Emerging novel metal electrodes not only serve as the collector of free charge carriers, but also function as light trapping designs in photovoltaics. As a potential alternative to commercial indium tin oxide, transparent electrodes composed of metal nanowire, metal mesh, and ultrathin metal film are intensively investigated and developed for achieving high optical transmittance and electrical conductivity. Moreover, light trapping designs via patterning of the back thick metal electrode into different nanostructures, which can deliver a considerable efficiency improvement of photovoltaic devices, contribute by the plasmon-enhanced light–matter interactions. Therefore, here the recent works of metal-based transparent electrodes and patterned back electrodes in photovoltaics are reviewed, which may push the future development of this exciting field.

1. Introduction

The photovoltaic devices require two electrodes to serve as collector of the free charge carriers (electrons and holes). Regarding to the direction of light illumination, the front electrode has the optical functionalities of allowing the transmission of light into active layer, while the opposite back electrode acts as the reflector that can be opaque or semitransparent. Concerning the widely used front electrode of indium tin oxide (ITO), it cannot be compatible to flexible substrate limited by its fragile feature. Moreover, the lack of the raw material hinders the development of low-cost optoelectronics based on ITO. The development of graphene, carbon nanotube (CNT), conductive polymer, and other transparent conductive oxides is proposed to replace the ITO as transparent electrode. However, there are critical issues of applying them as transparent electrodes. For instance, the monolayer graphene has the difficulties in mass production and the fundamental concerns on its horizontal conduction in large area. The large contact resistance at the junction should be addressed for CNT being alternative transparent electrode. Meanwhile, the long-term stability of conductive polymers (e.g., PEDOT:PSS) is also needed to pay attention. The other TOCs typically have low transmittance in the near-infrared region and the fabrication processes also involve the sputtering or vacuum deposition procedure. The metal transparent electrodes, including the metal nanowire (NW)-based conductive network, metal mesh, and ultrathin metal film, can be fabricated with the comparable optical and electrical properties, which are of great promising to substitute the ITO as front electrode in photovoltaic device because of the easy fabrication, low cost, and large-scale production. A metal film with hundreds of nanometers thickness is commonly used as the back electrode for collecting free charge carriers, which can also be used as back reflector to improve the light absorption of thin film active layer. Meanwhile, the plasmonic effects of the patterned metal back electrode, such as periodic, random, quasiperiodic, and bioinspired/prewritten structures, have been exploited to further enhance the light–matter interaction and the performance of thin film photovoltaic devices.

In this review, we systematically summarize the recent advances of metal-based front and back electrodes and their applications in organic and perovskite solar cells. The review has divided into four sections. Section 1 presents a brief introduction of the background and motivation of this review. Section 2 reviews the fabrication of metal transparent electrodes, including metal NW network, metal mesh, and ultrathin metal film. Then, the technical issues of their applications as the front electrode in the solution-processed organic and perovskite solar cells and the strategies to improve device efficiency through engineering the front electrode are also discussed. In Section 3, we summarize the patterns of periodic, random, quasiperiodic, and bioinspired/prewritten nanostructures for being back electrode of photovoltaic devices, and the mechanisms of enhancing photovoltaic performance are discussed. Finally, the conclusions and outlooks are presented in Section 4.

2. The Front Metal Electrode

Indium tin oxide and fluorine-doped tin oxide (FTO) are commonly used as the front electrode for light incoupling and charge carrier collection in most photovoltaic devices. However, their brittle properties and vacuum-based fabrication methods have limited them for the development of the low-cost and...
large-scale photovoltaic device. The metal of silver (Ag), copper (Cu), and gold (Au) have good electrical conductivity of $6.30 \times 10^7$, $5.96-5.80 \times 10^7$, $4.10 \times 10^7$ S m$^{-1}$ at the temperature of 20 °C, which are better than ITO and FTO. However, the bulk metal or thin film metal with several tens of nanometers is difficult to allow efficient transmission of visible light. In order to realize the metal-based transparent electrode possessing comparable optical transparency and electrical conductivity with ITO and FTO, special structural design on metal is necessary. Here, we review the fabrication of front electrodes based on metal NWs, metal mesh, ultrathin metal film, and their application in photovoltaic devices.

2.1. Metal Nanowire Based Conductive Network

The metal NW, such as silver, copper, gold, etc., based conductive network has become the promising candidate for being transparent electrode due to its attractive features of low cost, flexibility, and solution-processed and large-scale production. The tradeoff between the optical transparency and electrical conductivity is critical to the performance of the metal NW based conductive network. Properties of primary metal NWs and their formation on substrate determine the optical transmission of metal NW electrode. The contact resistance between metal NWs sets the fundamental limitation to its electrical conductivity. The stability of the metal NW network is also crucial during their commercialization. In this section, we summarize the strategies of forming the high-performed metal NW network on the aspects of NW synthesis, NW network formation, and their stability.

2.1.1. Metal Nanowire Synthesis

For the fabrication of metal NW network, the dispersed metal NWs in solvent are commonly used as the initial materials, which are generally synthesized through solution-based chemical approaches. Contributed by the rapid development of nanotechnology in recent 20 years, people have gained in-depth knowledge of the growth mechanism of metal nanostructures, including metal NWs. There are several reviews with the focus on the growth mechanism of metal nanostructure. Regarding the application of metal NWs as transparent electrode, the fundamental properties of the initial metal NWs, such as material, length, diameter, etc., will intrinsically determine the electrical and optical performance of the electrode. Ag NWs have received greatest attentions by researchers due to the highest conductivity, moderate price, and low optical loss at visible range among metals. The transparent electrodes based on Cu NWs have also been intensively studied owing to the advantages of the low price and high conductivity. However, Cu NWs have the shortage of oxidation even at room ambient condition. Despite the high price of gold, the NWs of Au, possessing the merit of high stability is very attractive in the applications to resist oxidative and corrosive species. Previous simulation works have demonstrated that metal NWs with large aspect ratio of length and diameter would benefit the formation of transparent electrode with low sheet resistance and high optical transmission. Therefore, researchers put great effort to synthesize metal NWs with small diameter and large length. The ultrathin NWs will allow the surpassing of most light with negligible optical loss from the parasitic absorption and scattering by metal nanowire. The ultralong metal NWs allow less quantity of NWs or smaller NWs density on substrate for the built up of highly conductive network, which consequently will...
reduce the total optical loss and increase optical transparency of the electrode. Meanwhile, reducing the byproducts in the metal nanowire conductive paste, such as nanoparticles, nanoplates, and other nanostructures that will introduce additional optical loss, is also very important to achieve the transparent electrode with high electrical and optical performance. Therefore, we briefly summarize the strategies of synthesizing metal NWs with large aspect ratio and high productivity following the sequence of Ag, Cu, and Au.

The chemicals used in the synthesis of Ag NWs can be classified as solvent, Ag ion source, reduction agent, surfactant, and additive agent. The polyol method is the most popular technique among the chemical routines for the synthesizing crystalline Ag NWs, contributed by the low-cost and facile controllable process for large-scale Ag NW production. The polyol method was first reported by Sun et al. in 2002,[14] and has been modified and optimized in the following 15 years for achieving Ag NWs with desired properties. In general, the polyol method adopts polyol (e.g., ethylene glycol and glycerol) as both solvent and reduction agent.[15,16] The donation of electrons from the hydroxyl functional groups in polyol under high temperature (e.g., 120–210 °C) can reduce the Ag ions into Ag atoms for the nucleation and growth of Ag NWs.[15] Meanwhile, the growth of Ag NWs can be mainly divided into three stages: nucleation, the formation of seeds, and the growth of seeds to nanowires. Chloride ions are commonly used as additive agents facilitating the nucleation in the first stage to improve the production of Ag NWs. It is also well known that Ag NWs are epitaxial grown from decahedral seeds with the deposition of silver atoms at (111) facets, while keeping their (100) facets stabilized by surfactants (e.g., polyvinylpyrrolidone (PVP)). Through engineering the three stages, people have been able to obtain high yield of Ag NWs with average diameter ranged from 20 to 200 nm and average length ranged from 10 to 300 μm.

In order to increase the length of Ag NWs, previous strategies, such as adopting proper amount of chloride,[17,18] large molar weight of PVP,[19] low stirring speed,[20,21] and successive multistep growth,[22] have been demonstrated for the synthesis of ultralong Ag NWs with several hundred micrometers. The fabrication of ultralong Ag NWs can also be obtained in aqueous solution by adopting a hydrothermal reaction.[23] Since the transverse localized surface plasmon resonance of thin Ag NWs near ultraviolet (UV) region brings less optical loss at visible range, synthesis of large-scale ultralong Ag NWs with sub-30 nm diameter (i.e., resonance near UV region) is highly favorable for transparent electrode application. The recent strategy for shrinking the diameter of Ag NWs generally adopts a mixed additive agent, e.g., Cl− and Br− ions.[24–29] The reduction of diameter of Ag NWs by introducing Br− ions can be attributed to the increased number of nucleation sites for the growth of Ag NWs and the formation of AgBr which will decrease the reduction speed of Ag+ during the growth of Ag NWs.[26,30] Meanwhile, absorbed Br− ions and PVP with high molecular weight of 1300 000 g mol−1 on the surface of Ag NWs will restrain their lateral growth.[28] Contributed the effort on enlarging length and reducing diameter, the aspect ratios of the Ag NWs have been able to extend to 1000–4000, which definitely will improve the optical and electrical performance of transparent electrode based on Ag NWs.[18,22,23,26,28,29,31,32]

The growth of Cu NWs, also having a pentagonal pyramid with five (111) planes on the end and five (100) planes on the sides, is similar to the case of Ag NWs by adopting copper ion source, reduction agent, surfactant, and additive agent for the nucleation and 1D growth in solvent. Various approaches have been developed for the growth of Cu NWs.[33,34] Here, we will only review the approaches capable of large-scale synthesis of Cu NWs with high aspect ratio. Wiley and co-workers have performed great job by using ethylenediamine (EDA) as surfactant to synthesize Cu NWs and study their growth mechanisms.[35–40] Cu(NO3)2 and hydrazine are generally used as the Cu ion source and reduction agent, and the reaction is carried out in a heavy basic aqueous solution through the addition of NaOH. The rapid synthesis of Cu NWs with high aspect ratio of 5700 has been demonstrated.[36] Their recent work on the growth mechanism of Cu NW in the EDA-mediated approach claims that EDA is functioned as a facet-selective promoter of Cu atoms deposition on the {111} facets rather than a capping agent stabilizing the {100} facet to inhibit the lateral growth.[40] However, the reduction agent of hydrazine is highly toxic and dangerously unstable, which should be stored and used with particular attention.

Besides EDA,[41] the amine functional group ended chemicals, such as hexadecylamine,[42,43] octadecylamine,[44] oleylamine (OA),[45,46] and tetradecylamine,[47] have also been used as the surfactant for the growth of Cu NWs with high aspect ratio. The recent fabrication of ultrathin Cu NWs with a diameter of 16–17 nm is realized by heating the CuCl2 and oleylamine solution through the addition of nickel(II) acetylateon as a catalyst or using tris(trimethylsilyl)isilane as a mild reducing reagent.[48,49]

For the synthesis of highly crystalline Au NW with diameter of sub-10 nm, HAuCl4 and oleylamine are the two essential chemicals in the chemical reaction, in which OA is a key chemical and plays multiroles of solvent, surfactant to stabilize {100} facets, and reduction agent to reduce the gold ions from HAuCl4. The simplest approach for the synthesis of Au NWs can be achieved through direct mixing a gold precursor with OA followed by aging at room temperature (20–25 °C) for 4 d.[50] The growth of Au NWs can also happen in a mixed solvent of OA and a second organic solvent, such as toluene and hexane, with the proper addition of reduction agent or oleic acid.[51–54] However, long aging time ranging from several hours to several days would be necessary for the growth of Au NW to several micrometers. The silane-mediated approach, which adopts trisopropylsilane to the mixture solution of oleylamine and HAuCl4 in hexane, has been demonstrated to be a simple and highly effective approach for the rapid synthesis of single-crystal ultrathin Au NWs.[55–57]

2.1.2. Formation of Metal Nanowire Based Conductive Network

It should be mentioned that, despite the chemical approaches have been optimized for the synthesis of metal NWs with high yield, the byproducts during the chemical synthesis, such as nanoparticles (NPs), are still inevitable in the final product solution. Proper precipitation process for purifying the product is generally necessary to remove excess NPs, which is beneficial...
for the fabrication of highly performed transparent electrode.\textsuperscript{[26,29,32,58]} Successive sonication and washing by solvent of metal NWs dispersion will be helpful for the removal of excessive surfactants from their surfaces. However, long-time sonication of metal NWs dispersed solution will cause the breakdown of wires and reduce the aspect ratio, which should be avoided during the process.\textsuperscript{[59]} The washed metal NWs can be redispersed in various solvents for the preparation of conductive ink.

The advantages of metal nanowire based transparent conductor over commercial metal oxide thin film transparent electrode are attributed to their large-scale chemical synthesis; meanwhile, it has the capability to be deposited on substrate under ambient condition by adopting equipment with much lower price and energy consumption as compared the one based on vacuum physical vapor deposition. Various methods have been demonstrated to efficiently disperse metal NWs on substrate, such as spin coating, dip coating, drop casting, mayer rod, doctor blading, spray coating, slot die, vacuum filtration, gravure printing, brush painting, etc. It is well known that the metal NWs on the substrate formed through those coating methods are randomly distributed.

Besides the adoption of metal NWs with large aspect ratio for improving the figure of merit of the transparent electrode, proper design for the rational alignment of metal NWs will reduce the load of metal NWs on substrate for achieving the same sheet resistance as compared to the electrode with randomly distributed metal NWs, but exhibit increased optical transparency. Therefore, the strategy of large-scale assembling metal NWs through a cost-effective and solution-based process is favorable. Fortunately, previous experiences on the assembly of 1D inorganic material, such as semiconductor NWs and carbon nanotubes, pave the way for the fabrication of aligned metal NWs on substrate.\textsuperscript{[60–63]} The Langmuir–Blodgett and Langmuir–Schaef er technique has been demonstrated to be an effective approach for the fabrication of ordered metal NWs on substrate with parallel and orthogonal arrangement.\textsuperscript{[64–69]} The directional flow of solvent with metal NWs dispersed is also helpful to their regular alignment on substrate.\textsuperscript{[65,70–74]} As shown in Figure 1, the dragging of metal NW dispersed solution on a substrate by using mayer rod, PDMS plate, and nanopatterned PDMS stamp has been demonstrated to be a powerful approach for large-scale fabrication of transparent electrode with well-aligned metal NWs on the substrate.\textsuperscript{[75–78]} Such kind of method, taking the advantage of the shear force in solution and the capillary force at solvent/air interface, is compatible with the roll-to-roll techniques for large-scale fabrication.

