Platinum-Free Catalysts as Counter Electrodes in Dye-Sensitized Solar Cells

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1. Introduction

Since 1991, much progress has been made in the development of dye-sensitized solar cells (DSSCs).[1–3] When compared to traditional silicon solar cells, DSSCs possess several unique advantages, such as simpler fabrication procedures, higher plasticity, higher transparency, and a greater variety of colors. Generally, a DSSC can be described by three components: a photoanode (i.e., a dye-sensitized mesoporous semiconductor film); an electrolyte containing a redox couple; and a counter electrode (CE). Figure 1 is a schematic drawing of a DSSC. Under illumination, a sensitizer molecule (S) jumps to an excited state (S*), and the unstable S* releases a photoelectron (e−/C0) that injects into the conduction band (CB) of the semiconductor, leaving behind a sensitizer hole (S+). Actually, the excited state (S*) may relax to the ground state without release of a photoelectron, but this is not the main process. These processes occur according to Formulae (1) and (2). Next, the photoelectrons in the CB are collected by the substrate (SB), flow through the external circuit, and reach the CE [Formulae (3) and (4)]. The oxidation state of the electrolyte (Ox) is reduced to the reduction state (Red−/C0) by electrons at the CE, as shown in Formula (5). Meanwhile, S+ is regenerated by Red−, which is oxidized to Ox according to Formula (6) until a circuit circle is completed. The electron transfer processes are accompanied by electron recombination. The recombination processes occur between the photoelectrons (CB) and the sensitizer holes [Formula (7)] and between the photoelectrons and Ox of the redox couple [Formula (8)]. Recombination is a major cause of efficiency loss in DSSCs and other solar cells.[4–6]

In DSSCs, platinum deposited on fluoride-doped tin oxide (FTO) conductive glass is generally used as CE. Platinum acts as catalyst and FTO as electron collector. The preparation of platinum CEs comprises (i.a.) thermal decomposition,[7, 8] magnetron sputtering,[9, 10] electrochemical decomposition,[11–13] and chemical reduction.[14–16] As previously noted, Platinum acts as catalyst for the regeneration of the redox couple. In light of this fact, Hauch et al. analyzed the role of platinum in the regeneration of an I3−/I− redox couple in a DSSC system.[17] A mechanism was proposed for the charge transfer reaction between I3− and I− with the help of platinum. The mechanism can be divided into four steps as follows:

(i) \( I^- + Pt \rightleftharpoons I^- (Pt) \) (absorption of I− on the Pt surface, fast)

(ii) \( I^- (Pt) \rightleftharpoons I (Pt) + e^- \) (oxidation of I−, slow)

(iii) \( e^- (CB) \rightleftharpoons e^- (SB) \)

(iv) \( e^- (SB) \rightleftharpoons e^- (CE) \)

(v) \( Ox + e^- (CE) \rightleftharpoons Red^- \)

(vi) \( Red^- + S^+ \rightleftharpoons Ox + S \)

(vii) \( e^- (CB) S^+ \rightleftharpoons S \)

(viii) \( e^- (CB) Ox \rightleftharpoons Red^- \)

Figure 1. Schematic of dye-sensitized solar cells.

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The surface of a platinum CE can be considered homogeneous and smooth, thus, step (i) occurs quickly and the forward rate is proportional to the concentration of \( \text{I}^- \) and to the number of unoccupied platinum sites. Steps (iii) and (iv) are also fast, and the rates of the forward reactions are equal to those of the reverse reactions. Step (iii) shows that platinum is a perfect catalyst for the adsorption and dissociation processes. Step (ii) is the slowest step, indicating that it is the rate-determining step for the redox couple \( \text{I}_3^- / \text{I}^- \). In addition, Hauch et al. found that platinum can be contaminated by components in the air.

We have investigated the effects of platinum film thickness on catalytic activity.\(^{18}\) The film thickness, ranging from 2 nm to 415 nm, was controlled by the sputtering time. For platinum films ranging from 2 to 10 nm no obvious mirror image was observed, while the other films, ranging from 25 to 415 nm, showed obvious mirror images, which was favorable because it increased the likelihood that incident photons are collected. A platinum film thickness of 2 nm was sufficient to obtain good catalytic activity. In the case of thicker platinum films (>2 nm), the additional thickness had no significant influence on the catalytic activity of the platinum CEs.

The substrate for the platinum CEs was usually FTO conductive glass. We have also evaluated platinum CEs on various substrates, in the form of nickel, steel, copper, and aluminum sheets. Moreover, organic polymers have been used as substrates to prepare flexible and transparent platinum CEs. These polymers include poly(ethylene naphthalate) films coated with tin-doped indium oxide (ITO-PEN), poly[3,4-ethylenedioxy-thiophene] (PEDOT), poly(ester), poly(styrene) and poly(ethylene).\(^{19}\) A stability test was performed on each substrate.

Platinum has become a benchmark in the field of CE catalyst development owing to its high catalytic activity, and thus remains a popular research topic in the field of DSSCs.\(^{20–22}\) Nevertheless, platinum has obvious disadvantages (high costs and limited availability) that restrict its application to the mass production of DSSCs. In addition, Olsen et al. have found that platinum might be dissolved in electrolytes containing the \( \text{I}_3^- / \text{I}^- \) redox couple, producing PtI\(_4\).\(^{20}\) Previously, the CE was not considered to be a key component and reports on CE catalysts were less extensive than those on sensitizers and semiconductors. As shown in Figure 2, the number of reports on CEs for DSSCs was limited from 2002 to 2006. However, since 2009, with the introduction of a series of low-cost, high-efficiency CE catalysts, such as CoS and TiN,\(^{24,25}\) this trend has been reversed and the number of studies on new CE catalysts has increased drastically. This breakthrough in CE catalysis promotes research towards reducing the costs of DSSCs, making them more competitive among various photovoltaic devices.

In the following sections, we give a comprehensive summary of platinum-free CE catalysts for DSSCs. These platinum-free catalysts can be divided into five types: metals, carbon materials, inorganic compounds, polymers, and composites. We highlight the advantages and disadvantages of each type of platinum-free catalyst and share techniques for guiding the design of catalysts in future research.

2. Platinum-Free Counter Electrode Catalysts

2.1. Metals

Platinum-free catalysts designed to replace the expensive platinum should possess the following properties: high catalytic activity, low cost, easy availability, and stability. Nickel and palladium are logical candidates because they are in the same group of the periodic table as platinum (Group VIII A metals). A nickel CE has been prepared by depositing a nickel film onto FTO glass by using an electroplate method. The DSSC showed a poor fill factor (FF) of 0.15, and a low open-circuit voltage (\(V_{oc}\)) of 468 mV.\(^{26}\) The low FF and \(V_{oc}\) were caused by a reaction between \( \text{I}_3^- \) with Ni. The stability of a CE prepared from palladium vapor-deposited onto FTO glass in an iodide species electrolyte had been previously investigated by Olsen. The palladium was not stable due to the formation of PdI\(_4\), according to a thermodynamical calculation. However, unlike the vapor-deposited layer, metallic palladium (a solid wire) did not react with the corrosive iodide species in the electrolyte, indicating that the deposition method may have an impact on the stability of metal CEs.\(^{23}\)

Sapp and colleagues used a gold CE in DSSCs with a cobalt (Co\(^{3+}/\text{Co}^{2+}\)) electrolyte.\(^{27}\) The gold-based DSSC showed a higher short-circuit current density (\(J_{sc}\)) that outperformed a platinum-based DSSC due to the fast regeneration of the cobalt redox species on the gold CE surface. Corrosion of gold in the cobalt electrolyte was not observed. Moreover, gold is more suitable than platinum for quantum-dot-sensitized solar cells (QSSCs) because the commonly used redox couple, \( \text{S}^2^- / \text{S}^2\)\(_2\), absorbs on platinum surface very well; this phenomenon is not observed with gold surfaces.\(^{28}\) Although gold possesses a high catalytic activity, its high cost, similar to platinum, may
restrict its application. More details of platinum-free CEs for iodide-free redox couples are discussed in section 2.6.

