I<sub>r</sub>/I<sub>s</sub> | 18.56 | 0.74 | 0.64 | 8.74 | 8.80 | Tangtrakarn et al., 2019 |
| Annealed-carbon | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.53 | 0.64 | 0.45 | 4.74 | 3.98 | Tangtrakarn et al., 2019 |
| PPy-MWCNTs | N719 | I<sub>r</sub>/I<sub>s</sub> | 14.99 | 0.71 | 0.62 | 6.56 | 7.20 | Towannang et al., 2012 |
| PPy-MWCNTs | N719 | I<sub>r</sub>/I<sub>s</sub> | 8.29 | 0.63 | 0.59 | 3.05 | 3.19 | Towannang et al., 2012 |
| MWCNTs/Pt | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.10 | 0.77 | 0.71 | 8.90 | 8.13 | Maiagure et al., 2012a |
| Co-N-MC | N719 | I<sub>r</sub>/I<sub>s</sub> | 15.00 | 0.72 | 0.70 | 7.57 | 8.22 | Hasin et al., 2017 |
| Ni-N-MC | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.60 | 0.73 | 0.70 | 8.42 | 8.22 | Hasin et al., 2017 |
| Co-N-MC | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.00 | 0.70 | 0.60 | 6.80 | 5.25 | Hasin et al., 2017 |
| Ni-N-MC | N719 | I<sub>r</sub>/I<sub>s</sub> | 16.00 | 0.71 | 0.62 | 6.95 | 5.25 | Hasin et al., 2017 |
| Carbon/NiS<sub>2</sub> | N719 | I<sub>r</sub>/I<sub>s</sub> | 20.75 | 0.75 | 0.62 | 9.64 | 8.38 | Maiagure et al., 2015b |

(Continued)
corrosion resistance toward iodine, high reactivity for triiodide reduction, and suitable chemical compatibility with other elements (Grätzel, 2003). The use of magnesium nanoparticles and molecular dopants such as aniline (AN) and nitrobenzene (NB) on carbon nanostructures can provide high-performance catalysts for DSSCs based on iodide and cobalt-based electrolytes (Pimanpang et al., 2009; Rakspun et al., 2020). Furthermore, mixed powders containing MWCNTs and cement were coated onto a fluorine-doped tin oxide (FTO) substrate at a 29:71 ratio using a simple painting method without heating, resulting in a greater efficiency (9.60%) than that of a pure carbon DSSC (4.99%) (Chindapasirit et al., 2019).

An annealing treatment is commonly proposed to improve the electrical and electrocatalytic activities of DSSC materials. Siriroj et al. (2012) reported that hydrothermally depositing MWCNT onto a CE annealed at 180°C improved the efficiency of the DSSC from 2.37% (non-annealed) to 7.66%. Wang et al. (2011) reported that a DSSC using N-doped resistive diamond-like carbon (DLC) films as a catalyst exhibited an efficiency of only 1.57%; however, Park and Kim (2011) reported that the efficiency of a DSSC with a DLC film increased to 5% when using a 600°C annealing treatment on the DLC film. Similarly, the diamond-like and graphite-like composites films obtained by annealing a hydrogenated DLC film have been applied as efficient catalysts (Uppachai, 2015); annealing a DLC film at 500°C increased DSSC efficiency from 0.24 to 7.61%.

Nanoporous carbon microspheres (CMS) have been synthesized using a hydrothermal deposition method with carrot juice as the natural carbon source. An annealing process was then performed to increase the conductivity and surface area (149.10 m²/g) of the resulting microspheres. The efficiency of the cell using this CMS CE was 0.17% before annealing and 7.71% after annealing (Lowpa et al., 2015). Maiaugree et al. (2015a) synthesized a mangosteen peel carbon (MPC) using a sintering process and applied it as a catalyst with a large surface area of 125 m²/g, in a DSSC comprising a T₂/T⁻ electrolyte. The efficiency of this DSSC reached 2.63%, which was higher than that of a DSSC with a Pt CE (1.47%).

The electrocatalytic activities of the T₂/T⁻ electrolyte and non-metal catalysts have also been investigated. Tangtrakarn et al. (2019) synthesized a post-annealed evaporated-carbon CE for a DSSC with a T₂/T⁻ electrolyte, achieving a solar efficiency of 8.04%. A short-term stability test was also performed over 50 days; the efficiency of the carbon DSSC was observed to remain constant, whereas that of the Pt DSSC decreased by 26%.

A cofunctioning catalyst was proposed to further enhance the electrocatalytic activity and surface area of the CE, resulting in improved solar cell performance. Enhanced DSSC performance was obtained by Towannang et al. (2012) and Maiaugree et al. (2012a) by using a polypyrrole (PPy) cocatalyst mixed with MWCNTs and MWCNTs/Pt, respectively. Similarly, the efficiency of a DSSC using an I₃⁻/I⁻ or T₂/T⁻ electrolyte was found to increase with the addition of the nanoparticle composites of cobalt or nickel to N-doped mesoporous carbon (Hasin et al., 2017). A pronounced 3.59% improvement in performance, close to that of a Pt DSSC (3.84%), was achieved by compositing TiC with carbon as the catalyst (Towannang et al., 2012). Furthermore, a combination of chemical bath deposition, an arc evaporation process, and annealing was used to synthesize a bilayered carbon-decorated Ni₃S₂ composite nanowall film as a cocatalyst (Maiaugree et al., 2015b). The large surface area of the nanostructure and its high electrocatalytic activity improved