Since the transportation of free electrons in metal nanowire based transparent conductor under electrical bias is bridged
by tremendous 1D metal NWs, the contact between the NWs is crucial to the sheet resistance of electrode with random or aligned metal NWs. Contact resistance is mainly limited by the residual surfactant on metal NWs and the contact area of NWs. An electrical barrier will be formed between the NWs due to the closely surrounded surfactant on their surface. Despite the surfactant can be washed and minimized by various solvent with the aid of successive sonication and centrifugation, it is difficult to completely remove the surfactant from the metal surface. Too many times washing cycles may reduce the dispersive property of the metal NWs in solvent and induce aggregation of metal NWs in conductive ink, which will decrease the performance of transparent electrode and should be avoided.

Thermal heating on the as-prepared metal NW electrode is the most commonly used approach for removing the remained solvent and welding NWs to reduce the contact resistance. However, the temperature of over 100 °C would be necessary for the welding of metal NWs, which is even higher for welding metal NWs with larger diameter. The approach will be greatly restricted in the application of metal NWs on flexible substrate, such as PET, whose morphology and properties are highly sensitive to the temperature. The low-temperature or room-temperature process is favorable for the posttreatment on the as-prepared metal nanowire electrode. The approach of incorporating secondary material into the metal nanowire electrode for the formation of composite transparent conductor has received great attentions, which can improve the electrical performance of metal nanowire transparent electrode and preserve the advantages from both materials as well. Carbon-based 1D and 2D nanomaterials, such as carbon nanotubes,[79-81] graphene oxide,[82-85] reduced graphene oxide,[86-89] and graphene,[90-94] have demonstrated to improve the electrical conductivity of metal nanowire electrode, contributed by the enhanced conductivity at the junction region compensated by the conductive or semiconductive carbon nanomaterials. Inorganic semiconductor nanomaterial, such as TiO₂,[95,96] ZnO,[97,98] ITO,[99-101] FTO,[102] AZO,[103-105] IZO,[106,107] ATO,[108] SnO₂,[109,110] and MoO₃[111,112] can also improve the conductivity of metal nanowire electrode through the vacuum-based film deposition or the solution-processed nanoparticles and sol-gel coating. The combination of metal NWs and the conductive polymer, such as PEDOT:PSS, has been shown to be a good candidate of transparent conductor.[113,114]

Meanwhile, welding strategies without introducing a secondary material and optical loss have been intensively investigated for the fabrication of highly transparent conductive metal network, which will broaden their application in various fields without the constraint by the secondary solder materials. Although removing the surfactants on metal NWs would be harmful to their dispersion in solvent, the surfactant removal after the NWs deposited on substrate can effectively minimize the electrical barrier between NWs and allow their intimate contact or fusion, which is helpful to the conductivity of metal nanowire based transparent electrode. Plasma etching,[75,115,116] solvent washing,[117] and chloride ions treatment[118,119] on Ag NW electrode are found to remove PVP from the Ag surface, and the treatment of Cu NW by lactic acid[104] and acetic acid[120] can help the removal of organic capping molecules and oxidation layer. The approaches of mechanically pressing on the metal NWs and merging NWs at their contact can reduce the contact resistance and surface roughness of the transparent electrode, which have received great interest due to their compatibility with roll-to-roll techniques.[30,121-125] Bending the metal NWs at their contact for increasing the contact area and conductivity has been demonstrated through moisture treatment on the electrode, which takes the advantage of the capillary force.[126,127]

The formation of crystalline metal bonding between metal NWs can achieve the lowest contact resistance theoretically, contributed by the increased contact area by metal material for reducing the scattering of free electrons during their transportation. Local heating and welding specifically at the junction region can help the formation of crystalline bonding, which have been demonstrated by two pathways: plasmonic welding from light and joule heating from electricity. Due to the extremely large optical field confined at the metal nanowire junction, the photoinduced annealing at the junction is contributed by the heat generated from photothermal effect of metal nanomaterials through using various light sources.[67,128-135] Large contact resistance will cause the accumulation of joule heat and annealing at the junctions when the metal nanowire electrode is applied with electrical bias. This phenomenon has been utilized for electrical improvement of metal nanowire electrode.[136,137] The exposure of metal nanowire electrode to large-pulsed electron beam is also helpful to the welding of metal NWs at the junctions.[138] Chemical welding, being another class of welding strategy for crystalline metal bonding, has attracted even more attentions due to the low-temperature and solution-based process. In general, a precursor containing metal ion source is dropped on the metal nanowire electrode on substrate; alternatively, the electrode is immersed in the precursor solution, which is followed by the reduction of metal ions and the deposition of metal atoms at the junction regions due to the preferential growth on the concave-type surface with high chemical potential or plasmon-mediated chemical reduction at the junction.[139-144] Figure 2 presents two representative results of Ag NW based conductive network with crystalline Ag solder at the junction of metal NWs. The native oxidation layer of nanowires can also serve as the metal source that will be reduced by reduction agents and help the formation of metal solder.[145] Selective etching at the junction of metal nanowires by H₂O₂ or chloride and followed welding have been demonstrated to fuse the metal NWs together.[119,123,146-148] This method, however, should be optimized on the solution concentration and exposure time in the process, to avoid the overetching which otherwise will make the conductivity of the electrode in an opposite direction. It should be further mentioned that, despite a number of strategies have developed to improve the performance of metal nanowire based transparent electrode, the combination of different strategies is the trend for making the electrode to meet the requirements in practical applications.

Regarding the fabrication of flexible metal NW network, it can be obtained through direct coating metal NWs on the flexible substrate, followed by mechanical pressing or other welding strategy for the formation of a conductive network.[149-152] Proper design on the formulation of metal nanowire conductive ink and functionalized substrate would be necessary to
improve the dispersion of metal NWs on the flexible substrate and adhesion between them. The transfer of metal NW network from a rigid substrate or a membrane filter to the flexible substrate is also commonly used for the fabrication of flexible transparent electrode. Meanwhile, the freestanding metal conductive network floating on aqueous surface can be transferred to other surface straightforward, which is much easier than graphene that needs further solvent treatment for the removal of polymer support. Besides the strategies of direct coating and transferring metal NWs on flexible substrate, recent effort on developing flexible conductor has dedicated to the fabrication of flexible composite with metal NWs embedded in a polymer film. In a typical fabrication process, the metal NW network is first fabricated on a substrate. Then, polymer material in solvent with proper concentration is deposited on metal conductive network, which is cured by thermal annealing or light exposure depending on the polymer property for the formation of metal NW network and polymer composite film. Finally, the flexible transparent conductor is peeled off from the substrate with metal NWs embedded at the surface of the composite film. Various polymer materials, such as PVA, PDMS, PMMA, polyimide, polyelectrolyte, poly(acrylate), etc., have been investigated for the fabrication of flexible transparent electrodes to meet specific requirements in practical applications. Pei and co-workers have made a lot of contributions in this area and various polymer materials have been developed for the application of optoelectronic devices.

Figure 2. a) SEM image of an Ag NW based conductive network with the integration of Ag nanoparticles at the junctions indicated by the red arrows fabricated through the plasmon-mediated photochemical method. b,c) The enlarged SEM images of the nanostructures indicated by the red frames. Reproduced with permission. Copyright 2015, American Chemical Society. d) SEM image of Ag conductive network locally welded by crystalline silver solder at the junction of NWs. e) TEM image of the conductive network, and the inset is microarea electron diffraction (MAED) pattern of the solder. Reproduced with permission. Copyright 2015, John Wiley & Sons, Inc.

2.1.3. Stability of Metal Nanowire Based Conductive Network

As a substitute for commercial metal oxide based transparent electrode, beside the optical transparency and electrical conductivity, the stability is the most critical issue to evaluate metal NW network during their commercialization. The stabilities of metal NWs are vulnerable that will be affected under various situations in practical applications. Metal NWs with extremely large surface-to-volume ratio, especially for Ag and Cu NWs, are easily attacked by various species existing in air, such as moisture, oxygen, and sulfide. The degeneration of transparent electrode will be accelerated with metal NWs exposed to light irradiation, high temperature, and current flow. The low thermal stability of metal NW network will limit their application in the devices needing high-temperature annealing process. Joule heat will be generated when the transparent electrode is applied with electrical bias, which will affect the stability of metal NW network and is crucial to the performance of optoelectronic devices under operational condition. Improving the mechanical stability of flexible transparent electrode is also important to their application in flexible devices. In this section, we summarize the strategies for improving the chemical, thermal, and mechanical stabilities of metal nanowire based transparent electrode.

Actually, strategies of welding metal nanowire electrode through depositing additional materials on metal NWs are also helpful to the chemical stability of transparent electrode, contributed by shielding metal NWs from the outer environment. The metal oxide thin film through sol–gel process and physical vapor deposition method can be fabricated with a compact layer, which inhibits the permeation of various spices to deteriorate the metal NW network. Carbon-based 2D materials, such as graphene, graphene oxide, and reduced graphene oxide, and conductive polymer have also been demonstrated to block metal NWs from the outer environment to avoid the gradual degeneration. Depositing additional materials, such as metal, metal oxide, polymer, and 2D carbon material, on flexible transparent electrode with metal NWs embedded in polymer substrate will create a “sandwich” structure for metal NWs with part of their surface area protected by polymer substrate and another part protected the additional material, which is helpful to the stability of flexible transparent electrodes. In order to assess the stability...
of metal NW network, much harsher conditions, such as high humidity, high temperature, UV–ozone, H₂O₂, Na₂S, etc., are generally applied on the electrode to monitor the resistance variation.

Recently, the strategy of coating another highly stable metal layer on metal nanowire surface for the formation of core–shell metal alloy NWs has been proposed and demonstrated to improve the stability of the transparent electrode. For example, the thin layer of Au, Ni, and Pd, which are highly stable in air, have been adopted as the overcoating on Ag NWs.[213–220] Meanwhile, the Cu NWs, which is even more unstable than Ag in air, have also been overcoated by a second metal layer, such as Au, Ni, Zn, Sn, Pt, and Ag, to improve the stability of metal nanowire electrode in air.[39,221–230] Wiley and co-workers have broadly investigated on various metal overcoating on Cu NWs and their practical applications.[39,226–230] Precise engineering on the growth process for the formation of uniform metal shell is crucial to the stability of transparent electrode with the core–shell NWs. Meanwhile, carbon-based 2D nanomaterials have also been demonstrated to be good shell materials on both Ag and Cu NWs for the stability improvement of transparent electrode.[206,231–233]

In some cases, high-temperature thermal annealing is required for the fabrication of optoelectronic devices. The application of metal NW network in such kind of devices will be restrained by their stability upon heat. Tolerance of metal nanowire based transparent electrode to thermal annealing is different, which depends on the material and diameter of the metal NWs. While thermal annealing on the transparent electrode will produce a uniform distribution of heat on the entire surface, joule heat is majorly generated from the contact regions, which have large resistance as compared to the crystalline metal NWs. The rapid accumulation of heat in these regions will induce breakdown at the contact and increase the resistance of transparent electrode after long-time electrical bias.[139,202,234] Soldering the contact of Ag NWs by crystalline Ag materials would definitely decrease the contact resistance and lead the uniform generation of joule heat from the entire electrode, which helps to improve the stability of the transparent electrode under electrical bias.[139,143] The coverage of 2D materials at the contact of metal NWs can improve the conductivity of transparent electrode, on the one hand. On the other hand, joule heat generated at the contact region will be quickly dissipated to the surrounding area due to the high thermal conductivity of 2D carbon materials, which is also helpful to improve the thermal stability of metal nanowire based transparent electrode.[235] Additional metal oxide coating on metal NWs is also beneficial for the enhancement of thermal stability of transparent electrode due to the high melting point of metal oxide, which will restrain the deformation of metal NWs.[234,236–237]

Regarding the metal nanowire based flexible transparent electrodes, the strategies of welding metal NWs for the formation of conductive network can reinforce the bonding between metal NWs as well as the adhesion between substrate and the conductive network, which subsequently will improve the mechanical properties of metal nanowire based transparent conductor during bending and twisting.[129,156,218–241] Meanwhile, designs on both aspects of metal nanowire and polymer substrate have been devoted to improve the stretchability of metal nanowire based flexible electrode, which will induce much larger shape deformation of the electrode than bending and twisting. As compared to the normal transparent electrode that composed of random or aligned metal NWs with linear structure, the transparent electrode with metal NWs having curved, wavy, or noncoplanar zigzag configuration has been demonstrated to exhibit enhanced stretchability.[242–245] Contributed by the storage of strain in metal NWs with such kind of morphology, the metal NWs can release the strain without broken when the electrode is applied by pulling force, which allows the recovery to original conductivity when the force on electrode is released. Besides the use of intrinsic stretchable polymer as the substrate of flexible transparent electrode, healable polymer materials are attractive for the application of flexible electrode with improved stretchability.[246,247]

2.2. Metal Mesh

As it is well known, the optical transparency and electrical conductivity of metal nanowire based transparent electrodes are dependent on the material composition, aspect ratio, contact resistance, and alignment of the metal NWs on substrate. Meanwhile, the metal meshes have the attractive features of contact-free or negligible contact resistance, programmable aspect ratio, and pattern of the wires on substrate, which have recently received more attentions for the application of transparent electrode. Actually, contributed by the rapid development in microelectronic field, people have been able to fabricate metal strip and grid with integration of photolithography and physical vapor deposition technologies. The patterned photoresist masks or templates, received from interference light exposure or direct laser writing, have been utilized for the deposition of metal mesh, and a large amount of metal, such as Ag, Cu, Au, Al, Ni, Pt, Pd, Ti, etc., can be selected for physical vapor deposition to meet different requirements.[248–252] After the removal of photoresist on substrate by organic solvent, the metal mesh can be achieved on a solid substrate. Meanwhile, the metal mesh can also be achieved through chemical etching of metal film or metal nanowire film covered by patterned photoresist and leaving the metal mesh protected by photoresist, which is lately removed by organic solvent.[253,254] The nanoimprint lithography technique has also developed for transferring the metal mesh on patterned soft template, which is stamped from a metal film or directly coated by physical vapor deposition, to solid or flexible substrate through applying proper pressure at the back of the template.[255–258]

However, the use of vacuum-based physical vapor deposition technology for fabricating metal mesh would greatly increase the cost of transparent electrode. It is desirable to fabricate metal mesh in the template through solution-based approaches. For example, the silver precursor is deposited on a PMMA template from nanoimprint technique, allowing the nucleation and growth silver nanomaterials in the valley of the template. Combined the treatment of rapid thermal annealing, the transparent electrode comprised of highly crystalline Ag grid is achieved.[259,260] Metal NPs or NWs can be used as the building block to fill in the valley of the polymer template. After proper welding process to reduce the contact resistance between each
building block, the metal NPs or NWs will be integrated for the formation of metal mesh. The patterned polymer template can also be fabricated on a conductive substrate, which allows the electrodeposition of metal mesh in the valley with the conductive layer directly exposed to the electrolyte. The aforementioned routine of fabricating the composite electrode of metal nanowire and polymer is also applicable to fabricate metal mesh embedded in a polymer substrate as flexible transparent electrode.