We have used the sputtering method to prepare molybdenum and tungsten CEs on a titanium sheet. The molybdenum and tungsten CEs showed poor catalytic activity for the iodide redox couple. DSSCs using the molybdenum and tungsten CEs yielded low power conversion efficiencies (PCEs) of 0.30% (Mo) and 0.19% (W), respectively. However, Mo$_3$N and W$_2$N prepared by the sputtering method showed high catalytic activities (discussed below). Until now, no metal CE catalyst with low cost, high catalytic activity, and high corrosion stability has been found. In future studies, alloys could be considered for the development of new metal CE catalysts for DSSCs.

2.2. Carbon materials

In order to reduce the cost of DSSCs by a large margin great magnitude, the development of low-cost CE catalysts is a feasible path. Carbon is an element that exists in five stable polymorphs: diamond, graphite, C$_{60}$, carbon nanotubes (CNTs), and graphene (Figure 3). Carbon materials possess the merits of low cost, good catalytic activity, electrical conductivity, high thermal stability, and corrosion resistance.

![Figure 3. Polymorphs of carbon.](image)

Due to the aforementioned advantages of carbon materials, they have been widely used in DSSCs. In 1996, Grätzel et al. introduced graphite and carbon black (Cb) into a monolithic DSSC as CE, and obtained a PCE of 6.7 %. The high catalytic activity of this carbon CE can be attributed to two factors: (1) graphite improved the lateral conductivity of the CE, and (2) Cb granted the CE a large surface area. The results reaffirm that carbon is a promising candidate to replace platinum. Activated carbon (AC) is a type of amorphous carbon with a diamond structure that Takahashi et al. used as a CE catalyst in DSSCs. The photovoltaic performance can be improved by increasing the roughness factor of the AC CE. At the same time, such an increase of the roughness factor decreases the charge-transfer resistance ($R_u$) in the CE/electrolyte interface. A DSSC using a AC CE showed a PCE of 3.89%, close to that of a DSSC using a platinum CE (4.30%). Grätzel et al. also investigated the application of Cb for CE catalysts in DSSCs. They found that the thickness of the Cb film significantly affected the FF and PCE. The FF increased from 0.463 to 0.685 as the thickness increased from 0.85 μm to 14.47 μm. The PCE demonstrated the same trend, whereas $V_{oc}$ and $J_{sc}$ varied very little as the Cb film thickness increased. Based on analyses by electrochemical impedance spectroscopy (EIS), the $R_u$ proved inversely proportional (nonlinear) to the thickness. A DSSC using a Cb CE with 14.47 μm thickness produced a high PCE of 9.1%. However, they did not evaluate the performance of the Cb CEs with thicknesses of more than 14.47 μm, and so our group performed a systematic investigation of which the results are discussed below.

Zou et al. fabricated fiber-shaped DSSCs using carbon fiber (Cf) as CEs. A DSSC using a Cf CE gave a PCE of 2.7%. Platinum deposited onto a Cf and combined metal wire could improve the catalytic activity, increasing the corresponding PCE value to 5.8%. EIS measurements indicated that the $R_u$ value did not change dramatically as a result of the modifications with platinum and metal wire. The series resistance ($R_s$) value, however, was reduced by a factor of three, contributing significantly to the improved photovoltaic performance.

Wang et al. prepared mesoporous carbon (Cm) as follows: phloroglucinol and formaldehyde were used to form a phenolic resin incorporated into a pluronic F127 template, which was then carbonized at 800 °C, producing Cm. The specific surface area of the Cm was 400 m$^2$ g$^{-1}$ and a DSSC using this CE yielded a PCE of 6.18%. Ramasamy and Lee used mesocellular silica as the hard template and divinylbenzene as the carbon source in order to prepare a ferrocene-derivatize, large-pore mesocellular carbon foam (Fe-MCF-C). A DSSC using this Fe-MCF-C as CE yielded a PCE of 7.89%, 12% higher than that of a DSSC using a pristine MCF-C CE. Cyclic voltammetry (CV) results showed that the $\Delta E_p$ (peak-to-peak separation) was 68 mV for Fe-MCF-C and 87 mV for MCF-C. The $\Delta E_p$ varies inversely with the charge transfer rate ($k$). According to the Nicholson method, the authors calculated the $k$ values for Fe-MCF-C and MCF-C as 0.0116 cm$^{-1}$ and 0.0034 cm$^{-1}$, respectively. Meng et al. fabricated an incorporated-carbon CE by using a flexible graphite sheet as the substrate and AC as catalyst. Due to the high electrical conductivity of graphite and the high catalytic activity of AC, low $R_s$ and $R_u$ values were observed for this carbon CE. A DSSC using this CE showed a PCE of 6.46%, surpassing the performance of a DSSC using a platinum CE (6.37%).

Lee et al. investigated the impact of the carbon particle size on the catalytic activity. Two kinds of carbon materials were involved in their research: the first was nanocarbon (surface area 100 m$^2$ g$^{-1}$) with an average size of 30 nm; the second was microporous carbon (surface area 0.4 m$^2$ g$^{-1}$) with a size of 2–12 μm. They found that the particle size strongly impacted the catalytic activity. A DSSC using the nanocarbon CE gave a PCE of 6.73%, much higher than a DSSC using the microporous CE. This difference in behavior between the two types of carbon material arises from the surface area and the conductivity. The
small surface area and high electrical resistance lead to high $R_s$ values, resulting in a low $FF$.[40]

CNTs were discovered in 1991.[41] CNTs in general comprise single-walled CNTs (SWNTs), double-walled CNTs (DNTs), and multi-walled CNTs (MNTs). CNTs can be designed as a semiconductor or metallic material according to the varied chiralities (the arrangement of the carbon honeycomb with respect to its axis).[40] In DSSCs, CNTs can be applied directly as CE catalyst. Using CNTs to replace platinum can endow the CEs with the following advantages: nanometer-scale transfer channels, large specific surface areas, low costs, high catalytic activities, and light weight.[30] A DSSC using SNTs as CE yielded a PCE of 4.5%, comparable to a DSSC using a (sputtered) platinum CE.[42] Lee et al. used MNTs as CE in DSSCs. Compared to the conventional platinum CE the MNT CE showed a low $R_{\text{ct}}$ due to the high density of defect-rich edge planes with an improved electrode/electrolyte interface. DSSCs using MNT and platinum CEs yielded PCE values of 7.67% and 7.83%, respectively, under 1 sun illumination (100 mw cm$^{-2}$, air mass 1.5 G).[44]

Zhu et al. investigated the differences between SNTs, DNTs, and MNTs as CEs in anthocyanin-based DSSCs under the same conditions.[46] A DSSC using SNTs as CE showed the best photovoltaic performance (1.46%) when compared to two other DSSCs using DNTs (0.45%) and MNTs (0.62%) as CEs. Among the three kinds of CNTs, the SNTs had the highest electrochemical activity for regeneration of the $I_3^-/I^-$ redox couple due to the 1D nanofeatures, which provided good electron transport. Furthermore, the impurities (iron, amorphous carbon) in SNTs can significantly affect the catalytic performance. For example, a DSSC using purified SNTs as CE showed a PCE of 1.46%, while a DSSC using “raw” SNTs as CE yielded a poor PCE of 0.57%. This can be attributed to catalyst poisoning: impurities occupying the catalytic sites. In contrast, the purification process introduces many oxygen functional groups that form new catalytic sites.

The technique adopted to prepare the CNT-based CEs is crucial for achieving high catalytic activity. Kim et al. have prepared CNT CEs by using screen printing and chemical vapor deposition (CVD) techniques. The CNTs of printed CEs were randomly oriented and woven into each other, whereas the CNTs of CVD CEs grew directly on the conductive glass surface, as shown in Figure 4. A DSSC using the printed-CNT CE showed a PCE of 8.03%. When the well-aligned CNTs prepared by CVD were used as CE, the PCE value increased to 10.04%. To the best of our knowledge, this is also the champion carbon-based DSSC using CNTs as CE.[35] The superiority of CVD CNTs can be attributed to the high conductivity arising from the well-aligned arrangement. In addition to screen printing and CVD, CNT CEs can also be fabricated by using the spraying technique.[46] The impact of spraying time for the CNT paste (i.e., CNT film thickness) on the performance of the CNT CEs was investigated. As the spraying time was increased from 5 to 30 s, the $J_s$ increased rapidly and the PCE value improved from 0.68% to 3.39%. With the increase in time, the $V_{oc}$ changed only slightly while the $FF$ increased dramatically. When the spraying time reached 200 s, the highest PCE of 7.59% was obtained. In their research, the PCE increased continuously with the spraying time (0–200 s). From our experiences, we believe there exists an optimal spraying time (i.e., thickness).