### Table 1

| Counter electrode | Dye-sensitizer | Electrolyte | J<sub>SC</sub> (mA/cm<sup>2</sup>) | V<sub>OC</sub> (V) | FF | PCE (%) | PCE/Pt (%) | References |
|------------------|----------------|-------------|-------------------------------|----------------|---|--------|-----------|------------|
| AH+TiC-carbon    | N719           | T⁻/I₂      | 10.12                         | 0.65           | 0.55 | 3.59   | 3.84      | Towannang et al., 2015 |
| NiₓS₂@MWCNTs     | N719           | I⁻/I₃      | 17.25                         | 0.75           | 0.56 | 7.48   | 7.24      | Maiaugree et al., 2019 |
| Metal-based and composite materials | | | | | | | | |
| PVP-capped Pt    | N719           | I⁻/I₃      | 10.50                         | 0.65           | 0.41 | 2.84   | 2.79      | Wei et al., 2006 |
| PANI             | N719           | I⁻/I₃      | 14.60                         | 0.71           | 0.69 | 7.15   | 6.90      | Li et al., 2008 |
| PPy              | N719           | I⁻/I₃      | 15.01                         | 0.74           | 0.69 | 7.66   | 6.90      | Wu et al., 2008 |
| MWCNT/PEDOT:PSS  | N719           | I⁻/I₃      | 15.5                          | 0.66           | 0.63 | 6.50   | 8.50      | Fan et al., 2008 |
| AC-1R-PPy        | N719           | I⁻/I₃      | 14.58                         | 0.74           | 0.43 | 4.72   | 7.59      | Keothongkham et al., 2012 |
| PEDOT-PSS-30L    | N719           | I⁻/I₃      | 17.30                         | 0.73           | 0.67 | 8.49   | 7.50      | Maiaugree et al., 2012b |
| NiS₄/PEOT-PSS     | N719           | I⁻/I₃      | 8.79                          | 0.65           | 0.54 | 3.05   | 3.64      | Maiaugree et al., 2013 |
| 0.3Ni₃S₄/NP/PEDOT-PSS | N719   | I⁻/I₃      | 16.05                         | 0.76           | 0.67 | 8.18   | 8.62      | Maiaugree et al., 2017 |
| STO_Co 0.075     | N719           | I⁻/I₃      | 21.22                         | 0.71           | 0.55 | 8.39   | 8.27      | Maiaugree et al., 2018 |
| Pt-WC            | N719           | T⁻/I₂      | 11.93                         | 0.60           | 0.59 | 4.29   | 3.80      | Towannang et al., 2012 |
| Pd-WC            | N719           | T⁻/I₂      | 11.79                         | 0.60           | 0.29 | 2.01   | 1.46 (Pd) | Towannang et al., 2018 |
| FTO/PNO/Pt       | N719           | T⁻/I₂      | 17.16                         | 0.69           | 0.69 | 8.17   | 7.23      | Maiaugree et al., 2014 |
| WO₃,β            | N719           | I⁻/I₃      | 13.44                         | 0.76           | 0.51 | 5.25   | 6.96      | Uppachai et al., 2014 |

Continued
the efficiency of a pure evaporated-carbon DSSC. The increased active surface area of nickel sulfide (NiS2) nanoparticles coated on MWCNTs prepared using a hydrothermal deposition process was also found to enhance DSSC performance (Maiaugree et al., 2019).

**Metal-based and Composite Materials**

An advantage of metal-based and composite CE cocatalyst materials is that they can be used in DSSCs instead of a pure PPy or PEDOT:PSS conductive polymer (Wu et al., 2008; Keothongkham et al., 2012). The composite catalyst materials, such as PEDOT-PSS+TiO2 (Maiaugree et al., 2012b), NiSO4+PEDOT:PSS (Maiaugree et al., 2015), NiS+PEDOT:PSS (Maiaugree et al., 2017), and SrTi1-xO3+PEDOT-PSS (Maiaugree et al., 2018), have been prepared by using various methods employing doctor-blade applications, electrodeposition, or hydrothermal deposition processes. The efficiencies of DSSCs employing these composite materials were found to be significantly increased because multiple catalysts were excited. Tonnannang et al. (2018) used a hydrothermal process to fabricate a tungsten carbide (WC) CE catalyst with Pt or Pd particles for DSSCs with a T2/T- electrolyte, resulting in considerably improved cell efficiency. Maiaugree et al. (2014) synthesized the connected networks of sputtered Pt on porous nickel oxide (PNO) nanosheets for use as a catalyst. The solar conversion efficiency of the FTO/PNO/Pt DSSC was 8.17% compared to the 7.23% efficiency of the FTO/Pt DSSC, as the electrocatalytic activities were enhanced and the electroactive areas were increased. A tungsten oxide (WO3-x) CE was easily prepared via thermal annealing of a tungsten sheet under a low-pressure O2 atmosphere (Uppchai et al., 2014); the resulting presence of W6+, W5+, and W4+ valence states in the sub-stoichiometric WO3-x produced excellent catalytic activity and electrical conductivity.

**CONCLUSIONS**

Functional materials based on cost-effective and low-cost substrates, produced using practical and facile fabrication processes, can be transferred to large-scale DSSC production with optimized materials, components, and manufacturing processes (Amornkitbamrung et al., 2015; Chindapasirt et al., 2019). Cocatalysts and composite materials that provide low resistivity, high catalytic activity, and large surface area are particularly promising. The low-cost approaches using facile fabrication processes detailed in this review can reduce production time while remaining environmentally friendly.

**AUTHOR CONTRIBUTIONS**

VA: conceptualization and supervision. PU and ST: manuscript preparation and revision. All authors have read and agreed to the published version of the manuscript.

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