Besides the template fabricated through photolithography, the periodic or random arranged microspheres on substrate can also act as the template for the deposition of metal film with micrometer size holes, which allow the penetration of light. Thin film with the formation of cracks inside, in most cases, is normally regarded as poor quality. However, Ren and co-workers and Kulkarni and co-workers have been able to engineer the uniform and large-area formation of random cracks in the film prepared from inorganic or organic colloidal solution, which can be used as template for the physical vapor deposition of transparent and conductive metal mesh. The metal mesh can also be obtained from the crack template in indium film from magnetron sputtering or silicon nitride thin film from chemical vapor deposition. The solution-processed fabrication of metal mesh in the crack template has also been demonstrated through electroplating or electrolysis metal deposition, as well as using the metal NPs or NWs as building blocks for the formation of metal wire. Meanwhile, the bioinspired templates, such as spider’s silk web and vein structure of leaf, have been adopted as the scaffolding for metal deposition and electroless plating for the formation of conductive and transparent metal mesh.

The polymer fiber through electrospinning technology can be fabricated with controllable diameter, length, composition, and spatial alignment on any substrate or freestanding, and has proven to be a powerful platform for the fabrication of metal transparent electrode. The direct mixture of metal precursor or metal conductive ink into the polymer solution has been used for the fabrication of polymer fiber network, which is lately reduced or welded for the formation of transparent and conductive metal mesh. However, the direct patterning of metal mesh through electrospinning technique should be optimized on each step for the formation of high-quality metal mesh, which otherwise will be comprised of metal wires with low aspect ratio and low conductivity. Meanwhile, the use of the polymer fiber network as support template for the deposition of metal film through physical vapor deposition approach is beneficial for the fabrication of highly conductive transparent electrode. The coating of freestanding polymer fiber network from both sides will form the metal/polymer core-shell mesh structure. The mere coating metal film on one side of polymer fiber network, permitting the removal of the polymer fiber by organic solvent, helps the formation of highly transparent and conductive nanotrough network, which can be transferred to different substrates and exhibit high mechanical flexibility. Through proper selection of metal and metal oxide sources as well as multiple layer coating on polymer fiber network, the chemical stability of the metal mesh can be significantly improved. By electrospinning polymer network on metal film to protect the metal film beneath after thermal annealing, the metal mesh can also be fabricated by etching of the metal film without polymer fiber covered and lift-off the polymer fiber later. The metal mesh from such method has the advantage of low surface roughness. Furthermore, solution-processed approaches have also developed for the fabrication of metal mesh through electroless metal growth on the polymer fiber template. The use of wave-like polymer fiber network is also helpful to improve the mechanical stretchability of metal mesh fabricated on that. Actually, the strategies of improving mechanical flexibility of metal NW network discussed in previous section should be applicable to the transparent electrode of metal mesh.

The interfacial self-assembly of nanocrystals is a well-known “bottom-up” approach for the fabrication of various patterns. Due to the self-assembly of nanoparticles at the air/liquid interface, “coffee ring effect” has been demonstrated to fabricate metal meshes comprised of closely packed metal nanoparticles with interconnected ring pattern and reticular pattern through an inkjet-printing process. Recently, a pillar-structured micropattern shown in Figure 3a has been applied to effectively manipulate the pattern of 2D liquid foam in metal colloidal solution, which serves as template and helps the formation of Ag mesh after the evaporation of solvent. As shown in Figure 3b–e, the morphology and geometry of the Ag NP comprised metal mesh can be varied through changing micropatterned substrate and the concentration of Ag NPs, which will determine the optical and electrical properties of the Ag mesh. Meanwhile, the maskless fabrication of metal mesh can be achieved by either selective laser sintering of metal nanoparticle film for the formation of conductive wires and removing the nanoparticles without sintering or selective ablation of metal film by pulsed laser. Through eliminating the coffee ring effects, the direct printing of metal conductive ink lines on flexible substrate through an inkjet-printing process has also been demonstrated for the fabrication of conductive metal mesh.

Besides metal NPs, the metal NWs with high aspect ratio can also be used for the building blocks for the self-assembly of conductive and transparent metal mesh. Ultrathin Au NWs with a diameter of several nanometers and stabilized by oleylamine can be assembled to superlattice nanomembrane at the air/liquid interface through the Langmuir–Blodgett process. Meanwhile, the partial removal of surfactants from ultrathin Au NWs leads to the formation of metal mesh at the air/liquid interface, which can be transferred to hydrophobic or hydrophilic substrates as transparent electrode. The self-assembly of metal NWs at oil/water interface has also been used for the fabrication of metal mesh through creating tremendous microdroplets of a reversed-phase solvent in the as-coated metal NW film. Due to the different vaporization speeds of the two solvents, the self-assembled NWs comprised of metal mesh will finally form after the evaporation of both solvents, which has been demonstrated to fabricate metal mesh from Ag NWs and Au NWs. Template-assisted self-assembly of Au NWs for the formation of metal mesh has been reported through imprinting the NW solution by a patterned PDMS template as shown in Figure 3f–i, which has also been demonstrated for large-scale fabrication through the roll-to-roll technique.
The superposition of Ag NW conductive network and mesoscale copper strip has been theoretically and experimentally demonstrated to decrease the sheet resistance of the new multiscale electrode in one order, while bringing negligible optical loss as compared to the bare Ag NW based transparent electrode. The large improvement of the multiscale electrode can be contributed by the additional path for free electron transportation by the ultrahigh conductive mesoscale metal wires with large diameter. Based on this concept, highly conductive and transparent electrode is achieved through the integration of solution-processed Ag nanowire and Ag conductive ink assembled metal grid.

2.3. Ultrathin Metal Film

Different from the transparent electrodes of metal nanowire and metal mesh that allow the penetration of visible light through the voids without occupying metal material, the ultrathin metal film with thickness from several to a dozen nanometers covers the entire surface, which should be ultrasmooth and continuous to minimize the optical loss caused by the surface plasmon resonance and improve the conductivity through reducing the defect in the film. Previous strategies for achieving transparent electrode based on ultrathin metal film are majorly dedicated to the metal oxide/metal/metal oxide or dielectric/metal/dielectric (D/M/D) multilayer structure through engineering the materials, thickness of each layer, and optimizing the parameters during physical vapor deposition process; and the efforts on improving optical transparency, electrical conductivity, and stability of the transparent electrode based on ultrathin metal film are still constantly put into. Meanwhile, the recent strategies of fabricating the composite transparent electrode are not confined to the traditional metal oxide for supporting the ultrathin metal film. Polymer and small molecule layers have been used to improve the wetting of metal film, and the special
physical vapor deposition strategies have also been adopted to improve the quality of metal film. Proper selection of the capping layer on metal film will further improve the transmission of transparent electrode based on multilayer film. Here, we briefly summarize the recent strategies on the fabrication of transparent electrode based on ultrathin metal film.

It is well known that the preferable growth mechanism of film on substrate is greatly dependent on the lattice mismatch between the film and substrate. Low lattice mismatch between them will induce the epitaxial growth of atomic layer on substrate. Meanwhile, the traditional supporting layers for ultrathin metal film deposition are glass, quartz, or flexible substrate. The bonding between metal and traditional supporting substrate is weak, which will induce the formation of metal islands at the preliminary stage during deposition. More metal material would be necessary to form the continuous metal film with several tens of nanometers, which will result in low transmission or impenetrable to visible light. The previous strategy of coating a metal oxide layer on substrate can help the formation of continuous and smooth ultrathin metal film allowing the partial transmission of visible light. Recently, the strategy of molecule treatment on the substrate or the metal oxide layer, such as (3-mercaptopropyl)trimethoxysilane (MPTMS), oxygen plasma treated ornmear, 11-mercapto-undecanoic acid, polyethyleneimine (PEI), polyallylamine, poly(N-vinylcarbazole), and bathocuproine (BCP) can greatly improve the wetting of metal film on the substrate, by taking advantage of the strong bonding between metal atoms and the functional groups of thiol or amine in the molecules to minimize the coalescence of metal atoms into clusters.\[339–348\] Sub-10 nanometer metal film with smooth and continuous surface can be achieved through this approach, which enables the high transparency and conductivity of the electrode. In addition, the work function of the electrode can also be altered due to the metal film modification by the dipole layer of small molecules, which is advantageous to the performance of optoelectronic devices.

The wetting feature of metal film can also be improved through modifying the strategy of physical vapor deposition during the film deposition process. For example, the mixture gas of trace content of oxygen or nitrogen and inert gas has been used to deposit ultrathin copper film with sub-10 nanometers on the surface of metal oxide during the magnetic sputtering process.\[349,350\] Similar strategy has also been utilized to deposit ultrathin Ag film on ZnO film for achieving an average transmittance of 91% over the spectral range of 400–1000 nm and a sheet resistance of 20 $\Omega$ $sq^{-1}$ on a flexible substrate.\[351\] The cosputtering of silver and alumina is helpful for the formation of ultrasmooth and thermally stable ultrathin Al-doped silver film on metal oxide surface with high conductivity.\[352–354\] The precoating of the 1 nm Al layer acting as buffer layer is also beneficial for the deposition of continuous and ultrathin Ag film.\[355\] Through the combination of two strategies using metallic buffer layer and cosputtering of metal alloy, the Ca:Ag blend film with the 1 nm Al seeding layer has achieved a low sheet resistance of 27.3 $\Omega$ $sq^{-1}$ and an extraordinarily high mean transmittance of 93.0% in the visible spectral range.\[356\]

Since the ultrathin metal film is based on a multilayer structure, the transmission of the transparent electrode will be greatly dependent on the thickness and dielectric constant for each layer. Through engineering the dielectric layer of antireflection coating, the optical transmission of electrode can be selectively engineered to reduce the light reflection and improve the light incoupling at specific wavelength region. For example, an Al-doped ZnO film has used as antireflective layer on the surface of ultrathin Ag film supported by TiO$_2$ film.\[357\] A transparent electrode with a transmission of 91.6% at 550 nm and a sheet resistance of 5.75 $\Omega$ $sq^{-1}$ has been obtained based on such antireflection transparent conductor, whose figure of merit is four times larger than that of commercial indium tin oxide film.\[336\] To further improve the performance of transparent electrode formed by ultrathin metal film, Choi and co-workers proposed the double-stacked configuration of WO$_3$/Ag/WO$_3$/Ag structure.\[318\] Through tuning the thickness of the spacer WO$_3$ between the two ultrathin Ag film, the good conductivity (<3 $\Omega$ $sq^{-1}$) and high transparency (≈90%) can be achieved simultaneously.

The other types of ultrathin metal film, such as Cu, aluminum (Al), nickel (Ni), etc., have also been used as the transparent electrode due to their low cost and easy accessibility. Similarly, the strategy of achieving the transparent electrode based on these metals is relied on the metal oxide/metal/metal oxide multilayer structure for achieving high transparency and conductivity.\[350,358–360\] The weakly oxidized Cu thin film sandwiched between ZnO films exhibits good optical and electrical performance due to the improved wettability. An average transmittance of 83% over the visible spectral range of 400–800 nm and a sheet resistance of 9 $\Omega$ $sq^{-1}$ can be achieved.\[349\] Kim and co-workers proposed the deposition of bilayer metal film of the Ni (5 nm) and Au (5 nm) for the uniformly distributed Au NPs.\[361\] After the thermal annealing in ambient O$_2$, the transparent Ni/Au electrode will change into the structure consisted of uniformly NiO$_x$ and Au NPs. The optical transmittance of 93% at 450–700 nm and a low sheet resistance of 14 $\Omega$ $sq^{-1}$ can be attained with this strategy.

### 2.4. Metal Transparent Electrode for Photovoltaic Applications

In this section, we majorly discuss the application of metal transparent electrode, including the metal NW network, metal mesh, and ultrathin metal film, in the solution-processed organic solar cells (OSCs) and perovskite solar cells (PVSCs), and the technical issues during their application as bottom and top electrodes in photovoltaic devices. Prior to the discussion of the metal transparent electrode in practical photovoltaics, we briefly discuss the strategies of patterning metal transparent electrode, which is also very important in their application of various optoelectronic devices.

Since the fabrication of metal nanowire transparent electrode is initialized from their dispersed solution, the direct coating metal NWs on a substrate though a mask can deliver a patterned transparent electrode.\[357\] Meanwhile, the as-coated metal NWs without any posttreatment generally have weak adhesion with the substrate, which allows the metal NWs can be selectively removed or transferred to another substrate by a patterned tape or stamp.\[362\] By using the photomask, patterned metal nanowire transparent electrode can also be achieved through direct exposure by high pulse laser, contributed by the
photothermal effect. Under the irradiation of pulse laser with proper power, the metal NWs will be welded together and gradually embedded into the polymer substrate, while the metal NWs without light irradiation can easily be removed by solvent or tape due to the poor bonding between nanowire and polymer substrate.\textsuperscript{[363–365]} On the other hand, ablation of metal NWs will happen when the power of pulse laser is high enough. That is also a strategy of patterning metal nanowire electrode by leaving the NWs without irradiation.\textsuperscript{[366]} The selective treatment of the polymer surface to exhibit attractive bonding with metal NWs, such as UV-ozone treatment on PDMS substrate through photomask, is helpful for the formation of patterned electrode after metal NWs coating process.\textsuperscript{[367,368]} Moreover, the traditional photolithography is also applicable for patterning metal transparent electrode following the processes of photoresist coating, selective exposure, washing, etching, and lift-off.\textsuperscript{[161,369,370]}

2.4.1. Organic Solar Cells

Metal Nanowire Based Conductive Network and Metal Mesh as Transparent Electrode: In order to utilize metal NW network or metal mesh as transparent electrode in OSCs and achieve a comparable OSC performance to the one with commercial ITO, besides obtaining the similar optical transparency and electrical conductivity, more aspects should be considered before adopting them as bottom electrode in OSC applications. The critical issues including surface roughness of the electrode, surface wetting upon following coated materials, work-function alignment of whole devices, efficient carrier generation, and transportation in each layer should be simultaneously addressed. The small surface roughness of metal transparent electrode is one of the most important issues for successful application in thin film OSCs, especially for the electrode formed by random distributed metal NWs or self-assembled metal mesh. The large surface roughness brought by the stacking of more than two metal NWs with diameter ranged from 20 to 100 nm will easily induce the direct contact between cathode and anode of thin film OSCs. In addition, the morphology and film quality of the adjacent interfacial layers and active layer will be greatly affected by the large surface roughness of the bottom electrode, and the performance of optoelectronic devices may be deteriorated as compare to the one on ITO substrate.