In recent years, graphene has become a prominent topic of research in various fields. Graphene is a single layer of 2D graphite that has the advantages of high conductivity, transparency, hardness, and corrosion resistance.[36, 47, 48] Grätzel et al. used graphene to prepare optically transparent CEs for DSSCs.[49] The graphene CE performed better for the regeneration of $I_3^-/I^-$ in ionic liquid solvent than in a traditional organic solvent. The $R_{\text{ct}}$ value of the ionic solvent was smaller than the traditional solvent by a factor of 5–6. This means that the mechanism for the regeneration of $I_3^-/I^-$ in the graphene surface is determined by solution-related events, rather than viscosity. The catalytic activity of graphene is proportional to the concentration of active sites (edge defects and oxide groups). The authors suggested that graphene was a promising alternative to platinum and also to the FTO conductive layer, which had been confirmed by previous work.[50]

As previously noted, the catalytic activity is correlated to the concentration of oxide groups. Aksay et al. evaluated this statement, and found that the C/O ratio had a strong influence on the catalytic activity.[51] Based on analysis of CV results, the $\Delta E_P$ increased alongside an increase in C/O ratio, as long as the C/O ratio exceeds 13. This means that a small number of oxide groups leads to a large $R_{\text{ct}}$, and, subsequently, poor catalytic activity. A DSSC using an optimal graphene CE showed a PCE of 5.0%, close to that of a DSSC using a platinum CE (5.5%). Jeon and colleagues fabricated a graphene CE by using the electrophoretic deposition (EPD) technique for DSSCs.[52] In their study, graphene was reduced from graphite oxide. They found that the number of oxygen functional groups decreased due to annealing, whereas DSSCs using graphene CEs (annealed at the highest temperature, 600 °C, with the fewest number of oxygen functional groups) performed best (5.69%). In other words, the catalytic activity increased as the number of oxygen functional groups decreased. We contend that the graphene prepared with the EPD technique has many oxygen functional groups, leading to a large $R_{\text{ct}}$ (confirmed by EIS tests). Building on previous results,[51] we claim that there is an optimum number of oxygen functional groups for graphene to achieve optimal catalytic activity. The PCE values for the DSSCs
in the works mentioned above were all less than 6%, leaving much room for improvement by modifying the concentration of the oxygen functional groups or lattice defects. Nevertheless, more studies are required to fully evaluate these statements.

Our group has performed a comprehensive study on nine kinds of carbon materials: AC, Cb, conducive carbon (Cc), carbon dye (Cd), Cf, CNTs, ordered mesoporous carbon (Com), discarded toner (Cp), and C60.[53] AC, Cb, Cc, Cd, Cf, CNTs, and C60 were purchased. Cp was obtained from discarded toner. Com was synthesized by a simple chemical method. As shown in Figure 5 a and b, Com is stacked with carbon blocks, which are, in turn, made up of rows of well-ordered carbon walls with a width of approximately 10 nm. This carbon wall configuration forms many channels in the CE body. The carbon walls are composed of minute carbon nanoparticles. Figure 5c shows a cross-sectional image of the well-ordered carbon walls, which have a typical mesoporous structure. The channels and mesoporous structure can increase the area of contact between the electrolyte and the CE. A DSSC using a Com CE yielded a high PCE of 7.5%, comparable to that of a DSSC using a platinum CE. Next, we compared the performance of nine kinds of carbon materials under the same conditions. Figure 6 shows the surface morphologies of these carbon materials. For the photovoltaic performance of the DSSCs using these carbon CEs, the traditional carbon materials (Ca, Cb, Cc, CNTs, and Cf) showed decent catalytic activity and the DSSCs yielded PCE levels ranging from 6.3% to 7.0%. Similar to Com, Cd showed high catalytic activity and the DSSC gave a high PCE of 7.5%. Even the discarded toner showed some catalytic activity and the DSSC gave a PCE of 4.3%. In this work, we also used impure C60 as CE catalyst for a DSSC which reached a poor PCE of 2.8%. As predicted, C60 performed as effectively as other carbon materials due to its superior electrical conductivity, stability, and other attributes.[54, 55] The low PCE, however, may be caused by the impurities in C60.

During the course of this work, we found that the main disadvantage of carbon CEs is the poor bonding strength between the carbon films and the substrate. To overcome this, we attempted to add TiO2 to improve this bonding strength. However, it was found that adding too much TiO2 can weaken the catalytic activity of the carbon CE due to the bad conductivity of TiO2. The optimal amount of TiO2 to be added was determined.[53] At the same time, we investigated the effect of carbon film thickness on catalytic activity. To achieve a high catalytic activity, a carbon film with 25 μm thickness was appropriate. An excessively thin carbon film can lead to insufficient catalytic activity while an excessively thick carbon film can crack and detach from the substrate. This separation can be attributed to interfacial stress between the carbon films and the substrate as well as the internal stress of the carbon film body itself. As mentioned above, the Grätzel group also reported the impact of Cb film thickness on the performance of the DSSCs.[34] In their work, the thickness of Cb layers ranged from 0.85 to 14.47 μm. The Jsc and Voc changed slightly whereas the FF increased as the thickness of the carbon films increased. These results, combined with our own findings, demonstrate that the thickness of the carbon films significantly affects the FF.

Carbon is indeed a good CE catalyst in DSSCs, however, we still believe the main disadvantage of carbon CE is the poor bonding strength between this material and the substrate. This could be a factor that endangers long-term use. Depositing the carbon film on the substrate by in situ techniques could resolve this issue. In addition, fabricating an incorporated CE of pure carbon may be another solution. On the other hand, opacity is another disadvantage of carbon materials. We believe that developing transparent carbon CEs for DSSCs will become a promising research direction in the future.

2.3. Organic polymers

Transparency and flexibility are two unique properties of DSSCs. To achieve these qualities requires a transparent and
flexible photoanode, a transparent electrolyte, and a transparent and flexible CE. Platinum deposited onto ITO–PET or ITO–PEN substrate is a conventional transparent and flexible CE. Due to the high costs of these materials, it is essential to develop new catalysts for transparent and flexible CEs. In 1988, Johas et al. fabricated an electrical conductive organic polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) with a high conductivity, transparency, and stability.\(^{[57, 58]}\)

![Figure 7. Chemical structures of PEDOT, PSS, and TsO.](image)

We have concerned ourselves with catalytic activity for the regeneration of \(I_3^-/I^-\).\(^{[59]}\) Poly(styrenesulfonate) (PSS, Figure 7) has been used as a dopant to improve the solubility as well as the electrical conductivity by preparing soluble PEDOT-PSS pastes. PEDOT-PSS paste is now available commercially and provides a convenient way to prepare PEDOT CEs.\(^{[60]}\) Hayase et al. have used PEDOT-PSS CE for quasi-solid DSSCs, discovering that this CE performed better than platinum when using anionic liquid electrolyte (ILE).\(^{[61]}\) They investigated this phenomenon by testing the \(R_{ct}\) at the electrode/ILE interface. The \(R_{ct}\) value for the PEDOT-PSS/ILE was merely one-tenth of the value for the Pt/ILE. In contrast, for the organic liquid electrolyte (OLE), the opposite was true: the \(R_{ct}\) for PEDOT-PSS/OLE was larger than the \(R_{ct}\) of Pt/OLE. Yanagida et al. gave a definitive explanation for this phenomenon.\(^{[62]}\) They used p-toluene-sulfonate (TsO, Figure 7) doped PEDOT (PEDOT-TsO) as CE. The high viscosity and low conductivity of ILE necessitate high \(I_2\) concentrations; therefore, the porous PEDOT-PSS CE is more suitable for ILE than Pt. In addition, for both OLE and ILE, the \(R_{ct}\) of PEDOT-TsO/ electrolyte declined as the thickness of PEDOT-TsO film increased. This can be attributed to the increase of surface area due to the porous structure of the PEDOT-TsO film.