To resolve the concerns of large surface roughness, selecting the metal NWs with small diameter will be helpful for the fabrication of transparent electrode with relatively low surface roughness. In addition, improving the dispersion of metal NWs on substrate or avoiding the aggregation of multiple metal NWs during their coating process needs the efforts on increasing the dispersion of metal NWs in solvent and the engineering on the coating strategy. Both of the strategies are vital to the fabrication of metal NW network with high electrical/optical performance in practical application. Meanwhile, additional treatment on the electrodes is necessary to further reduce the surface roughness. Interestingly, the strategies discussed in the previous section for welding metal nanowire electrode by coating additional materials can also benefit to reduce surface roughness, and most of the materials can be directly used as the hole or electron transporting layer in OSCs. Applying mechanical pressure on the metal nanowire electrode can also effectively decrease the gap between metal NWs and substrate for reducing the electrode surface roughness.\textsuperscript{[125,371,372]} The embedment of metal nanowire electrode into a matrix formed by metal oxide NPs or polymer layer is generally used to fabricate ultrasmooth transparent electrode.\textsuperscript{[101,103,192,212,373–376]} For transparent electrode comprised of large diameter nanowire, owning better electrical stability than the electrode by small diameter nanowires, more overcoating materials will be necessary to flatten the electrode, which however introduces a thick layer of interfacial layer between metal surface and active layer. Great amount of charge carriers generated from active layer will be lost during their transportation to the electrode, and the device will exhibit poor power conversion efficiency. The selective filling of voids among metal nanowire conductive network can be achieved through spin-coating silicon dioxide nanoparticles with diameter similar to the metal nanowire, which has been demonstrated for the reduction on surface roughness and the planarization of electrode by further polymer material coating.\textsuperscript{[141]}

After resolving issue of surface roughness, the surface wetting property upon the solution of following coated interfacial or active materials is another important issue for the transparent electrode. It is difficult to form a uniform layer on the transparent electrode surface with poor surface wetting through solution-based approach. Defects, such as pinholes and cracks, will exist in the following coated interfacial film or active layer. For the poor quality of interfacial layer, the majority carrier transportation and blocking against opposite minority carriers will be greatly affected, and the existence of direct contact between active layer and bottom electrode will greatly increase the current leakage. Likewise, for the poor film quality of active layer, it will not only affect the generation of charge carriers under light illumination and thereafter drift/diffusion in active layer, but also induce the direct contact of two interfacial layers due to the discontinuous active layer. All of these conditions would apparently deteriorate the performance of photovoltaic devices. For example, the metal transparent electrode coated by graphene, which is hydrophobic, is difficult to be fully covered by interfacial layer through solution process. To solve the problem, surface modification on the composite electrode by evaporating ultrathin metal oxide layer or proper addition of surfactant into the solution of interfacial material has been demonstrated to improve the quality of interfacial layer formed on the composite electrode.\textsuperscript{[377,378]} Fortunately, due to the broad range of materials dissolved in various solvents for the coating of interfacial layer, the metal transparent electrodes have been demonstrated to be either anode or cathode depending on the property of interfacial layer. In fact, through addressing the critical issues of surface roughness, surface wetting, work-function alignment, efficient charge generation, and transportation, the application of Ag NWs, Cu NWs, and metal mesh in organic photovoltaic devices can exhibit comparable performance to that of device fabricated on commercial ITO substrate.\textsuperscript{[95,141,229,374,379–384]} Here, we do not list all published strategies of adopting the transparent metal nanowire/mesh network to fabricate high-performance OSCs. The strategies of synthesizing metal NWs with high aspect ratio and their rational alignment on substrate are beneficial to the fabrication
of metal NW network with better optical/electrical performance than commercial ITO. It is thus reasonable to expect better performance of the organic photovoltaic devices based on metal transparent electrode.[71,74] Likewise, similar issues need to be addressed for flexible OSCs during the fabrication of metal transparent electrodes.[373,385,386]

To employ metal NW network and metal mesh as transparent top electrode in OSCs, it is generally processed after the formation of active layer and the top interfacial layer. There are two major issues for achieving high-performance OSC, i.e., avoiding the damage against underneath layers during the formation of above transparent electrode and improving the electrical contact between the top electrode and interfacial layer. The direct coating of metal nanowire solution on the surface of device might have negative effects by dissolving the underneath layers. Therefore, the lamination process is first adopted for the fabrication of metal NW network or metal mesh on the top of device.[319,377,387–389] During the lamination process, there is no employment of solvent that minimizes the damage to underneath layer, and the mechanical pressure applied on the transparent electrode will also improve the contact between the electrode and interfacial layer and benefit charge carrier transportation. Meanwhile, the fabrication of metal oxide layer through sol–gel processed or physical vapor deposition on active layer can effectively protect active layer from damage by the solvent during the coating of metal NWs, which is further coated by another layer of metal oxide for achieving the dual functions of welding metal nanowire and improving the electrical contact of metal NWs with the interfacial layer.[99,109,390] PEDOT:PSS is also commonly used as a protective layer for the active layer from damaging by the solvent of metal NWs. In addition, the strong bonding between PEDOT and metal NWs helps the formation of excellent electrical contact, which has successfully demonstrated as the top electrode of OSCs.[391–393] Through the combination of strategies of fabricating metal transparent electrode as the bottom and top transparent electrodes, the fully solution-processed semitransparent OSCs have also demonstrated.[383,394]

**Ultrathin Metal Film as Transparent Electrode:** Since the ultrathin metal film based multilayer transparent electrodes are commonly obtained through vacuum-based physical vapor deposition process, it can be readily used as the top or bottom electrode in OSCs without the consideration of difficulties existing in the metal NW network and metal mesh. The technical concerns during their applications in OSCs majorly come from (1) selection of materials and thickness of each layer, by considering the optical/electrical performance of transparent electrode; (2) work-function alignment of the adjacent layer in the device; and (3) light incoupling for improving optical absorption of active layer. Besides the requirements of high optical transparency and low sheet resistance, more aspects of the transparent electrode based on dielectric/metal/dielectric should be taken into account for its application in photovoltaic devices. One of the dielectric layers adjacent to active layer will act as interfacial layer, whose work function and thickness are critical to the extraction of photogenerated charge carriers in device. Meanwhile, another dielectric layer along with the direction of incident light is also important to incouple light into device.

The photon conversion efficiency of photovoltaic device based on D/M/D transparent electrode is greatly dependent on the optical/electrical performance of the electrode, and the efficiency can be better than the reference device based on ITO film. For example, the ZnO/Ag:AgOx/ZnO (ZAOZ) transparent electrode using an AgOx (O/Ag = 3.4 at%) layer deposited on polyethylene terephthalate (PET) substrates at room temperature shows an average transmittance of 91%, over spectral range 400–1000 nm and a sheet resistance of 20 Ω sq−1. After adopting the ZAOZ as transparent cathode, power conversion efficiency (PCE) of organic device based on ZAOZ structure has improved to 6.34% compared to that of 5.76% for the conventional transparent cathode of ZnO/ITO.[351] The MoOx/Ag/ MoOx (MAM) structure not only shows a comparable optical transmittance but also reveals a superior sheet resistance as compared to the ITO/PEDOT:PSS film.[395] Specifically, the current density–voltage (J–V) characteristics of MAM-based large-area devices demonstrated a less efficiency degradation as compared to that of ITO-based device. The efficiency of MAM-based device just decreases from 4.47% (0.2 cm2) to 3.17% (25 cm2) with efficiency degradation of 30%, while the efficiency degradation is up to 68% (from 5.67% to 1.80%) for ITO-based device. Notably, the DMD structure, as compared to ITO, is good for large-scale production of photovoltaic device due to the area-scaling sheet resistance.

Guo and co-workers reported the NiO/Ag/NiO (NAN) transparent electrode, in which NiO has a high conduction band for electron blocking and a low valence band for efficient hole transport.[396] The NAN-based cells deliver the comparable PCEs of 6.07% and 5.55% as deposited on glass and PET, respectively, which are competitive with those of ITO-based devices (5.90% and 4.42%). In a subsequent work, they reported the low-work-function transparent cathode with structure of SnOx/Ag/SnOx/Bi2O3 (SASB).[397] The introduction of the Bi2O3 lowers the work function of SASB electrode to 4.22 eV, which matches the lowest unoccupied molecular orbital level of fullerene-based acceptor for better electron extractions. The proposed SASB electrode has a low energy level alignment between cathode and acceptor and also delivers the excellent optical transmittance of 88% and low electrical sheet resistance of 9 Ω sq−1. The PCE of 6.21% is achieved for PBDTTT-C:T:PC70BM-based solar cells, which is comparable to that of ITO-based device (6.53%).

The ultrathin Ag film has been fabricated on the active layer of PBDTTTF-B:PC71BM, and the device configuration with ultrathin metal film and ITO as the front electrode are shown in Figure 4a. The high index material of TeO2 has adopted as the antireflection capping layer on ultrathin Ag cathode. The OSCs with TeO2 coated on thin Ag electrode revealed an improved photocurrent as compared to that of ITO-based planar device (see Figure 4b). The best PCE of 8.5% can be achieved for OSCs with both glass and plastic as substrate. In another work, Jen and co-workers reported a similar device configuration of the ultrathin Ag film deposited on the substrate of glass, in which the high index TeO2 is sandwiched between the transparent Ag and glass.[138] The optical designs of ultrathin Ag film as transparent electrodes are studied to enhance the light incoupling and trapping via the high refractive index TeO2 layer. As shown in Figure 4c, the adopted TeO2 layer with the optimized thickness...
of 40 nm can not only lowers the surface reflection but also maximizes the light intensity in active layer as compared to the one without high index TeO2 layer. Besides, the high index TeO2 layer can facilitate the growth of smooth, highly conductive, and optically transparent Ag film (12 nm), which lead to a superior performance for the device with the proposed TeO2/Ag transparent electrode that even exceeds the one with ITO electrode. Guo and co-workers further demonstrated the usage of another high index material Ta2O5 for improving the light transmittance of thin Al-doped Ag film. The use of small amount of Al during co-deposition of Ag produces an ultrathin and smooth Ag film, while the high index Ta2O5 improves the light incoupling. The synergetic improvement by the doped Al and high index Ta2O5 layer leads to a champion performance of both transmittance and conductivity as compared to other proposed hybrid transparent electrode (see Figure 4d).

Besides acting as antireflective coating for improving light transmission, the front dielectric layer can also be engineered into specific pattern to offer an additional degree of freedom for manipulating light incoupling to photovoltaic device. Lee and co-workers reported the designs of hybrid dielectric/metal/polymer as top transparent anode by replacing top dielectric with polymer. The proposed device structure is illustrated in Figure 5a. The polymer of PDMS with a small refractive index will reduce the reflection loss at the front interface and achieve a high transmittance with the insensitive polymer thickness. Patterning the polymer into a well-ordered nanostructure on the top Ag electrode can further improve the transmittance of the hybrid electrode. The resultant PCE is improved from 4.46% to 6.75% for PTB7:PC70BM-based OSCs, which is mainly attributed to the both high transmittance and excellent haze of the patterned structure. In the subsequent work, Lee et al. have proposed the asymmetric configurations of the polymer/metal Ag (8 nm)/dielectric WO3 (30 nm) film as transparent bottom anode (see Figure 5c). The soft polymer materials of the ormoclear are adopted to replace the inorganic dielectric materials, which improve the surface wettability of the subsequently deposited Ag. The proposed structure exhibits low sheet resistance of 4.8 Ω sq−1 and high transmittance of 96.3% at 535 nm, which result in an enhanced PCE of 7.63%. In addition, as shown in the inset of Figure 5d, the ormoclear can be further patterned into a well-order structure by the nanoimprint lithography. The photocurrent can be further improved to 16.6 mA cm−2 as compared to that of the ITO-based device (14.2 mA cm−2). In another study, a similar asymmetric electrode with structure of PEI/Ag/PEDOT:PSS is
proposed as bottom cathode on the substrate.\footnote{341} The hybrid electrodes reveal the good optical, electrical properties, and flexibility including a visible-range transmittance $>95\%$, a sheet resistance $<10\ \Omega\ \text{sq}^{-1}$, and bending radius $<1\ \text{mm}$.

The Strategies of Light Trapping for Transparent Metal Electrode: As it is well-known, the direct replacement of ITO with transparent ultrathin metal film and the combination with the back thick metal electrode will form an optical microcavity in the thin film photovoltaic device. Jen and co-workers adopted the ultrathin Ag film as cathode and thick Ag as anode to form the microcavity configuration, and the resonant microcavity effect contributed to a substantial improvement of photon collection.\footnote{401} The use of antireflective coating as the first dielectric layer along the direction of incident light could greatly increase the transmission of light into the device, which consequently will improve the magnitude of the optical field in the microcavity.\footnote{354,398} The light confinement of microcavity at the active layer can also be improved by introducing the optical spacer between the active layer and transparent top metal electrode.\footnote{402,403} In addition, the transparent metal film can also function as the interconnecting layer in tandem solar cells, which can form the microcavity with the adopted front transparent metal electrode for improving the light trapping in tandem cells.\footnote{404}

Besides the simple formation of microcavity, the plasmonic effects can also be exploited in the ultrathin metal film with the patterned hole array, and the excited surface plasmon can be utilized to favor the light harvesting. The metal film with hole array is reported to reduce the light reflection and achieve a balanced transmittance and conductivity.\footnote{405} Pei and co-workers demonstrated the formation of Au nanomesh with the closely packed polystyrene (PS) nanosphere.\footnote{406} The Au nanomesh induced plasmonic effects has improved the short-circuit current density ($J_{SC}$) from 7.02 to 14.2 mA cm$^{-2}$. As shown in Figure 6a, the periodicities of the Au nanomesh can be modulated to excite surface plasmon at different resonant wavelengths, which can selectively improve the light absorption of active layer.\footnote{276} Figure 6b is the cross-sectional SEM image of the representative Au nanomesh incorporated OSCs.\footnote{407} Due to the excitation of plasmonic resonance, the $J_{SC}$ is significantly improved (Figure 6c). However, the excited plasmonic resonance of the Au nanomesh, which is a narrow bandwidth, cannot explain the broadband enhancement in EQE spectra as shown in Figure 6d. The formation of the microcavity between the Au nanomesh and back thick Al electrode should be another mechanism for confining light in active layer. Wang and co-workers further studied the optimization and fabrication of the metal nanomesh with the hexagonally arrayed periodic circular hole as the electrode in P3HT:PCBM-based OSCs.\footnote{408}

Recently, the ultrathin metal film has adopted as one of the transparent electrodes in the semitransparent photovoltaic devices, which can also be used as both anode and cathode.
simultaneously in one single transparent solar cell.\textsuperscript{[409–411]} However, the efficiency of such kind of device could be limited by the relative low light absorption of active layer due to the shortened light path. The essential light trapping design is highly desirable for semitransparent solar cells. Choy and co-workers proposed a hybrid optical nanostructure dielectric/metal/nanoparticle:dielectric (D/M/NP:D) as transparent electrode to enhance the light incoupling.\textsuperscript{[412]} The D/M/NP:D nanostructure consists of high index and low-loss nanoparticles (Si NP scatter) and index matching material (Alq 3) on ultrathin Ag film, i.e., MoO 3/Ag/Si NPs:Alq 3, as the top hybrid electrode (Figure 7a). The hybrid nanostructure can complementarily improve the light incoupling in long- (due to Si NPs) as well as short-wavelength regions (due to Alq 3 layer) with additional synergetic improvement (due to hybrid D/M/NP:D nanostructure). For demonstration, the semitransparent OSCs (st-OSCs) with or without the hybrid transparent electrode were fabricated. As shown in Figure 7b, the incident photon-to-current efficiency (IPCE) spectra revealed a broadband enhancement feature for the st-OSCs with the hybrid light incoupling structure as compared to control st-OSC with the bare ultrathin Ag electrode. The final PCE is improved from 3.61% to 4.83% with enhancement.