Subsequently, they examined the impact of different dopants (e.g., PPS, TSO, CI\(\text{O}_4^-\) for PEDOT CEs) on the catalytic activity.\(^{[63]}\) PEDOT-TsO was prepared most often with a chemical oxidation method, which introduced 1–5% of Fe\(^{III}\) into this material. This can lead to PCE loss.\(^{[64]}\) It is therefore imperative to develop new methods for preparing PEDOT without introducing impurities. In their work,\(^{[65]}\) PEDOT-TsO, PEDOT-PSS, and PEDOT-CI\(\text{O}_4^-\) were deposited galvanostatically or by cyclic voltammetry on FTO glass. In CV measurements for \(I_3^-/I^-\) species, all of the PEDOT films showed high catalytic activity as compared to platinum. Additional oxidation/reduction peaks at the lowest potential could be attributed to dedoping/doping of CI\(\text{O}_4^-\) or TsO\(^-\). However, there were no additional peaks observed for PSS. This indicates that the dopants, CI\(\text{O}_4^-\) and TsO\(^-\), play a significant role in the doping/dedoping process, while PSS can actually suppress the doping/dedoping process, making PEDOT-PSS a proper candidate in the PEDOT series of CEs for DSSCs. However, DSSCs using doped PEDOT CEs showed a PCE of 4.0–4.4%. This means that there is no measurable difference for the impact of CI\(\text{O}_4^-\), PSS, and TsO on the catalytic activity of the doped PEDOT CEs. Ho et al. treated PEDOT-PSS with dimethyl sulfoxide (DMSO), N,N-dimethyl for- mamide (DMF), N,N-dimethyl acetamide (DMAc), and dichloro-methane (DMC).\(^{[65]}\) The PEDOT-PSS film treated with DMSO exhibited the highest conductivity (85 ± 15 S cm\(^{-1}\)). The conductivity of the films without treatment and of those treated with DMF, DMAc, and DMC were 2 ± 0.05 (no treatment), 45 ± 10 (DMF), 36 ± 7 (DMAc), and 20 ± 6 S cm\(^{-1}\) (DMC). The \(R_{ct}\) value declined from 14.5 to 11.1 \(\Omega\), and the diffusion resistance declined from 39.4 to 20.1 \(\Omega\) after DMSO treatment. Therefore, the PCE improved from 1.90% to 2.41% after treatment.

Transparency is a special merit of PEDOT polymers. The Kang group attempted to add MNTs sorbitol to PEDOT-PSS to improve the CE transparency and conductivity.\(^{[66]}\) They found that the amount of sorbitol molecules on the MNTs strongly affected the transparency and conductivity of PEDOT-PSS significantly. However, they did not use this kind of PEDOT-PSS film in DSSCs as CE. The substrates in the studies discussed above are all rigid FTO glass, which cannot sufficiently exhibit the specific properties of PEDOT. Pringle et al. prepared PEDOT film on an ITO-PEN flexible substrate by electrodeposition.\(^{[67]}\) CV results showed no obvious differences in peak current among various PEDOT electrodes prepared with different deposition times (5–45 s). That is, a very short deposition time (5 s) is enough to achieve a highly effective and transparent PEDOT film. In addition, this method is suitable for roll-to-roll manufacturing. A DSSC using this CE and OLE (or ILE) reached a high PCE of 8.0% (or 5.7%), and to our knowledge, 8.0% is the highest PCE using the PEDOT series of CEs.

PEDOT has its own advantages of high catalytic activity, transparency, but also its disadvantages. Giřtu et al. investigated the behavior of PEDOT in the \(I_3^-/I^-\) electrolyte using X-ray photoelectron spectroscopy (XPS).\(^{[68]}\) The XPS results showed that PEDOT had the ability to form charge transfer complexes with iodide. This phenomenon had also been observed by Biallozor et al. through CV measurements.\(^{[69]}\) This is a potential hazard associated with PEDOT CEs for \(I_3^-/I^-\) electrolyte. There are two ways to overcome this issue: First, one can develop new organic polymer catalysts to replace PEDOT CEs for \(I_3^-/I^-\) electrolyte. Second, one can develop new redox couples for PEDOT CEs.

In addition to PEDOT, poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine) (PProDOT-Et\(_2\)) has been proposed as a CE catalyst for DSSCs.\(^{[70]}\) A PProDOT-Et\(_2\) film was deposited onto...
FTO substrate by electropolymerization with various charge capacities (10, 20, 40, 80, 120, 160, 200 mC cm$^{-2}$). The PProDOT-Et$_2$ film had the largest active surface area when the deposited charge capacity was 40 mC cm$^{-2}$, resulting in catalytic activity similar to that of platinum. When the deposited charge capacity was increased further, the PProDOT-Et$_2$ aggregated, which reduced the surface area. A DSSC using this polymer CE yielded a PCE of 5.20%, close to that of a DSSC using a platinum CE. Subsequently, Ho et al. compared the catalytic activities of various organic polymers containing PEDOT, PProDOT, and PProDOT-Et$_2$. A DSSC using PProDOT-Et$_2$ CE showed a high PCE of 7.88%, significantly higher than that of DSSCs using PEDOT CE (3.93%). The PProDOT also exhibited high catalytic activity and the corresponding DSSC gave a PCE of 7.08%.

Wu et al. prepared polypyrrole nanoparticles (PPy, Figure 8) using a pyrrole monomer with the help of iodide.$^{[71]}$ An SEM image showed that the particle size ranged from 40 to 60 nm. Although CV showed only one redox pair for the iodide electrolyte, the current density was so large as to guarantee high catalytic activity. Moreover, the good linear relationship between the peak current density and the square root of the scan rate demonstrated that there was no specific interaction between the iodide species redox couple and the PPy electrode. A DSSC using PPy CE showed a high PCE of 7.66%, surpassing the photovoltaic performance of a DSSC using a platinum CE (6.90%).

Very recently, Xia et al. fabricated PPy CE on FTO glass with vapor-phase polymerization (VPP) and electropolymerization (EP) methods.$^{[72]}$ The PPy particle prepared by VPP had a uniform size of 85 nm. DSSCs using these CEs yielded PCE of 3.4% (VPP-PPy) and 3.2% (EP-PPy), both lower than that of the platinum DSSC (4.4%). In addition, spherical PPy nanoparticles with a uniform size of 100 to 150 nm and the EP-PPy had a larger particle size of 200 to 300 nm. DSSCs using these CEs yielded PCE of 4.26% at rear illumination. The transparent DSSCs had broader applications as building integrated photovoltaics. If this CE was fabricated on a flexible substrate, a flexible DSSC could be used more comprehensively due to its transparency, lightweight, and good plasticity.

In the presence of ammonium persulfate and perchloric acid as a dopant, Wu et al. prepared mesoporous PANI through an oxidative polymerization of aniline monomer.$^{[75]}$ The prepared PANI Triton X-100 solution was coated onto an FTO glass surface by the “dip-tugging” method, followed by drying at 150 °C for 2 h, and the PANI CE was prepared. The SEM image showed that PANI CE had a mesoporous structure which was conducive to high catalytic activity. A DSSC using this CE reached a PCE of 7.15%, higher than that of a DSSC using Platinum CE (6.90%).

Although organic polymer CEs possess the advantages of transparency, high catalytic activity, easy availability, and low cost, their stability (i.e., chemical, thermal, and photostability) may be a serious problem for practical applications. Reports on stability tests for DSSCs using polymer CEs are still lacking. There remains much work to be done for the development of new, stable, flexible CEs, but nonetheless, significant progress has been made.