Figure 6. a) SEM images of plasmonic gold nanohole arrays with the periodicities of 570 and 1040 nm. Reproduced with permission.\textsuperscript{[276]} Copyright 2017, Nature Publishing Group. b) Cross-sectional SEM of Au nanomesh incorporated OSCs, and the inset shows the schematic illustration of the device with Au nanomesh. c) Typical J–V characteristics of control and Au mesh incorporated OSCs and the Au-incorporated OSCs have an enhanced PCE by 52%, and J_{SC} and FF by 41% and 6% respectively. d) EQE spectrum of the OSCs with control ITO and Au nanomesh as electrode. Reproduced with permission.\textsuperscript{[407]} Copyright 2013, OSA Publishing.

Figure 7. a) Device structure of semitransparent OSCs with hybrid electrode structure, and the inset shows the cross section of the hybrid structure. b) IPCE spectra of st-OSCs with and without light incoupling structure, and the summarized J–V characteristics of the st-OSC are listed in the inset. Reproduced with permission.\textsuperscript{[412]} Copyright 2015, Elsevier.
of 34% due to the optical incoupling by the hybrid electrode. Therefore, through carefully engineering the device configuration, the light manipulations and electrical optimization can be achieved simultaneously in hybrid transparent electrode, which is of great promising for extend the solar energy application.

The distributed Bragg reflector (DBR) consisted of alternative high and low index materials can form a photonic bandgap and inhibit the light transmission at the specific wavelength region, which is a good reflector in photovoltaic application especially for the semitransparent cells. Martorell and co-workers proposed the multilayered structure on the Ag film (15 nm) to improve light harvesting in transparent OSCs.[413] Two kinds of transparent devices are schematically shown in Figure 8a, one transparent cell adopted only one layer of LiF atop the thin cathode Ag (Tn-Ag), while another one is with three-layered MoO3/LiF as the back reflector (PC-Tn-Ag) for the thin Ag film. The EQE in Figure 8b clearly indicates the considerable improvement of the light incoupling induced by the multilayered structure. As

Figure 8. a) Schematic view of the two transparent OSCs. b) Experimentally measured EQEs for the opaque cell (Tk-Ag), the semitransparent cell of the 10 nm thick Ag layer (Tn-Ag), and the cell incorporating the photonic crystal (PC-Tn-Ag). Reproduced with permission.[413] Copyright 2013, Nature Publishing Group. c) Schematic illustration of the semitransparent cell architecture incorporating the photonic crystal structure between the glass and the thin Au electrode and antireflection coating layer above the Ag thin metal electrode. d) Measured J–V curves for both semitransparent devices, STC1 and STC2, and for the opaque solar cell. Reproduced with permission.[414] Copyright 2015, John Wiley & Sons, Inc. e) Device architecture of semitransparent OSCs with eight pairs of 1D photonic crystal (PC). f) Transmittance spectra of 1DPCs. Reproduced with permission.[415] Copyright 2014, Elsevier.
compared to the Tn-Ag cell, the enhanced EQE results in an increase of the $J_{SC}$ from 8.5 to 10.7 mA cm$^{-2}$, and the corresponding PCE from 3.6% to 5.2%, which recover the efficiency up to 80% as compared to the opaque cell. In the subsequent work, the formation of microcavity configurations through replacing ITO by transparent Au electrode has demonstrated to further improve the efficiency of transparent cell.[414] The device structures are depicted in Figure 8c, the transparent cells have adopted the thin Ag film as anode and thin Au film as cathode, and the antireflection coating layer composed of LiF (low refractive index)/MoO$_3$ (high refractive index) is deposited on the transparent Ag anode for improving the light incoupling. Differently, one transparent cell has the multilayered SiO$_2$/TiO$_2$ as the back reflector sandwiched between the transparent Au and glass as back reflector (STC1), while in another one the transparent Au cathode is directly deposited on the glass (STC2). The $J–V$ characteristic shown in Figure 8d reveals that the STC1 outperforms the STC2 and has the comparable photocurrent as the opaque cells. The final PCE of STC1 assisted by the near-infrared light trapping reaches 90% of the opaque counterpart and simultaneously 21% visible transparency is maintained.

The mechanisms and modulations of the DBR have been well studied, in which the influence of layer number of the alternative layered structures on light reflection wavelength has been systematically unveiled.[415–418] Chen and co-workers demonstrated the 1D photonic crystal (WO$_3$/LiF)$_n$ as the back reflector (Figure 8e).[415] and the eight layers of WO$_3$/LiF can induce a total photonic bandgap in the wavelength region of 400–500 nm. Since the light cannot transmit through the 1D (WO$_3$/LiF)$_8$ structure at 400–500 nm (Figure 8f), the PCE of 4.84% and transmittance of 25.4% have achieved for the total transparent OSCs with active layer of PCDTBT:PC$_{70}$BM. In addition, through tuning the thickness of the alternative WO$_3$ and LiF materials, the photonic bandgap of 1D photonic crystal can be relocated at 580–780 nm.[416] Besides light trapping offered by the photonic bandgap of 1D photonic crystal, the other optical modes have also exploited to improve the performance of transparent OSCs. The concepts of the optical Tamm states and phase difference have also been used for improving transparent device performance.[419,420]

### 2.4.2. Perovskite Solar Cells

Perovskite solar cells, which have been regarded as the next generation of solar cells contributed by the low-cost and solution-processed device fabrication and the high-power conversion efficiency, are attracting more and more attentions from both academia and industry. Diverse aspects ranging from fundamental research to practical application of the PVSCs have been intensively investigated. The study of metal-based transparent electrode in PVSCs is also important in order to meet more requirements of the next generation of solar cells.

However, it is well known that the organic/inorganic hybrid perovskite film is very sensitive to the environmental conditions, such as humidity, light, heat, etc. Inappropriate treatment on the perovskite film will affect the interface and quality of film, which are critical to the cell efficiency. Therefore, through physical vapor deposition process of fabricating transparent electrode of dielectric/ultrathin metal/dielectric on the top of device in a vacuum condition, the damage against perovskite film will be minimal. Combined the strategies discussed in Section 2.3 for achieving high transparent and conductive electrode, different kinds of transparent electrode with multilayer structure have successfully demonstrated as the top electrodes for PVSCs.[344,346,421–427] Table 1 briefly summarizes the structures of ultrathin metal film based transparent electrodes and the performance of single junction PVSCs by using them as the transparent top electrode. Meanwhile, the application of metal NW network and metal mesh in PVSCs as the transparent top electrode can also be achieved through lamination method due to the solvent free process (see Figure 9a,b). Before the lamination process, the metal transparent electrode is preformed on a flexible substrate, which is then laminated on perovskite film capped by a thick polymer interfacial layer after applying proper pressure, benefiting the embedment of metal nanowire into the polymer film for achieving good electrical contact and charge carrier transportation in the photovoltaic device.[144,428–430] In addition, coating the flexible metal transparent electrode with another interfacial layer with proper addition of adhesive agents is helpful to improve the adhesion and electrical contact between the top electrode and the bottom electrode.[428,430]

In contrast, more problems will be confronted for direct fabricating metal nanowire based transparent electrode through solution process on the top of perovskite devices. Avoiding damage against the underneath perovskite film during the process is the primary issue for achieving the high-performance PVSCs due to the highly unstable perovskite film. A thick polymer layer or thin metal oxide layer from atomic layer deposition without any pinhole or crack has been demonstrated to be a good protector for the deposition of metal nanowire electrode on top.[431,432] The barrier effect can be further improved with additional layer of metal or metal oxide layer on the polymer interfacial layer, which can also improve the electrical contact and charge carrier transferring between metal nanowire and interfacial layer contributed by the work-function alignment.[433–435] Details of the metal transparent electrode and their performance in single junction PVSCs through lamination process and solution process have listed in Table 1.

Different with application of metal transparent electrode as top electrode, in which the major concern arises from the damage against the perovskite film during the fabrication process, the bottom electrode of metal transparent electrode may have the possibility of being attacked by the halides, which are the essential component for the perovskite film. The penetration of halides in liquid or gas state through interfacial layer and adsorption on metal surface can happen during and after the formation of perovskite film, and the reactivity of halides with metal will be enhanced in the presence of moisture, oxygen, heat, electricity, light, etc. Adopting the metal materials with high stability or unreactive to the halides for the fabrication of transparent electrode could be a good solution to resolve this concern. For example, the transparent electrode of Au mesh has proven to exhibit much higher stability than the one from Ag NWs after the fabrication of perovskite film.[436] The thin film transparent electrodes of Au/NiO$_x$ and ultrathin Au film have been demonstrated in PVSC with comparable performance to the device fabricated on ITO glass.[437] However,
the high price of gold material would be a major obstacle for their application in low-cost PVSCs. Before the application of transparent bottom electrode from silver, copper, and other metal material with a relatively low price in PVSCs, the stability issue should be addressed. The formation of a conductive or semiconductive blocking layer without pinhole or crack on the metal transparent electrode by a compact metal oxide during the fabrication of perovskite film.\textsuperscript{[345]} The strategy of covering the metal transparent electrode by a compact metal oxide layer from physical vapor deposition process is also applicable to the metal mesh and the solution process metal NW network for improving their stability against corrosion by halides, which have been demonstrated in the application of PVSCs.\textsuperscript{[203,441]}

Fabricating stable transparent electrode through all solution and low temperature process is highly desirable in organic photovoltaic device as well as PVSCs. Graphene, being a good gas barrier due to its unique 2D structure of atomic-scale hexagonal lattice made of carbon atoms, is a promising candidate for protecting the metal transparent electrode and eliminating the penetration of halides. The composite flexible transparent electrode of polymer/Ag NWs/graphene with enhanced anticorrosive property has been demonstrated in PVSC application, in which a thermal evaporated MoO\textsubscript{3} interfacial layer is used to improve surface wetting of the electrode and benefit the formation of solution-processed perovskite film.\textsuperscript{[442]} Meanwhile, the flawless film stacked from graphene oxide flakes has also been demonstrated

<table>
<thead>
<tr>
<th>Technique</th>
<th>Transparent top electrode (TTE)</th>
<th>Device configuration</th>
<th>PCE [%] (bottom illumination)</th>
<th>PCE [%] (top illumination)</th>
<th>PCE [%] (reference electrode)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamination</td>
<td>PET/Ni mesh/ PEDOT:PSS</td>
<td>Glass/ITO/c-TiO\textsubscript{2}/mp-Al\textsubscript{2}O\textsubscript{3}/MAPbI\textsubscript{3}/Cl\textsubscript{2}/spiro-OMeTAD/PEDOT:PSS/TTE</td>
<td>9.8 ± 1.7</td>
<td>13.3 ± 1.8</td>
<td>14.3 ± 2.2 Opaque Au film</td>
<td>[428]</td>
</tr>
<tr>
<td>Lamination</td>
<td>PET/Ag NWs</td>
<td>Glass/ITO/c-TiO\textsubscript{2}/mp-Al\textsubscript{2}O\textsubscript{3}/MAPbI\textsubscript{3}/Cl\textsubscript{2}/spiro-OMeTAD/PEDOT:PSS/TTE</td>
<td>12.7</td>
<td>-</td>
<td>12.7 Opaque Au film</td>
<td>[429]</td>
</tr>
<tr>
<td>Lamination</td>
<td>PI/Cu NWs</td>
<td>Glass/ITO/c-TiO\textsubscript{2}/mp-Al\textsubscript{2}O\textsubscript{3}/MAPbI\textsubscript{3}/Cl\textsubscript{2}/spiro-OMeTAD/PEDOT:PSS/TTE</td>
<td>-</td>
<td>9.13 ± 0.71</td>
<td>12.19 ± 0.92</td>
<td>[144]</td>
</tr>
<tr>
<td>Lamination</td>
<td>PET/Ag-mesh/ PEDOT:PSS</td>
<td>Glass/ITO/c-TiO\textsubscript{2}/mp-Al\textsubscript{2}O\textsubscript{3}/MAPbI\textsubscript{3}/Cl\textsubscript{2}/spiro-OMeTAD/PEDOT:PSS/TTE</td>
<td>8.8 ± 1.0</td>
<td>6.7 ± 0.6</td>
<td>10.1 ± 1.8</td>
<td>[430]</td>
</tr>
<tr>
<td>Thermal evaporation</td>
<td>MoO\textsubscript{3}/Ag/MoO\textsubscript{3}</td>
<td>Glass/ITO/PCBM</td>
<td>13</td>
<td>9.7</td>
<td>-</td>
<td>[423]</td>
</tr>
<tr>
<td>Thermal evaporation</td>
<td>MoO\textsubscript{3}/Ag/ZnS</td>
<td>Glass/ITO/c-TiO\textsubscript{2}/MAPbI\textsubscript{3}/Cl\textsubscript{2}/spiro-OMeTAD/TTE</td>
<td>12.8 ± 0.44</td>
<td>-</td>
<td>14.0 ± 0.59 7 nm MoO\textsubscript{3}/ Opaque Ag film</td>
<td>[424]</td>
</tr>
<tr>
<td>Thermal evaporation</td>
<td>BCP/Ag/MoO\textsubscript{3}</td>
<td>Glass/ITO/PCBM</td>
<td>10.66 ± 0.35</td>
<td>7.18 ± 1.52</td>
<td>12.7 ± 1.60 BCP/ Opaque Ag film</td>
<td>[346]</td>
</tr>
<tr>
<td>Atomic layer Deposition</td>
<td>SnO\textsubscript{2}/Ag/SnO\textsubscript{2}</td>
<td>Glass/ITO/PCBM/AlO\textsubscript{3}/TTE</td>
<td>11.8</td>
<td>8.6</td>
<td>12.5 Opaque Ag film</td>
<td>[423]</td>
</tr>
<tr>
<td>Thermal evaporation</td>
<td>MoO\textsubscript{3}/Cu/SnO\textsubscript{2}</td>
<td>Glass/ITO/PCBM/AlO\textsubscript{3}/TTE</td>
<td>9.6</td>
<td>-</td>
<td>-</td>
<td>[426]</td>
</tr>
<tr>
<td>Thermal evaporation</td>
<td>PEIE/Ag/MoO\textsubscript{3}</td>
<td>Glass/ITO/PCBM/AlO\textsubscript{3}/TTE</td>
<td>11.92</td>
<td>12.26</td>
<td>-</td>
<td>[427]</td>
</tr>
<tr>
<td>Spin coating</td>
<td>Ag NWs</td>
<td>Glass/ITO/PCBM</td>
<td>13.55</td>
<td>8.41</td>
<td>14.50 with back reflector</td>
<td>[431]</td>
</tr>
<tr>
<td>Spray coating</td>
<td>Ag NWs</td>
<td>Titanium foil/c-TiO\textsubscript{2}/mp-Al\textsubscript{2}O\textsubscript{3}/MAPbI\textsubscript{3}/spiro-OMeTAD/TTE</td>
<td>10.55 ± 0.42</td>
<td>-</td>
<td>16.15 ± 0.20 Opaque Ag film</td>
<td>[432]</td>
</tr>
<tr>
<td>Spray coating</td>
<td>Ag NWs</td>
<td>Glass/ITO/PCBM/AlO\textsubscript{3}/TTE</td>
<td>8.49</td>
<td>-</td>
<td>10.68 Opaque Ag film</td>
<td>[433]</td>
</tr>
<tr>
<td>Spin coating</td>
<td>Ag NWs</td>
<td>Glass/ITO/c-TiO\textsubscript{2}/MAPbI\textsubscript{3}/spiro-OMeTAD/TTE</td>
<td>11.07</td>
<td>6.10</td>
<td>-</td>
<td>[434]</td>
</tr>
<tr>
<td>Spray coating</td>
<td>Ag@Au NWs</td>
<td>Glass/ITO/PTAA/PCBM/AlO\textsubscript{3}/TTE</td>
<td>11.0</td>
<td>-</td>
<td>-</td>
<td>[435]</td>
</tr>
</tbody>
</table>