2.4. Inorganic compounds

As shown in Figure 2, the year 2009 witnessed an explosion in the volume of research on CE catalysts for DSSCs. In 2009, Grätzel et al. introduced an inorganic compound, CoS, into DSSCs as a novel CE catalyst.$^{[24]}$ Semi-transparent CoS on a flexible ITO-PEN electrode was obtained by a one-step electrochemical deposition. The Tafel-polarization curve showed a large slope for the CoS CE, which indicated that a large exchange current density ($I_0$) existed on the CoS electrode surface, comparable to that of a platinum electrode. The Tafel polarization results showed that CoS was a promising CE catalyst for $I_0$ reduction. The photovoltaic performance of a DSSC was assembled in their study. This DSSC gave a PCE of 6.54% at front illumination, and a PCE of 4.26% at rear illumination. The transparent DSSCs had broader applications as building integrated photovoltaics. If this CE was fabricated on a flexible substrate, a flexible DSSC could be used more comprehensively due to its transparency, lightweight, and good plasticity.

Figure 9. Photograph of a large-area bifacially active transparent DSSC with PPy CE.$^{[76]}$ Copyright American Chemical Society 2011.

Recently, Zhao and colleagues fabricated a transparent polyaniline (PANI) CE via in situ polymerization on FTO glass, to use as CE for DSSCs.$^{[74]}$ The PANI CE exhibited good transparency in the visible region (450–750 nm). As shown in Figure 9,
using a CoS CE also confirmed this, and the DSSC showed a PCE of 6.5%, equal to that of a DSSC using a platinum CE. The $R_t$ value (obtained by EIS measurements) of CoS was 1.8 $\Omega$ cm$^2$, close to that of platinum (2.2 $\Omega$ cm$^2$). This confirmed that CoS was an excellent catalyst for the $I_3^-$ reduction. CoS had perfect stability. A long-term stability test under light soaking at 60 $^\circ$C showed that, after 1000 h, the PCE retained 85% of its initial value. Another recent work also proved that CoS is an excellent CE catalyst in DSSCs.

Also in 2009, Gao et al. synthesized TiN nanotube arrays by the anodization of Ti foil, followed by simple nitridation. A DSSC using the TiN nanotube on the Ti sheet as CE showed a PCE of 7.73%, which matched the performance of a DSSC using platinum CE (7.45%).[25] TiN had a $R_t$ value of only 5.68 $\Omega$ and a $R_c$ of 1.51 $\Omega$, much lower than those of Pt (21.88 $\Omega$ and 7.38 $\Omega$). This indicates that TiN has a higher catalytic activity for the regeneration of $I_3^-$/I$^-$/I$^-$ redox couple than platinum. The photovoltaic performance of a TiN-DSSC should be much higher than that of Pt-DSSC, however, the difference between the PCE values for the two DSSCs was not distinct. This can be attributed to the large diffusion resistance for TiN (104.9 $\Omega$ $\cdot$ cm$^2$) compared to that of platinum (8.34 $\Omega$). The overall impedance of TiN and platinum CEs gave them comparable photovoltaic performances. On the other hand, TiN has an excellent electrical conductivity (4.6 $\times$ 10$^{-4}$ $\Omega$ $^{-1}$ $\cdot$ cm$^{-1}$) alongside its catalytic property.[77] Ko et al. used TiN to replace TCO to collect electrons in the photoanode, where the photovoltaic performance was highly dependent on the thickness of the TiN film.[79]

Early transition metal carbides and nitrides (TMCs, TMNs) possess platinum-like catalytic behavior, a property which has been proved by previous studies. These metal carbides and nitrides have also been used in the fields of ammonia synthesis, CO$_2$ methanation, hydrogcnation, dehydrogenation, and methanol oxidation, among others, as a replacement for the noble metal.[79–81] Since 2009, many inorganic compound catalysts have been applied in DSSCs as CEs. These inorganic compounds can be divided into five classes: carbides, nitrides, oxides, sulfides, and phosphides. The following sections will introduce and examine each of these five compounds.

### 2.4.1. Carbides

In 1973, Levy and Boudart first noted that tungsten carbide (WC) had a platinum-like catalytic behavior due to its special electronic structure.[82] Lee et al. prepared polymer-derived WC (WC-PD) and microwave-assisted WC (WC-MW), and introduced both in DSSCs as CE catalysts.[83] The DSSCs based on these CEs yielded PCE of 6.61% (WC-PD) and 7.01% (WC-MW), which were still lower than that of the DSSC using platinum CE (8.23%).

It is already well established that crystallinity heavily impacts the catalytic activity. To this point, Park et al. prepared tungsten carbide by sintering the precursor (WO$_3$·H$_2$O) in a CH$_4$/H$_2$ atmosphere at varying temperatures. They investigated the impact of sintering temperature on the crystallinity and the subsequent impact on the catalytic activity.[84] At a sintering temperature of 700 $^\circ$C, W$_2$C/WC (with possible traces of WO$_3$) was obtained; at 800 $^\circ$C, W$_2$C/WC (WC dominant); and at 900 $^\circ$C, pure WC. The DSSCs using these three CEs showed PCE of 0.20% (W$_2$C/WC with traces of WO$_3$), 4.2% (W$_2$C/WC with WC dominant), and 3.0% (pure WC). The W$_2$C/WC (WC dominant) CE showed the highest catalytic activity, while still lower than that of platinum (5.22%).

At the same time, our group investigated tungsten and molybdenum carbides as CE catalysts for DSSCs.[85] DSSCs using these commercial materials as CEs showed PCEs of 5.35% (WC) and 5.70% (Mo$_2$C), much lower than the corresponding PCE of the platinum DSSC (7.89%). This can be attributed to the large size of the two carbides. There are two techniques for improving the catalytic performance of the carbides: the first is to synthesize the catalysts with small particle size; the second is to evenly disperse the catalyst particles into another carrier.

![Figure 10.](image-url) a) XRD patterns of the synthesized W$_2$C and WC. b, c) SEM images of W$_2$C and WC. d) Current density–voltage curves of DSSCs using W$_2$C, WC, and Pt CEs.
For the first technique, we synthesized nanometer-sized WC and W$_2$C using metal-urea route. WCl$_6$ was used as a tungsten source while urea was used as a carbon source. As shown in Figure 10a, given that the urea/WCl$_6$ molar ratio was 5, pure W$_2$C with good crystallinity was obtained and the peaks could be assigned to the crystal planes of (100), (002), (101), (102), (110), (103), (112), and (201) for W$_2$C (35–0776, PDF 2 database). When the urea/WCl$_6$ molar ratio reached 7, WC was successfully synthesized and the peaks at 32.06°, 35.84°, 47.78°, 63.46°, and 75.10° could be assigned to the crystal planes of (001), (100), (110), and (200), respectively, for WC (25–1407, PDF 2 database). Figure 10b and c showed that W$_2$C has the form of a spindle with diameter 20–50 nm while WC was a relatively large pyramid (50–100 nm). DSSCs using carbides as CEs achieved high PCEs of 6.68% (W$_2$C) and 6.23% (WC), as shown in Figure 10d. Compared to the large WC particles, the nanometer-scale WC had a much improved catalytic activity.

For the second technique, we synthesized WC and MoC imbedded in ordered mesoporous carbon (MoC-OMC, WC-OMC). The DSSCs using the two composite CEs yielded high PCE of 8.18% (WC-OMC) and 8.34% (MoC-OMC), which would be discussed in the section 2.5.

### 2.4.2. Nitrides

In addition to carbides, some nitrides, TiN, MoN, MoN, W$_2$N, WN, Fe$_2$N, and NiN were also introduced into DSSCs as CE catalysts. 27, 29, 87 We prepared MoN and W$_2$N films on flexible Ti sheets by the sputtering method and used them as CEs for DSSCs. The corresponding DSSCs produced PCEs of 6.38% (Mo$_2$N) and 5.81% (W$_2$N), and reached 91% (Mo$_2$N) and 83% (W$_2$N) of the photovoltaic performance of a DSSC with a platinum CE (7.01%). The high performance of nitrides-based DSSCs indicates high catalytic activity of MoN and W$_2$N for the I$_{3-}$/I$^-$ redox, a property that has been proven by EIS measurements.

The $R_s$ value for Mo$_2$N was 1.1 Ω and for W$_2$N was 1.8 Ω. A similar value was observed for other metal substrate. 29 This can be attributed to the excellent electrical conductivity of the Ti sheet and the good bonding strength between the Mo$_2$N or W$_2$N film and the Ti sheet, which, in turn, promoted the collection of electrons from the external circuit. In addition, the $R_s$ value for Mo$_2$N was 7.9 Ω and for W$_2$N was 8.4 Ω, close to that of Pt (6.3 Ω). This confirms that Mo$_2$N and W$_2$N both hold high catalytic activity.

The reason for the relatively low performance of the Mo$_2$N and W$_2$N based DSSCs was the large diffusion resistance of the I$_{3-}$/I$^-$ redox couple in the electrolyte of the CE as previously reported. 20 We found that the $V_{oc}$ value of the Mo$_2$N-DSSC was lower than that of the W$_2$N-DSSC, which can be attributed to large charge transport resistance ($R_s$) in the W$_2$N-DSSC. This means that the photoelectrons of W$_2$N-DSSC need to overcome a relatively larger resistance when they cross the TiO$_2$ films, producing high electron density on the conduction band of TiO$_2$, thereby causing the Fermi level to rise. According to Formula (9), one can deduce that the $E_C$ of the TiO$_2$ for Mo$_2$N-DSSC is lower than that of the W$_2$N-DSSC, assuming the same applied voltage for both. This also indicates that in the W$_2$N-DSSC, the Fermi level of TiO$_2$ is higher than that in Mo$_2$N-DSSC, leading to a higher $V_{oc}$ in the W$_2$N-DSSC. 89

$$R_s = R_0 \exp \left( \frac{E_F - E_C}{k_B T} \right)$$

where $R_s$ is equal for all DSSCs, $E_F$ is the Fermi level of TiO$_2$, $E_C$ is the bottom of the conduction band of the TiO$_2$ anode, $E_{F, redox}$ is the Fermi level of the electrolyte, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $V$ is the bias voltage, $e$ is the elementary charge, and $A$ is a constant.

Similar to TiN, all of MoN, WN, and Fe$_2$N were prepared by nitridation of the oxide precursors (MoO$_3$, WO$_3$, Fe$_2$O$_3$) in ammonia atmosphere, after which they were introduced as CE catalysts into DSSCs. 87 The corresponding DSSCs gave the following PCE values: MoN (5.57%), WN (3.67%), Fe$_2$N (2.65%), and Pt (6.56%). These results confirm that nitrides are promising replacements for platinum. The relatively low PCE was also caused by the large diffusion resistance, a phenomenon shared in previous results. 25, 29

Gao et al. used surface-nitrided Ni foil as the CE in DSSCs, producing a PCE of 5.68%, much lower than that of the platinum DSSC (8.41%). 88 This is due to the compact nitride film, without a mesoporous structure. In order to achieve a high-performance nitride catalyst, they prepared NiN CE using NiN film with a mesoporous structure. A DSSC using this NiN CE showed a high PCE of 8.31%, which confirmed again that a large surface area was critical for high catalytic activity.

Despite these results, the question remains: What is the fundamental reason for the high platinum-like catalytic activity of the carbides and nitrides? The theory holds that small atoms, such as carbon or nitrogen, when inserted into the interstitial sites of early transition metals, produce a series of interstitial compounds, such as TMCs or TMNs, with unique physical and chemical properties. While it is evident that the electron structure of the host metal can be modified by the alien atoms through electron transfer process, the direction and extent of electron transfer, on the other hand, has been debated and is discussed elsewhere (i.e., host metal to interstitial atom or interstitial atom to host metal). 80, 81, 91–93

The surface structure and energy level of the host metal are drastically changed as a result of electron transfer, which can modify the electron density at the Fermi level. 88, 96–98 The subsequent result is that TMCs and TMNs exhibit catalytic behavior distinct from metal hosts and that their activity closely resembles that of platinum. In addition, the carbides and nitrides combine the merits of several materials: the hardness of covalent solids, the high melting temperature of ionic crystals, and
the electric and thermal conductivity of transition metals. Here, what should concern us still more is the platinum-like catalytic activity of these compounds. We believe that transition metal carbides and nitrides are promising low-cost catalysts to replace platinum. The TMCs and TMNs can be used in many fields, such as fuel cells, hydrogenation of aromatic hydrocarbon, hydrogenation of unsaturated alkene and so on; they need not be limited to the DSSC systems.

2.4.3. Oxides

Tungsten oxides (WO$_x$, 0 $<$ x $<$ 3) have attracted a great deal of interest as versatile materials applied in the photo-oxidation of H$_2$O to O$_2$ as photocatalysts, gas sensors, electrochromic devices, and field emitters.$^{[99–102]}$ Zheng et al. used WO$_3$ as a photoanode semiconductor to replace conventional TiO$_2$. The WO$_3$-based DSSCs showed poor PCE of 0.56–0.75 % and a large dark current was found.$^{[103]}$ The authors attributed the low performance to the following two issues: (i) The Fermi level of WO$_3$ tends toward positive at approximately 0 V relative to NHE. This causes a low $V_{oc}$ (around 400 mV) for WO$_3$-based DSSCs using the I$_3^-$/I$^-$ electrolyte. (ii) In contrast to TiO$_2$, WO$_3$ cannot absorb dye molecules efficiently due to its acidic surface.

In addition to the two reasons mentioned above we believe there may be other critical reasons for the poor performance. We found that WO$_3$ can be used as a catalyst for the reduction of I$_3^-$ to I$^-$. And a DSSC using WO$_3$ CE showed a PCE of 4.67 %. If WO$_3$ is used as the photoanode semiconductor, the direct contact between WO$_3$ and I$_3^-$ species may cause the I$_3^-$ to be reduced by the electrons in the conduction band of WO$_3$ due to the autocatalytic activity. That is, a number of the electrons cannot be collected by the substrate and, thus, flow into the external circuit. The autocatalytic activity of WO$_3$ can result in a large dark current density, which has been observed. This can be the key reason for the poor performance of the DSSCs using WO$_3$ as photoanode semiconductor. In our research, we found that the synthesized WO$_3$ nanorods had excellent catalytic activity and that the DSSC using a WO$_3$ CE showed a high PCE of 7.25 %, close to that of a platinum DSSC (7.57 %). This is an unexpected result. The fundamental reason for the high catalytic activity of WO$_3$ is still unclear and requires further study.

Very recently, our group synthesized H-Nb$_2$O$_5$ (hexagonal), O-Nb$_2$O$_5$ (orthorhombic), M-Nb$_2$O$_5$ (monoclinic), and T-Nb$_2$O$_5$ (tetragonal) via a simple chemical method by merely adjusting the sintering temperature and then used the four niobium oxides as CE catalysts in DSSCs.$^{[105]}$ DSSCs using niobium oxide CEs showed PCEs of 5.68 % (H-Nb$_2$O$_5$), 4.55 % (O-Nb$_2$O$_5$), 5.82 % (M-Nb$_2$O$_5$), and 7.88 % (T-Nb$_2$O$_5$). We can conclude that NbO$_2$ performs best amongst the four niobium oxides and that the crystal form significantly influences the catalytic activity, as previously reported.$^{[104]}$ In an earlier study, Papageorgiou mentioned the $R_i$ value for RuO$_2$ CE was 20 $\Omega$ cm$^2$, however he did not report the performance of DSSCs using RuO$_2$ CE.$^{[106]}$ In light of its $R_i$ value, RuO$_2$ may be a promising CE catalyst. Unfortunately, we could not find consequent reports on RuO$_2$ as a CE in DSSCs by Papageorgiou or other researchers. We guess that the reason for the lack of further study is the high cost of RuO$_2$. Xia et al. used V$_2$O$_5$ as CE in solid DSSCs.$^{[107]}$ The performance of the solid DSSCs depends on the thickness of V$_2$O$_5$ films. If the V$_2$O$_5$ is too thin to cover the Spiro-OMeTAD layer, it can cause a short-circuit. In contrast, if the V$_2$O$_5$ film is too thick, it can result in bad conductivity. After optimization, a solid DSSC using a 10 nm thick V$_2$O$_5$ CE reached a PCE of 2.0 %, close to the performance of the DSSC using Ag CE. New CE catalysts for iodide-free redox couples are discussed in Section 2.6.