Table 1. Summary of metal-based transparent top electrodes in perovskite solar cells.
to improve the anticorrosive property of Ag nanowire based conductive network, which however have poor conductivity at longitudinal direction due to the multilayer film with great amount of carboxyl and hydroxyl groups attached on each layer. The strategy of partially reducing the graphene oxide for the formation of flawless film on Ag nanonetwork can synthetically address the issues of anticorrosion, longitudinal conductive, surface wetting, and work function of the transparent electrode, which has been demonstrated in the application of PVSC on both glass and PET substrate (see Figure 9c,d). The fully embedment or coverage of metal transparent electrode by the conductive polymer with continuous film morphology is also helpful to the stability of metal transparent electrode, which has been realized through a slot die process for the formation of a thick PEDOT:PSS film on the Ag NW electrode.

As shown in Figure 9e,f, the high-performance and stable PVSCs have been demonstrated on the hybrid electrode of metal mesh and PH1000, which exhibit a high PCE of 14.0% and is highest among the metal-oxide-free flexible PVSCs. A brief summary of the structures and the fabrication techniques

Figure 9. a) Schematic structure of perovskite solar cells with laminated Cu NW top electrode and b) SEM cross-sectional image of the PVSC. Reproduced with permission. Copyright 2016, John Wiley & Sons, Inc. c) Schematic diagram of a PVSC on the flawless anticorrosive GO film protected Ag nanonetwork bottom electrode and d) SEM image of the cross section of a typical device. Reproduced with permission. Copyright 2016, Royal Society of Chemistry. e) Image and structure of the large area flexible PET substrate with embedded Ag mesh (FEAM), and f) device structure and cross-section SEM images of the PVSC with structure of hybrid electrode/PEDOT:PSS (35 nm)/MAPbI3 (B280 nm)/PCBM (B60 nm)/Al (100 nm). Reproduced with permission. Copyright 2017, Nature Publishing Group.
of transparent bottom electrode as well as perovskite device configuration and their performance are listed in Table 2.

2.4.3. Stability of Solar Cell Based on Metal Transparent Electrode

Contributed by the efforts from all aspects, the metal-based transparent electrodes have been successfully demonstrated as cathode or anode in the application of both OSCs and PVSCs, which can exhibit comparable performance with the devices fabricated on the commercial metal oxide based conductive film. Besides the comparable PCE of the photovoltaic device with metal transparent electrode, long-term stability of photovoltaic device under operational condition is another crucial parameter to be assessed before their commercialization, which however is still lack intensive investigation. The metal-based transparent electrode in PVSCs under operational condition exhibits much higher chemical reactivity than the electrode in ambient condition, owing to the presence of a large amount of free electrons on the surface of metal electrode inclining to transfer to the surrounding materials, which will induce the degeneration of metal transparent electrode. Under work condition of solar cells, the exposure of light and heat will even speed up the degeneration of metal transparent electrode.

Encapsulation of the photovoltaic devices to inhibit the penetration of various vapors is helpful to the stability of metal electrode, but it is difficult to avoid the reaction of metal transparent electrode with the essential materials of the devices. For example, Bormann et al. found that the encapsulated OSC fabricated on the flexible Ag NW/Norland Optical Adhesive 63 (NOA) composite electrode still experienced a large decrease of PCE maintaining only 20% of initial values after 20 ± 5 h. Enhanced chemical reaction between Ag NW and NOA under light exposure or electrical bias was attributed to the failure of metal nanowire based transparent electrode.\textsuperscript{[447]} Even worse situation could be expected on metal transparent electrode in PVSCs. Owing to the instability of the perovskite film and the diffusion of ion under electrical field, the decomposed halides will reach the metal transparent electrode.

Table 2. Summary of metal-based transparent bottom electrodes in perovskite solar cells.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Transparent bottom electrode (TBE)</th>
<th>Device configuration</th>
<th>PCE [%] (bottom illumination)</th>
<th>PCE [%] (flexible device)</th>
<th>PCE [%] (reference electrode)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal evaporation</td>
<td>SU-8/MoO\textsubscript{2}/Au</td>
<td>TBE/PEDOT:PSS/MAPbI\textsubscript{1.63}Cl\textsubscript{0.37}/PCBM/Ca/Ag opaque film</td>
<td>9.05</td>
<td>9.05</td>
<td>12.13 ITO/glass</td>
<td>[436]</td>
</tr>
<tr>
<td>E-beam evaporation</td>
<td>Glass/Au:TiO\textsubscript{2} film</td>
<td>TBE/MAPbI\textsubscript{1}/C\textsubscript{60}/Bphen/Ag opaque film</td>
<td>10.24</td>
<td>–</td>
<td>10.85 PEDOT:PSS/ITO/glass</td>
<td>[437]</td>
</tr>
<tr>
<td>E-beam evaporation</td>
<td>WO\textsubscript{3}/Ag/WO\textsubscript{3}</td>
<td>TBE/PEDOT:PSS/MAPbI\textsubscript{1}/C\textsubscript{60}/Bphen/Ag opaque film</td>
<td>9.73 ± 0.57</td>
<td>8.04</td>
<td>10.51 ± 0.75 ITO/glass</td>
<td>[438]</td>
</tr>
<tr>
<td>ALD + RF magnetron sputtering</td>
<td>SnO\textsubscript{2}/Ag/SnO\textsubscript{2}</td>
<td>TBE/SnO\textsubscript{2}(ozone)/MAPbI\textsubscript{1}/spiro- MeOTAD/MoO\textsubscript{2}/Ag opaque film</td>
<td>11</td>
<td>–</td>
<td>13.9 ± 0.7 ITO/glass</td>
<td>[439]</td>
</tr>
<tr>
<td>Magnetron sputtering</td>
<td>Glass/ITO/Ag grid/AZO</td>
<td>TBE/ZnO/MAPbI\textsubscript{1}/spiro- MeOTAD/Ag opaque film</td>
<td>13.86</td>
<td>–</td>
<td>12.37</td>
<td>[440]</td>
</tr>
<tr>
<td>Solution approach +</td>
<td>c-ITO/Ag</td>
<td>TBE/PEDOT:PSS/MAPbI\textsubscript{1}/PC\textsubscript{61}BM/BCP/Ag opaque film</td>
<td>14.15</td>
<td>–</td>
<td>15.38 ITO/glass</td>
<td>[203]</td>
</tr>
<tr>
<td>DC magnetron sputtering</td>
<td>c-ITO/Cu</td>
<td>TBE/PEDOT:PSS/MAPbI\textsubscript{1}/PC\textsubscript{61}BM/Ag opaque film</td>
<td>12.95</td>
<td>–</td>
<td>12.08 ITO/PET</td>
<td></td>
</tr>
<tr>
<td>Solution approach +</td>
<td>Glass/ZrO\textsubscript{2}/MPTMS/Ag/MUTAB</td>
<td>TBE/PC\textsubscript{61}BM/MAPbI\textsubscript{1}/PTAA/Ag opaque film</td>
<td>14.48 ± 0.64</td>
<td>–</td>
<td>14.30 ± 0.61 ITO/PEI</td>
<td>[345]</td>
</tr>
<tr>
<td>vacuum evaporation</td>
<td></td>
<td>TBE/PC\textsubscript{61}BM/FAPbI\textsubscript{1}/PTAA/Ag opaque film</td>
<td>15.01 ± 0.67</td>
<td>–</td>
<td>15.11 ± 0.68 ITO/PEI</td>
<td>[345]</td>
</tr>
<tr>
<td>Solution approach +</td>
<td>PET/Ag NWs/ZnO:F</td>
<td>TBE/b-TiO\textsubscript{2}/MAPbI\textsubscript{1}/spiro- MeOTAD/Ag opaque film</td>
<td>3.29</td>
<td>3.29</td>
<td>2.95 FTO/glass</td>
<td>[441]</td>
</tr>
<tr>
<td>pulsed laser deposition</td>
<td></td>
<td>TBE/c-ZnO/mp-Al\textsubscript{2}O\textsubscript{3}/MAPbI\textsubscript{1}/spiro- MeOTAD/Ag opaque film</td>
<td>6.12 ± 0.8</td>
<td>–</td>
<td>9.97 ± 0.7 FTO/glass</td>
<td>[444]</td>
</tr>
<tr>
<td>Solution approach</td>
<td>Polymer/Ag NWs/graphene</td>
<td>TBE/MoO\textsubscript{2}/MAPbI\textsubscript{1}/PCBM/BCP/Ag opaque film</td>
<td>10.419</td>
<td>10.419</td>
<td>10.231 ITO/PET</td>
<td>[442]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TBE/MoO\textsubscript{2}/MAPbI\textsubscript{1}/PCBM/PCBM/Ag opaque film</td>
<td>9.233</td>
<td>7.92</td>
<td>12.488 ITO/glass</td>
<td>[443]</td>
</tr>
<tr>
<td>Solution approach</td>
<td>PET/Ag mesh/PH1000</td>
<td>TBE/PEDOT:PSS/MAPbI\textsubscript{1}/PCBM/Al opaque film</td>
<td>14</td>
<td>14</td>
<td>13.9 ITO/glass</td>
<td>[446]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TBE/PEDOT:PSS/Triple cation perovskite/PCBM/Al opaque film</td>
<td>11</td>
<td>–</td>
<td>–</td>
<td>[445]</td>
</tr>
</tbody>
</table>
that exhibits extraordinary stability over more than 4500 h.\textsuperscript{[425]} Such compact SnO$_x$ layer on the top of device can also act as the encapsulated layer to protect the perovskite film from the attack by species in the outer environment, which is another important reason for the excellent stability performance of the device.

3. The Back Metal Electrode

Being an essential part of a solar cell, the back metal electrode majorly plays the role of collecting charge carriers generated from the active layer under the light illumination. The requirement on the transparency of the back electrode is not rigid, which can be either opaque or transparent. The semitransparent thin film solar cells possessing transparent cathode and anode have been attracting attentions due to their potential application in photovoltaic windows. Fabrication of metal transparent electrode on the top of photovoltaic devices has been reviewed in the previous section. Meanwhile, the opaque electrode of thick noble metal film generally exhibits high reflection, which has the ability of increasing the optical path in thin film solar cells and thereby power conversion efficiency. The opaque noble metal electrode can also be patterned with special structures, such as periodic, random, quasiperiodic, and bioinspired/prewritten pattern, to exhibit extraordinary optical properties, which have been demonstrated to improve the efficiency of thin film solar cells. In this section, we review the recent works of the patterned metal electrode that introduces the strong light–matter interactions for improving the optical absorption of active layer as well as the efficiency of both OSCs and PVSCs. The stability issue of metal back electrode in PVSCs is also briefly discussed.

3.1. Periodic Pattern

Engineering the back metal electrode into the repeatedly periodic pattern can offer the incident light with an additional momentum and then excite the surface plasmon polaritons (SPPs) along the periodic metal electrode interface, which facilitate the highly concentrated near field into subwavelength region and thereby boost the optical absorption of the active layer. The incorporations of metal nanostructures into solar cells have been reported since 20 years ago.\textsuperscript{[448]} The metal nanoparticles have been increasingly exploited to promote the light absorption of silicon solar cells by the localized surface plasmon resonances and scattering effect.\textsuperscript{[449–453]} Meanwhile, engineering the back metal electrode into periodically pattern also enables to enhance the optical absorption of the active layer. The soft lithographic method has been developed to pattern the active layer into periodic structure by a soft grating mold, and then the evaporated metal on the active layer as electrode will follow the pattern of active layer.\textsuperscript{[454–456]} Figure 10a shows
a typical schematic process flow of the fabrication sequences for OSCs with grating patterned electrode. The active layer of P3HT:PCBM was spin coated on the PEDOT/ITO substrate, the active layer reveals a flat feature as shown Figure 10b, and the cathode of Ca/Al is then thermally evaporated on the active layer, which is also a planar film (Figure 10c). In another case, PDMS mold with periodically grating patterns was put in conformal contact with the active layer, and after the annealing process, the active layer has replicated the PDMS pattern once peeling off PDMS mold and then a clearly repeated pattern can be observed (Figure 10d). The cathode of Ca/Al also replicates and follows the grating pattern of the active layer (Figure 10e). With the help of PDMS mold, the active layer and cathodes can be engineered into the periodically grating pattern.

The emerging theoretical studies have been conducted to investigate the excited SPPs in the silicon (e.g., amorphous silicon) and organic material (e.g., P3HT:PCBM, etc.) based solar cells. Through modifying the geometrical parameters of grating into nanowall grating, the ultra-small period and ultra-high aspect-ratio will enable to excite the enriched optical modes and lead to hot spots in-between the neighboring nanowalls and the surface plasmon at the corners of nanowall. The numerical results reveal that the optical absorption of active layer can be enhanced significantly over a broadband region. The geometrical parameters of the grating such as the period, depth, and dimension can be modulated to match the spectra of sunlight and result in a considerable enhancement of active layer absorption. The fundamental mechanisms of the attained photocurrent enhancement are generally attributed to the improved near-field intensity due to the excitation of SPPs mode. Sha and co-workers theoretically studied the angular response of OSCs with periodic Au back strip. A wide-angle absorption enhancement can be achieved which outperforms the Lambert’s cosine law over the wide incident angle, while the absorptivity of the reference cell without Au strip is below the absorptivity of the cosine law. The reasons are attributed to the Wood’s anomalies and surface plasmon resonances. In the subsequent work, Sha et al. systematically studied the underlying mechanisms of the optically enhanced absorption induced by the metal grating. They unveiled the existence of plasmonic band gap in metal grating structure that would induce a large group velocity at the plasmonic band edge. As shown in Figure 11b, there are three peaks in metal absorption spectra, and the corresponding near-field distribution clearly shows the bounded near field along the metal strip (Figure 11i–iii). Interestingly, the phase distribution of peak 2 indicates the standing wave characteristic of the plasmonic bandgap (Figure 11c), and peaks 1 and 3 are the plasmonic band edges, which are due to the coupling of the forward and backward evanescent waves. The periodically modulated surface significantly modified the original dispersion relation of semiinfinite plane of metal dielectric, which induces a plasmonic band gap and finally introduces

Figure 11. a) Total absorptivity versus a function of the incident angle θ under p-polarized light. The Lambert’s cosine law is defined as \( A_0 \cos(\theta) \), where \( A_0 \) is the absorptivity under normal incidence. Reproduced with permission. Copyright 2011, OSA Publishing. b) Optical absorption of the metal grating with a varied grating height thickness \( T \); i–iii) the near-field distribution corresponding to peaks 1–3, respectively. c) The phase distribution of Hz field at the plasmonic bandgap with respect to peak 2 in (b). Reproduced with permission. Copyright 2014, OSA Publishing.
the absorption enhancement at the three emerging peaks. Experimentally, Choy and co-workers have demonstrated the plasmonic bandgap of Ag grating electrode in promoting the OSC performance. They have used the PDMS mold with 750 nm periodicity to pattern the active layer. The subsequent deposition of the Ag film as the electrode replicates the 1D periodic grating structures of the active layer, which produces the plasmonic band edge modes. The plasmonic band edge modes contribute to the absorption enhancement peak at the long wavelength of 715 nm, and it together with the enhancement at the short wavelength of 400 nm by waveguide mode enhance the PCE by 19%. The 1D periodic grating has a significant enhancement under p-polarized light illumination due to the excitation of SPP modes, while the periodic structure cannot provide the additional momentum under s-polarized light illumination resulting in the weakened absorption enhancement. To overcome such drawback, the 2D grating with periodicity at two directions is proposed to achieve the polarization-insensitive enhancement. Choy and co-workers experimentally and theoretically demonstrated that the incorporations of 2D grating in OSCs outperform 1D grating incorporated OSCs due to the polarization independence of the plasmonic resonance. As shown in Figure 12a,b, the nanoimprint method is adopted to pattern the active layer into 1D and 2D grating. The AFM images clearly show the geometrical features of the 1D and 2D patterns. Chen and co-workers used a transferring process via nanosphere lithography to fabricate a simple light-harvesting system featuring 2D periodic granular-like electrode in OSCs. The combinations of the theoretical and experimental results indicate that the light trapping efficiency in patterned OSCs is enhanced due to the light scattering and surface plasmon resonance. Thus, the photocurrent of the bulk OSCs with low bandgap PTPTBT:PC70BM as active layer is increased by 20%. Heremans and co-workers demonstrated the usage of hole–mask colloidal lithography to design the nanostructured rear Ag electrode on the top of the OSC active layer. The optimized patterned rear Ag electrode with a strong light scattering can enhance the red absorption tail of the active layer. Sun and co-workers also used the holographic lithography technique to fabricate the 2D nanostructures with dual periodicities in glass substrate. The subsequently evaporated Au(15 nm)/MoO3(5 nm)/SubPc(15 nm)/C60(40 nm)/BCP(3 nm)/LiF(1 nm)/Al (80 nm) will follow the dual corrugated grating structures and achieved 31% PCE enhancement due to the SPR-induced field enhancement.

The shape of the grating can be tuned through adopting the different fabrication techniques. Schmidt-Mende and co-workers studied the ordered metal nanovoid array for confining the incident light and enhancing the absorption in an adjacent absorbing layer of organic semiconductor. The featured hexagonally packed arrays of Ag nanovoids can excite both the localized and propagating surface plasmon. Jung and co-workers proposed to use the 3D-nanopatterned PET substrate to form the microresonant cavity, and the cell efficiency of PCDTBT:PC70BM OSCs is significantly improved by 26.4% due to the enhancement of both optical light absorption and electrical carrier collection. Liu et al. demonstrated a simple rubbing hole injection layer to form surface relief grating on the active layers of OSCs. With the gratings successfully formed on the hole transport layer (PEDOT:PSS), photoactive layer (P3HT:PCBM), and cathode (Al) in sequence, the formed grating in the multilayered OSCs will increase the optical path lengths, interfacial areas between the photoactive layer and electrode, which result in both the optical and electrical improvement of the device performance with PCE up to 3.8%. Zhang and co-workers proposed a sauna-like method to fabricate the periodically textured metal electrode with a tunable height, duty cycle, periodicity, and inclination angle by adjusting the etching time of the PS microspheres. Peer and Biswas proposed to use the polymer micro-lens on the glass coupled with a photonic–plasmonic crystal at the metal cathode on the back of P3HT:PCBM-based OSCs (see Figure 12c). The light will strongly diffract into the active layer by the periodic microlenses, and the waveguide modes and plasmon modes raised by the back periodically corrugated metal cathode cooperatively enhance the long-wavelength absorption of the active layer. As shown in Figure 12d, the adoption of the
microlens combined with the photonic crystal array of the patterned Ag electrode reveal a better absorption and photocurrent than that of the OSCs with microlens only. The theoretical calculations indicated that the resultant absorption enhancement can be up to 38% corresponding to 36% photocurrent enhancement as compared to the flat cell.

Recently, the periodic nanopattern has been extended for the emerging PVSCs. Xu and co-workers proposed a molecule/polymer composite hole transport layer (HTL) with a periodic microstructure for morphology replication of a corrugated Au electrode in PVSCs, which improved the optical and electrical properties simultaneously. Optically, the structures of the periodic composite HTL with the conformal periodic Au electrode will induce the cavity effects that are the combination of the Fabry–Perot interference and surface plasmon resonance for improving the light harvesting. Electrically, the molecular packing and self-assembly of the patterned HTL will enhance the conductivity due to the elevation of hole mobility and density up to three times. The improvement of both optical and electrical properties results in the significant enhancement of the optical light absorption of perovskite materials and electrical carrier extraction, and thereby the device efficiency of up to 17% is achieved.

Besides the optical enhancement of active layer absorption induced by the patterned metal electrode, the plasmonic–electrical effect of metal grating electrode has been unveiled to electrically modulate the OSC performance. Choy and co-workers demonstrated the elimination of SCL by the incorporation of the nanopatterned Ag electrode into the inverted OSCs. The plasmonic–electrical effect of the metallic grating anode has been attributed to the redistribution of the exciton generation regions that move from region near cathode to near grating anode, which shorten the transport paths of low-mobility holes. The schematic illustration of transport paths for the electrons and holes in inverted OSCs with metallic planar and grating anode is shown in Figure 13a,b. It reported that the better balanced transport paths for charge carriers (electron and hole) would reduce the bulk recombination and hole accumulation resulting in the elimination of SCL. The inverted OSC device with structures of ITO/TiO₂ (20 nm)/active layer (220 nm P3HT:PCBM)/MoO₃ (10 nm)/Ag (with or without grating) (100 nm) were experimentally fabricated. The experimentally measured photocurrents (Jph) versus effective applied voltages (V₀ - V, V₀ is built-in potential) at different incident light intensities are shown in Figure 13c,d. When V₀ - V is less than 0.2 V (i.e., a low internal field), the approximately linear relationship between Jph and V₀ - V is mainly governed by the diffusion and drift current effects. As internal field starts to increase, a square-root dependence of Jph and V₀ - V emerges for the Ag-planar inverted OSCs as shown in Figure 13c (black line denoted by SCL region, i.e., existence of charge accumulation). When the internal field further increases (i.e., under a sufficiently large reverse

Figure 13. A schematic mechanisms of transport paths of charge carriers in inverted OSC devices. a) Inverted OSCs with a planar metallic anode, and b) inverted OSCs with a grating metallic anode. SCL characteristics for Ag-inverted OSCs measured at room temperature (T = 300 K) with photocurrents (Jph) versus effective applied voltage (V₀ - V, V₀ is the built-in potential) at different incident light intensities. Here, V_sat is the voltage that photocurrent Jph is saturated. c) Ag-planar-inverted OSCs, and d) Ag-grating-inverted OSCs. The black solid lines in (c) represent the square-root dependence of photocurrent on effective applied voltage (SCL region). Reproduced with permission. Copyright 2014, Nature Publishing Group.
bias), $J_{\text{ph}}$ become saturated and recombination does not occur (the critical effective voltage is denoted as $V_{\text{sat}}$). As shown in Figure 13d, the elimination of SCL region was conspicuously observed in inverted OSCs with Ag grating anode. Differently, regarding the normal OSCs device with structure ITO/PEDOT:PSS (30 nm)/active layer (220 nm)/Ca (10 nm)/Ag (with or without grating) (100 nm), the elimination of SCL region cannot be observed even with the Ag grating electrode because of the existence of charge accumulation. The existence of SCL phenomenon in the normal OSCs device even with the Ag grating cathode (for collecting the electron not hole) was explained by severely unbalanced transport paths of the high-mobility electrons and low-mobility holes because of inversely moving the exciton generation regions from near anode (ITO) to near cathode (Ag grating).[478] Both the results of normal and inverted OSCs with metallic planar and grating electrode confirmed that the resultant SCL elimination was due to the redistribution of photogenerated excitons by the plasmonic–electrical effect of the patterned Ag electrode. An appropriate manipulation of the exciton generation region by the patterned Ag electrode and better balanced transport paths of charge carriers would be beneficial to improve the performance of OSCs.

3.2. Random Nanostructure

The designs of the back metal electrode into periodically patterns enable the electrical and optical improvement of OSC performance with the excited optical modes. However, these optical modes typically have narrow bandwidth, while the random nanostructures have the advantages of broadband optical modes due to the enriched spatial frequency in k-space.[479–481] The back metal electrode is of promising potential for improving the active layer absorption over a wide spectral region. Different from the randomly distributed metal network, Kim and co-workers demonstrated a simple and easy approach employing polystyrene nanoparticle (PS NP) to create a randomly nanostructured Ag back electrode in inverted OSCs.[482] The nanopattern of the back electrode is produced through transferring the surface pattern of the PS NP (60 nm) blended PEDOT:PSS (50 nm) anode buffer layer. The randomly nanopatterned Ag back electrode allows the efficient light trapping resulting in enhancing the PCE to 5.7% with 18% improvement for P3HT:OXCBA-based OSCs. Teng and co-workers proposed a nanostructured back electrode through blending propylene glycol monomethyl ether acetate (PGMEA) into the P3HT:PC71BM solution, which induces the P3HT aggregation and gives rise to the micro-nanostructured morphology on the surface of the active layer, and the sequentially deposited Al electrode will follow the micro-nanopattern.[483] The schematic illustrations of the device configuration are shown in Figure 14a,b, and the active layer aggregation introduces a large surface roughness. The root mean standard (RMS) is 0.919 nm for the active layer without blending PGMEA, while the RMS increases to 3.78 nm after blending PGMEA. The following deposition of Al as back electrode will replicate the surface pattern and form a random patterned Al electrode, which will enhance the light diffraction and improve the light propagation path length. The $J$–$V$ characteristics and EQE spectra for the OSCs with planar and randomly patterned electrode are shown in Figure 14c,d. The patterned OSCs will lead to an increase in the $J_{\text{SC}}$ and FF resulting in the improvement of PCE up to 17.9% as compared to the planar device. The in-depth reasons are due to the enhanced scattering effect and carrier mobility. The improved charge carrier collection efficiency is attributed to the shortened carrier transfer path and enlarged interfacial area of the micropatterned active layer and electrode interface.

Loo and co-workers systematically exploited the wrinkles and deep folds that form on the polymer surfaces on the device performance.[484] Through modulating the compressive stress on the active layer, the wrinkle will be changed to the deep folds by means of self-contact of neighboring wrinkles. The $J$–$V$ characteristics of the constructed flat, wrinkled, and composite surfaces of wrinkles and deep folds are shown in Figure 15a. The insets are the schematic device structure and the active layer surface with the wrinkles and deep folds, and the folds are generated by neighboring wrinkles. The wrinkles and deep folds of the active layer will induce a patterned electrode and improve the electrical properties. The introduction of the wrinkles significantly improves the $J_{\text{SC}}$, and the formation of deep folds further increases the $J_{\text{SC}}$, The EQE and optical absorption spectrum of the P3HT:PCBM active layer are shown in Figure 15b,c. The OSC device with the composite surface shows substantial improvement in light harvesting in the near-infrared region. The EQE increases by more than 600% at a wavelength of 650 nm as compared to the flat device. Meanwhile, the range of solar energy conversion is extended by more than 200 nm, which results in the increment of the photocurrent by 47%. Differently, Tang and co-workers reported textured surface, i.e., the deterministic aperiodic nanostructure (DAN) into single junction OSCs by the nanoimprinting method.[485] The incorporation of the DAN patterns in OSCs will contribute to the broadband self-enhanced light absorption and optimum charge carrier extraction. The DAN-incorporated OSCs are schematically shown in Figure 15d, and the AFM image of the rear Al electrode (Figure 15e) reveals an aperiodic feature. The in-depth reason of the enhanced performance is attributed to the collective excitation and hybridization of several factors including the pattern-induced antireflection, light scattering, and surface plasmon resonance, together with a minimized recombination. The collective effect delivered a broadband enhancement in EQE spectra as shown in Figure 15f. As a consequence, it finally increases the photocurrent by 18% resulting in a PCE >10% for PTB7-Th:PC71BM-based OSCs.