2.4.4. Sulfides and Phosphides

As discussed above, the carbides, nitrides, and oxides of molybdenum and tungsten all showed high catalytic activity for the regeneration of the I$_3^-$/$I^-$ redox couple. However, to the best of the authors’ knowledge, no reports on the application of Mo and W sulfides as CE catalysts in DSSCs can be found, despite the fact that MoS$_2$ and WS$_2$ have been applied in many areas, such as lubricants, refractories, and H$_2$ evolution.$^{[108–112]}$ Molybdenum and tungsten carbides, nitrides, and oxides functioned well in DSSCs. Their sulfides are expected to behave in a similar fashion. We introduced MoS$_2$ and WS$_2$ into DSSCs as CE catalysts successfully.$^{[113]}$ Surprisingly, MoS$_2$ and WS$_2$ performed better than the corresponding carbides, nitrides, and oxides. The DSSCs using MoS$_2$ and WS$_2$ CEs yielded high PCEs of 7.59 % (MoS$_2$) and 7.73 % (WS$_2$), comparable to the performance of a platinum DSSC (7.64 %). In CV measurements, two pairs of redox peaks were observed for MoS$_2$ and WS$_2$. The profile, peak position, and peak current density were all similar to those of platinum, indicating the high catalytic activity of MoS$_2$ and WS$_2$. In EIS measurements, the $R_i$ values of MoS$_2$ and WS$_2$ were merely 0.5 $\Omega$ (MoS$_2$) and 0.3 $\Omega$ (WS$_2$), much smaller than that of platinum (3.0 $\Omega$), confirming high catalytic activity for both sulfides.

On the other hand, the Nernst diffusion resistance ($Z_d$) values of MoS$_2$ and WS$_2$ were much larger than that of Pt. Based on Formulae (10) and (11), a large $Z_d$ can result in a low diffusion coefficient ($D$) and a low limiting current density ($J_{lim}$). This means the redox couple (especially, I$_3^-$) suffers from a high resistance, causing it to diffuse slowly in the electrolyte. This is detrimental to the regeneration of the I$_3^-$/$I^-$ redox couple at the CE. The overall impedance is responsible for the comparable PCE values between the DSSCs using MoS$_2$ (WS$_2$) CEs and the DSSC using platinum CE.

\[
Z_d = \frac{W}{\sqrt{\Delta i_o}} \tanh \left( \frac{0.62}{\sqrt{k_i} \Delta o} \right)
\]

where $W = k_i T \sqrt{2 e C}$, $\Delta D = D/\delta^2$, $D$ is the diffusion coefficient of the I$_3^-$, $C$ is the concentration of the I$_3^-$, $n$ is the number of electrons transferred in the reaction, $k_i$ is the Boltzmann constant, $e$ is the elementary charge, and $\delta$ is the thickness of the diffusion layer.
where \( l \) is the spacer thickness, \( N_A \) is Avogadro’s constant; and \( D, C, e \) and \( n \) retain their established meanings.

Co and Ni both belong to the Group VIII A metals. CoS had been introduced into DSSC systems.[114] NiS was subsequently applied in DSSCs as CE.[114] Meng et al. prepared NiS CEs by periodic potential reversal (PR) and potentiostatic (PS) techniques. The DSSCs using PR-NiS and PS-NiS CEs showed PCE of 6.83% (PR-NiS) and 3.22% (PS-NiS). Their work proved the followings: (i) NiS is a promising catalyst to replace platinum; (ii) the preparation technique significantly impacts the catalytic activity; and (iii) PR is a favorable, low-temperature electrodeposition technique to prepare NiS-like CEs. Very recently, Lin et al. introduced copper zinc tin sulfide (CZTS) to DSSCs as CE catalyst. CZTS performed well for the regeneration of \( I_3^- \) from \( I^- \). A DSSC using the CZTS CE showed a PCE of 7.37% higher than the corresponding photovoltaic performance of the platinum DSSC.[115]

To the best of the authors’ knowledge, no reports on the application of phosphides as CE catalysts in DSSCs exist. We used Ni5P4 and MoP as CEs, and the respective DSSCs showed PCEs of 5.71% (Ni5P4) and 4.92% (MoP).

2.5. Composites

As the name implies, composite CEs commonly comprise two or more components, which can include, but are not limited to, WC or MoC imbedded in ordered mesoporous carbon (WC-OMC, MoC-OMC), TiO2/CNTs, Pt/carbon, carbon/PEDOT/PSS, carbon/TiO2, and CoS/PEDOT/PSS.[85,116–127] The advantage of this type of CE is, naturally, the combination of the best qualities of all components into one composite.

We synthesized MOC-OMC and WC-OMC by an in situ chemical method.[123] Compared to DSSCs using pure carbide CEs, the PCE values of DSSCs using WC-OMC and MoC-OMC CEs improved from 5.35% (WC) and 5.70% (MoC) to 8.18% (WC-OMC) and 8.34% (MoC-OMC), surpassing that of the platinum DSSC (7.89%). It is evident that WC-OMC and MoC-OMC have excellent catalytic activity for \( I^- \) reduction. In another study of composite CE, Gao et al. deposited TiN nanoparticles on CNTs and then used the composite (TiN/CNTs) as CE.[116] The DSSC had a PCE of 5.41%, higher than both the DSSC using TiN CE (2.12%) and the DSSC using pure CNTs CE (3.53%). The high catalytic activity can be attributed to the combination of the high catalytic activity and the high electrical conductivity into one composite. This strategy can be used to design effective catalysts in the future studies.

Wu et al. prepared the Pt/Cb composite by reducing \( H_2PtCl_6 \) with NaBH4 in Cb suspension and then introducing this composite into DSSCs as CE catalyst.[117] They found that loading 1.5 wt% Pt on Cb was enough to achieve high catalytic activity. The DSSC using the Pt/Cb (Pt, 1.5 wt%) CE had a PCE of 6.72%, comparable to that of the platinum DSSC (6.63%). Lan et al. deposited platinum on carbon fiber paper (CFP), where CFP functioned as the conductive substrate to replace FTO.[118] The DSSC using the Pt/CFP composite CE showed a PCE of 4.13%, higher than that of the DSSC using the sputtered platinum CE (3.94%).

As early as 2001, Hagfeldt et al. prepared a Pt/SnO2 composite CE on a plastic substrate by the compression method at low temperature.[119] The DSSC using this CE had a PCE of 4.9%. Chen and colleagues investigated the catalytic activity of a series of Ni1−xPtx (x = 0.02, 0.04, 0.06, 0.08) alloys for \( I^- \) reduction.[120] They found that Ni0.92Pt0.08 performed best amongst these alloys, and the DSSC showed a high PCE of 8.21% under standard conditions, higher than that of a DSSC using platinum CE (7.33%). Qiao et al. prepared a carbon/TiO2 composite CE in which carbon served as a catalyst and TiO2 as a binder.[121] A DSSC using a carbon/TiO2 CE showed a PCE of 5.5%, close to that of platinum DSSC (6.4%). Here, TiO2 worked as a binder. However, TiO2 was a semiconductor, thus, adding too much TiO2 can reduce the conductivity of the carbon/TiO2 CE. In our previous research, we have determined the optimal amount of TiO2.[122]

Shi et al. added varying amounts of graphene to PEDOT-PSS in order to fabricate a transparent PEDOT-PSS/graphene composite CE.[122] Compared with the pure PEDOT-PSS CE, the addition of graphene can increase the \( J_L \) and FF of the DSSCs significantly. This can be attributed to the fact that graphene contains large amounts of chemical defects that provide high catalytic activity. When the graphene content increased from 0 wt% to 1.0 wt%, the PCE of the DSSCs increased from 2.3% to 4.5%. Further increases of graphene caused no observable change in the PCE. Ouyang et al. prepared a composite CE of PEDOT-PSS/CNTs and a composite CE of PSS/CNTs.[123] The DSSC using PEDOT-PSS/CNTs CE showed a PCE of 6.5%, much higher than that of the DSSC using PSS/CNTs CE (3.6%). The nonconjugated PSS can easily be wrapped around CNTs, producing an insulating layer for electron transfer. By contrast, the conductive PEDOT wrapped around CNTs can not affect the electron transfer.

Recently, Kitamura and Shiratori used a mesoporous PEDOT-PSS/Cb composite CE as CE catalyst. They evaluated the impact of morphology, porosity, film thickness, and Cb content on the performance of the CEs. After optimization, the DSSC using this composite CE reached a PCE of 4.7%, slightly lower than that of the DSSC using Pt CE (5.1%).[124] Kobayashi et al. deposited ClO4−/PEDOT on mesoporous TiO2 film to prepare a mesoporous ClO4−/PEDOT/TiO2 composite CE. The DSSC using this composite CE showed a PCE of 4.78%, an improvement of 1.1% over the DSSC using ClO4−/PEDOT CE (3.68%).[125] Miyasaka et al. used a series of metal oxides (MO, such as TiO2, ZnO, NiO, Al2O3) to prepare mesoporous MO/ITO/PEDOT-PSS composite plastic CEs.[126] Based on CV and EIS measurements, they found that the TiO2-based composite CE showed the highest catalytic activity with respect to the high current density and low overpotential.

The ranking of PCE values, in descending order, is TiO2 > Al2O3 > NiO > ZnO. The plastic DSSC using TiO2 based composite CE reached a PCE of 4.38%, slightly lower than that of the DSSC using Pt CE (5.41%). In their work, adding oxides can prove feasibility for obtaining high-efficiency PEDOT CEs with...
a large surface area. Kang et al. used CoS/PEDOT/PSS as a composite CE catalyst, with the corresponding DSSC giving a PCE of 5.4%, comparable to that of the DSSC using Pt CE (6.1%). The high catalytic activity of this composite CE can be ascribed to the synergistic catalytic effect.[127]

2.6. Catalysts for iodide-free redox couples

In the studies discussed above, I$_3^-$/$I^-$ is the dominant redox couple in DSSCs. However, I$_3^-$/$I^-$ has its own downsides, such as absorbing visible light, sublimation of I$_2$, and corrosive effects with some metals (e.g., Ag, Au). Due to the disadvantages, some new redox couples have been introduced into DSSCs to replace I$_3^-$/$I^-$, containing T$_2$/T$^+$, Co$^{3+}$/Co$^{2+}$, BMT/McMT, among others.[128–130] More information on the redox couples can be found elsewhere.[131] What must be emphasized is that Grätzel et al. fabricated porphyrin-sensitized solar cells using Co$^{3+}$/Co$^{2+}$ redox couple, and the highest PCE of 12.3% was obtained.[132]

T$_2$/T$^+$ is a new organic redox couple. Its chemical structure is shown in Figure 11.[128] Our group found that some platinum-free catalysts were more suitable for regeneration of the T$_2$/T$^+$ redox couple.[133] AC, Cb, Cd, WC, and WC-OMC were chosen randomly to catalyze the regeneration of the T$_2$/T$^+$ redox couple. All performed better than platinum. The DSSCs using these platinum-free CEs showed PCE values between 4.75%–5.10%, much higher than that of the DSSC using platinum CE (3.68%). EIS results indicated that the $R_q$ values for these platinum-free CEs were much lower than that of platinum confirming the high catalytic activity for these platinum-free CEs. Subsequently, we used WO$_2$ and WO$_2$ imbedded in mesoporous carbon (WO$_2$-MC) to repeat this experiment, producing similar results.[134]

Boujtita and colleagues applied carbon as the catalyst for the regeneration of the Co$^{3+}$/Co$^{2+}$ redox couple.[135] The DSSC based on carbon CE and the Co$^{3+}$/Co$^{2+}$ electrolyte yielded a PCE of 1.2%, 30% lower than that of the DSSC based on the conventional platinum CE and I$_3^-$/$I^-$ system. We also found that TiC and Com catalysts were more effective than platinum for the regeneration of the Co$^{3+}$/Co$^{2+}$ redox couple. The Co$^{3+}$/Co$^{2+}$ based DSSCs using these materials showed PCE of 4.13% (TiC), 4.05% (Com) and 2.91% (Pt). Future works will provide more details and elaborate on this study. Sun et al. found that the regeneration of the organic redox couples on the PEDOT CE occurred more smoothly than that in the conventional Pt CE.[136]

As mentioned above, I$_3^-$/$I^-$ is widely used in DSSCs, especially liquid DSSCs. In the case of solid DSSCs, spiro-MeOTAD, PEDOT, PPV and similar materials function as hole conductors.[107, 137–141] In this type of DSSCs, Au and Ag are the most common CE catalysts because these high-work-function materials can effectively extract holes.[107]

In quantum dot (QD)-sensitized solar cells (QSCs), the I$_3^-$/$I^-$ electrolyte has been replaced by an aqueous polysulfide (S$_2^2$–/S$^-$) electrolyte because QDs suffer from photodegradation when applied in conjunction with the I$_3^-$/$I^-$ redox couple.[142] In some situations, Co$^{3+}$/Co$^{2+}$ and Fe$^{3+}$/Fe$^{2+}$ can be used as redox couples in QSCs.[143, 144] Previous research has proven that noble metals (e.g., Pt, Au) are not effective for the regeneration of the polysulfide redox couple due to the high over potential and low catalytic activity.[145] To overcome this issue, WC, CoS, NiS, Cu$_2$S, PbS, and carbon have been applied to catalyze the regeneration of the polysulfide redox couple.[146–152] Cu$_2$S showed high catalytic activity toward the polysulfide redox couple, whereas this catalyst suffered from short-term stability due to mechanical instability.[145, 146]

CoS has been proven to be a promising catalyst because of its high catalytic activity and high stability.[146] Chang et al. used CoS as the CE for QSCs, producing a high PCE of 3.4%.[146] The Meng group used carbon (AC/Cb, mass ratio 75%:25%) CEs for QSCs, producing a PCE of 1.47%, much higher than that of the QSCs using Pt CE (0.17%).[149] At the same time, Fan et al. also introduced two carbon materials (spherical carbon and AC) as CEs in QSCs. The QSCs both showed high PCE (3.90% for spherical carbon, 3.34% for AC) and the corresponding PCE of the Pt-QSC was only 2.33%.[150] More recently, Zaban and colleagues used PbS as the CE in a QSC, producing a PCE of 3.01% much higher than the Pt-QSC (0.75%).[152]

In this section we found that, similar to semiconductors and sensitizers, there exists fit issue between CE catalysts and redox couples. Platinum-free catalysts are more suitable for iodide-free redox couples. Great attention must be paid to this issue in the process of developing new CE catalysts or new redox couples.

3. Summary and Outlook

Over the past 10 years, DSSCs have attracted more attention and the field has advanced remarkably. As one of the key components in DSSCs, the CE functions as the catalyst at the location where regeneration of the redox couple takes place. Although the conventional choice of CE material, platinum, is a good catalyst for regeneration of the I$_3^-$/$I^-$ redox couple, its obvious disadvantages are high cost, limited supply, and corrosion by the I$_3^-$/$I^-$ redox couple. These shortcomings could hinder the long-term use of DSSCs in the future. To make DSSCs more competitive among various photovoltaic devices, developing low-cost and high-efficiency CE catalysts to replace platinum is critical. Fortunately, significant progress has been made, notwithstanding the fact that it is only recently
that researchers have focused their work on CE catalysts (as opposed to dyes and semiconductors).

In summary, a series of platinum-free metals and carbon materials have been introduced into DSSCs, each with unique advantages and disadvantages. Organic polymers also offer promising alternative as flexible and transparent CEs. Very advantages and disadvantages. Organic polymers also offer materials have been introduced into DSSCs, each with unique ad-

Moreover, the catalytic activity can be improved by combining two or more proper materials into a composite. This may highlight the importance of a proper match between CE cata-

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Keywords: catalysts · dyes · electrochemistry · platinum · solar cells

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Pt-Free Catalysts as Counter Electrodes in DSSCs


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