3.3. Quasiperiodic Nanostructure

The random pattern of the metal back electrode merits the broadband optical modes. Differently, the periodic counterpart reveals a distinct resonant feature at a specific wavelength. The quasiperiodic nanostructure inherits the characteristics of both random and periodic patterns, which not only delivers a broadband optical resonance but also promotes the light–matter interactions via the optical modes at a specific wavelength. It is very promising for the potential photovoltaic applications.
The quasiperiodic metal nanostructure combines plasmonic elements of different sizes and topologies, which can enhance the system’s Q factor and offers a confined mode over a wide bandwidth. One example is the quasiperiodic structure in which each strip is composed of metal nanoparticles. In another work, Choy and co-workers have demonstrated a macroscopically periodic (macroperiodic) and microscopically random (microrandom) structure, which has a broadband resonance due to the interactions of the localized, propagating modes and the hybridization of the local and propagating modes. With strategically preformed metal nanoseeds, the tunable macroscopically periodic pattern composed of microscopically random nanoplate-based Ag structures (see Figure 16c) is fabricated chemically through photon-driven growth using simple light source with low photon energy and low optical power density. The SEM images of the random, periodic, and macroperiodic and microrandom (quasiperiodic) structures are shown in Figure 16a,c,e, and the SEM images unambiguously show the geometrical differences. The Fourier transform of the SEM images indicates the distinction of the k-space for random, periodic, and quasiperiodic structures. As shown in Figure 16b,d, the k-space of the random structure reveals a uniform pattern, while several bright spots appeared for the periodic structure because of the interaction of the plasmon-Floquet modes, which resemble the reciprocal space for perfectly periodic structure. Differently, the k-space image of the macroperiodic and microrandom patterns (Figure 16f) is contributed by the superposition of the k-space image of both the perfectly periodic pattern and the completely random pattern. The enriched optical modes of the quasiperiodic structure will induce a highly concentrated near field. With the numerical simulations of the perfect and quasiperiodic structures, the distributions of electric field in the quasiperiodic structure are plotted in Figure 16g,h. The macroperiodic and microrandom structure exhibited more hot spots with higher field intensity as compared to that of perfect periodic structure. Finally, the extinction spectra of the quasiperiodic structure reveal a broadband feature for both transverse electric (TE)- and transverse magnetic (TM)-polarized waves, and the TM wave preserved the feature of the grating diffraction effect (Figure 16i).

Regarding the advantages of the quasiperiodic structures, Ostfeld and Pacifici reported the usage of the periodic and...
quasiperiodic hole arrays of the Ag film for improving the light absorption of an organic active layer. The periodic (square, triangular lattice) and quasiperiodic (Penrose, dodeca-grid, and heptadeca-grid) structures are fabricated by the focused ion beam milling method, and the corresponding SEM images are shown in Figure 17a–f. For the periodic structure, the 2D discrete Fourier transform spectra reveal a clearly reciprocal lattice with square and triangular feature (see the inset of Figure 17a,b). The Fourier spectrum of the random structure is uniform in the k-space. Interestingly, the Fourier spectra of the quasiperiodic structures with Penrose and dodeca-grid and heptadeca-grid patterns are highly relative to their geometrical periodicities, and a diffraction ring pattern is achieved in the Fourier spectrum of heptadeca-grid structure, which indicates the properties of the omnidirectional and polarization insensitivity. After spin coating P3HT:PCBM on the Ag film, the back Ag hole array of the periodic and quasiperiodic structures reveals an enhanced absorptance (defined as 1-reflectance). Figure 17g,h further verifies that the heptadeca-grid-based quasiperiodic structures reveal a spectrally broad, omnidirectional, polarization-insensitive absorption enhancement. Due to the enriched optical modes, the quasiperiodic structure with heptadeca grid is much more suitable for photovoltaic applications as compared to the reference cell with back flat and periodic Ag film.

Dostalek and co-workers proposed a multidiffractive plasmonic structure with multiple superimposed periodical modulations for coupling light into surface plasmon. The structure combines the advantages of the regular periodic and random structures. As shown in Figure 18a, the subsequently coated Al and thin P3HT:PCBM layers will follow the nanopattern of the UV-curable polymer. The AFM image in Figure 18b reveals the multidiffractive features. The spectral reflectivity of the patterned active layer will be significantly reduced under both TM
and TE waves (Figure 18c). Finally, the absorption of the active layer in spectra of 600–750 nm is enhanced by a factor of 2.9.

3.4. Bioinspired/Prewritten Nanostructure

Besides the periodic, random, and quasiperiodic structures that fabricated in laboratory, there are some patterns that are inspired in the nature or prewritten structures. The moth-eye structures are widely adopted in OSCs due to its easy process for nanoimprinting and enriched optical modes for light absorption improvement. Yu and co-workers proposed the biomimetic moth-eye nanoarchitecture in OSCs.[490] The 2D hexagonal periodic grating array on surface of both ZnO and active layer P3HT:ICBA, prepared by the soft imprint nano-patterning techniques, is shown in Figure 19a. The cross-sectional SEM image of OSC with dual patterns is shown in Figure 19b, and the patterns are incorporated into ZnO (period = 380 nm) and active layer (period = 650 nm), respectively. The Ag electrode replicates the periodic pattern of the active layer and then improves the light harvesting due to the prolonged light path brought by strong light scattering and plasmonic resonance. The $J_{SC}$ of the patterned device is increased from 10.9 to 13.31 mA cm$^{-2}$ corresponding to the PCE from 5.12% to 6.28% with 22.2% improvement. The angular dependence is also improved as compared to the control device when the incident angle is between 20° and 70°. Zhu and co-workers also reported the 2D moth-eye nanostructure in PTB7:PC$_{70}$BM based on OSC.[491] They also adopted the 3D simulation of the 2D rectangular grating of the P3HT:PCBM to theoretically study the moth-eye structure for optically improving carrier generation of $J_{SC}$ and electrically enhancing carrier extraction of FF.[492]

Tang and co-workers reported the usage of the biomimetic moth-eye structure in quasiperiodic gradient shaped active layer and an antireflective coating.[493] The fabrication procedure of patterned OSCs is depicted in Figure 19c; the first process is the transfer of the biomimetic moth-eye nanoarchitecture to the ZnO surface, and the perfluoropolyethers (PFPE) positive and negative molds are used in the soft nanoimprinting method for patterning ZnO. After the pillowing off PFPE mold in the second step, the spin-coated active layer of P3HT:ICBA replicates and follows the biomimetic eye pattern of ZnO. The third step is the deposition of the metal electrode with the thermally evaporation, in which the electrode also reveals eye structures. The last step is the incorporation of antireflective coating with biomimetic eye structure on glass substrate. The significant improvement of the $J$–$V$ characteristic can be observed as shown in Figure 19d; the incorporation of biomimetic eye structure in the active layer (Bio-AL) increases the $J_{SC}$ from 12.20 to 14.61 mA cm$^{-2}$ with 19.75% enhancement; and the integration of the antireflective
coating (AR) further pushes the $J_{SC}$ to 15.16 mA cm$^{-2}$. As a result, the PCE of 7.86% is achieved for P3HT:ICBA-based OSCs with 22.2% improvement. As shown in Figure 19e, the EQE spectra indicate that the broadband enhancement is achieved by the incorporated biomimetic eye structure. The substantial improvement is attributed to the broadband polarization-insensitive light trapping of biomimetic nanostructured active layer, and the reduction in surface reflection.

Figure 17. SEM images of periodic structure with a) square, b) triangle lattice and quasiperiodic structure with c) Penrose, d) dodeca-grid lattice, e) heptadeca-grid lattice, and f) random Ag hole array. The insets show the 2D discrete Fourier transform power spectra for each array, and the inset in left of (b) shows the P3HT:PCBM coated on triangular hole array. g) Absorptance spectra for P3HT:PCBM films spin cast on unpatterned and patterned Ag hole arrays. h) Absorption enhancement of P3HT:PCBM films on various patterns, normalized to the spectra of equally thick films on unpatterned Ag film. Reproduced with permission.[488] Copyright 2011, AIP Publishing.

Figure 18. The multidiffractive grating with Al and active layer P3HT:PCBM. a) Geometrical illustration and b) the corresponding AFM image; the inset is the height profile and the location is indicated by the white dash line in (b). c) The reflectivity of Al/active layer with/without the corrugated multidiffractive grating under TE and TM waves. Reproduced with permission.[489] Copyright 2016, John Wiley & Sons, Inc.
by antireflective coating and surface plasmon effect by the corrugated back metal electrode. In the subsequent work, they have incorporated the biomimetic moth-eye structure and antireflection layer in the PTB7:PC71BM system, and achieved the PCE of 9.33%.[494] Recently, Tang and co-workers further reported the incorporation of the bioinspired moth nanostructure into back electrode in the PVSCs. The corrugated back electrode with bioinspired pattern induces a broadband polarization-insensitive light scattering and surface plasmonic resonance, which outperform the control flat cell even in the periodic grating back electrode. Finally, the adopted moth-eye-patterned back electrode has improved the PCE of CH$_3$NH$_3$PbI$_3$–Cl$_x$-based PVSCs from 14.27% (control flat) and 15.46% (grating electrode) to 16.31% without sacrificing the electrical properties.

The predesigned, subwavelength nanostructures typically need the expensive fabrication process, while the prewritten pattern, e.g., blue-ray movie discs, can lower the expensive fabrication processes. Huang and co-workers demonstrated the blue-ray movie discs as extremely low-cost nanoimprinting templates for creating photon management nanostructures in thin-film solar cells.[496] The process for delaminating a blue disk (BD) and casting a PDMS mold on the exposed recording layer is shown in Figure 20a, and then the fabricated mold can be used as prewritten for patterning the active layer. The Fourier transform of the AFM image of mold with blue-ray pattern (Figure 20b) revealed a circular feature, in which two hot spots are still expected at the value of $|k_y|$. The optimized Fourier space indicated that the enriched optical mode existed in blue-ray patterns. The AFM image of the active layer with and without the blue-ray pattern is shown in Figure 20c, and the replication of the blue-ray pattern on the active layer has been realized. The deposited carrier transport layer and metal electrode will follow the pattern of active layer. The EQE spectra of the devices without and with pattern, and EQE enhancement ratio obtained by dividing the spectra of the patterned devices by that of the flat device. “F” denotes the Flat cell and “B” denotes the cell with biomimetic moth eye pattern. “A” denotes the cell with antireflection layer. Reproduced with permission.[493] Copyright 2014, John Wiley & Sons, Inc.
3.5. Stability of Back Metal Electrode in Perovskite Solar Cells

Regarding the application of back metal electrode in PVSCs, the selection of metal material will rely on the work-function alignment of the device and materials cost, on the one hand. The work function of the metal electrode plays an important role in determining the charge carrier extraction and the build-in field for achieving high PCE. On the other hand, the stability of back metal electrode on the device should be taken into account, due to the possible diffusion of halide from perovskite film to the metal surface, which will induce the corrosion to the metal electrode. From the aspect of device stability, Au is regarded as the most promising material for PVSCs, which is also normally adopted for the fabrication of highly stable solar cells. Ni, with relatively low price and high stability, could be a good candidate to replace Au for the fabrication of back electrode of PVSCs. Due to the relatively low work function and the low reflection to visible light, the PCE of PVSC is slightly lower than the device with Au anode. Ag and Al are also adopted as the back electrode, which however have the concern of corrosion by the halides as aforementioned. Strategies of inserting an electrical conductive barrier between the electrode and perovskite film to inhibit the diffusion of halides from the perovskite film to electrode as well as the diffusion of metal atom to the perovskite film may address the stability issue of both the back metal electrode and perovskite materials. Recently, Huang and co-workers demonstrated the interesting result that Cu could be a better selection for the back electrode of PVSC than Ag, Al, Cr, or Au, contributed by its corrosion resistance to the nonoxidizing acids (e.g., HI, HBr) and halogens. The PVSC using a Cu back electrode without encapsulation still has 98% of the initial efficiency after 816 h storage in an ambient environment. In addition, metal foils, such as titanium and copper foil, have also been adopted as the bottom electrode for PVSC with the combination of transparent top electrode.

4. Conclusion

We have reviewed the most recent works of the emerging novel metal electrodes from the fabrication to their application as front and back electrodes of organic and perovskite solar cells. The strategies of fabricating the metal-based transparent electrode, including metal NW network, metal mesh, and ultrathin metal film, with simultaneously high optical transparency and good electrical conductivity are summarized, which are the basic requirements for the application in photovoltaic devices. We have pointed out the technical issues existed in...
their application in photovoltaic devices and listed the strategies to overcome these issues for achieving high-performed metal transparent electrode in both OSCs and PVSCs. The manipulation of light in solar cells with the ultrathin metal film based transparent electrode is also discussed. In addition, we have unveiled the fundamental differences in the geometrical and spatial properties for periodic, random, quasiperiodic, and bioinspired/prewritten nanostructured back metal electrodes. The applications of these nanostructures in solar cells for improving the light absorption are also discussed.

However, the study of long-term stability of photovoltaic device based on metal electrode under work condition still needs more attention. The degeneration of metal electrodes in a photovoltaic device under light illumination and electrical bias could be more serious than the situation of their barely storage in ambient environment. Especially for the case of PVSCs, the metal bottom electrodes will affect the formation of the perovskite film and their stability will affect the PVSC performance. In addition, the unstable perovskite film will also affect the stability performance of the metal electrode, and the situation could be even worse for the device under work condition. The stability of PVSCs based on the metal bottom or top electrode could be a synergetic result from both the metal electrode and the perovskite film, as well as the design on the whole device. Meanwhile, the exploration of the well-defined nanopattern of metal electrode that can inherit both the periodic and random properties but with a low-cost and the simple fabrication process are of great importance for the future photovoltaic application. The effort on light management through the designs of front and back electrodes should be constantly devoted for boosting the efficiency of photovoltaic device, especially the emerging perovskite solar cells.

Acknowledgements
H.L. and X.R. contributed equally to this work. This work was supported by the University Grant Council of the University of Hong Kong (Grant Nos. 201611159194, 201511159225, and Platform Technology Funding2016-17), the General Research Fund (Grant Nos. 711813 and 17211916), the Collaborative Research Fund (Grant Nos. C7045-14E) from the Research Grants Council of Hong Kong Special Administrative Region, China, and Grant CAS14601 from CAS-Croucher Funding Scheme for Joint Laboratories. This work was also supported by the National Natural Science Foundation of China (Grant Nos. 11704293 and 61701003) and Hubei Provincial Natural Science Foundation of China (Grant No. 2017CFB286).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
electrical conductivity, light trapping, metal electrodes, patterned back electrodes, transparent front electrodes

Received: September 11, 2017
Revised: November 24, 2017
Published online: