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Multifunctional graphene and carbon nanotube films for planar heterojunction solar cells

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ABSTRACT

Graphene and carbon nanotubes, featured with outstanding electronic, photonic and mechanical properties as well as Earth abundancy, are perfect for use as carrier-selective transport and collecting layers in photovoltaics. In recent years, graphene and carbon nanotube films have underpinned significant advancement in the planar heterojunction (PHJ) solar cells, with reduced fabrication cost, improved power conversion efficiencies approaching 20%, and the great potential for scalable deployment. Here we discuss the state-of-art progress in graphene-based and carbon nanotube-based PHJ solar cells leveraging advanced nanocarbon technologies as well as industrial-compatible solar cell design and processing. Fabrication and functionalization strategies of graphene and carbon nanotube films for electronic and photonic optimization of PHJ solar cells are systematically reviewed. We also envision technological pathways and future prospects to exploit multifunctionality of graphene and carbon nanotubes to realize ubiquitous application of high-performance, flexible PHJ solar cells.

1. Introduction

Solar cells can directly convert solar energy to electric power without carbon footprint, and thus are promising to meet world energy consumption demands and fulfil low carbon scenario in future. As shown in Fig. 1, a typical planar heterojunction (PHJ) solar cell has three main components: a top electrode layer (or emitter) to create built-in potential for separating electron-hole pairs and selectively transporting electrons/holes, a photoactive layer to absorb solar energy and generate electron-hole pairs, as well as a bottom electrode layer (or base) to collect holes/electrons. The valence-band electrons in the photoactive material are excited by absorbing photons with energy greater than the bandgap energy, generating electron-hole pairs. The electric field at the junction between top electrode and photoactive layer separates the electron-hole pairs; the holes are then collected by the top electrode once they drift to the junction. The circuit completes once the holes pass through the load and meet up the electrons in the photoactive layer. Compared with p–n homojunction solar cells, PHJ solar cells have a simpler structure and do not require high-temperature dopant diffusion processes, which allows compatible and scalable manufacturing and reduces fabrication cost up to 30% [1–3]. The PHJ structure holds the promise to further improve PCE and decrease fabrication cost, thereby paving the way of realizing scale-up deployment of photovoltaics as a renewable source of electricity.

Currently, the most commercially competitive photoactive materials for PHJ solar cells include crystalline silicon (c-Si), cadmium telluride (CdTe), copper indium gallium selenide (CIGS) and perovskite materials. The highest power conversion efficiency (PCE) values achieved for c-Si, CdTe and CIGS solar cells so far are 26.3%, 22.1% and 21.7% [4], respectively, approaching the theoretical Shockley–Queisser thermodynamic limit. In recent years, the PCE of lead halide perovskite solar cells (PSCs) has increased from 3.8% [5] to 22.1% [6] since its first embodiment in 2009. It is worth mentioning that, although the absolute value of PCE is the most sought-after and eye-catching property of a solar cell in laboratory, it is only part of the big picture for industrial-scale application which incorporates stability, scalability, uncertainty, risk, cost and life cycle.

Photovoltaics are expected to be market-competitive and ready for subsidy-free utility-scale adoption at module costs of US$0.50–0.75 W^{-1}, which results in a levelized cost of electricity (LCOE) of US$0.06/kWh, comparable to the current fossil fuel-based electrical

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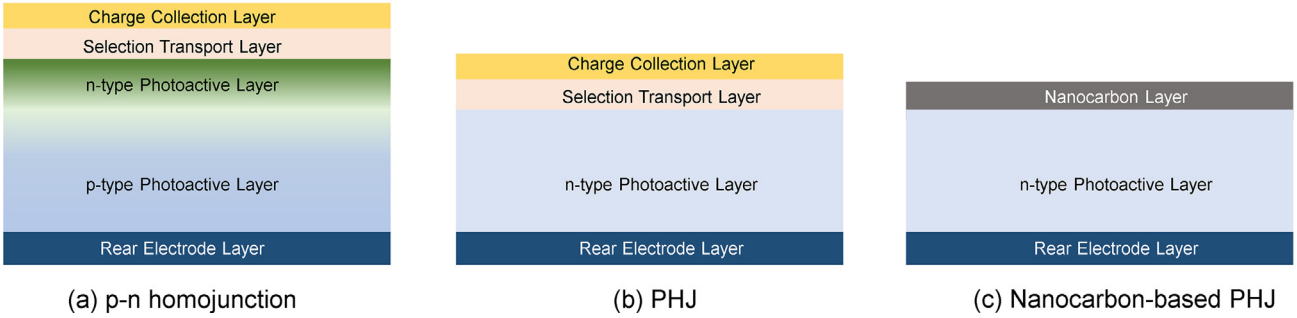

Fig. 1. Schematics of (a) p–n homojunction, (b) PHJ and (c) nanocarbon-based PHJ solar cells.

utility plants. With 75 GW installation in 2016, c-Si is dominating the solar-cell market, taking up to 93% of market share [7]. Currently, the estimated manufacturing cost of c-Si PV is US$1.29 W^{-1}, which is approaching the target but still has space for further cost reduction. Other inorganic photoactive materials such as CdTe and CIGS utilize less photoactive semiconductor material per watt than c-Si, however, both are expensive and contain rare-earth materials, and have issues in toxicity. Organic-inorganic hybrid perovskite materials have low formation energies for deposition and are compatible with low-cost, scalable manufacturing techniques such as roll-to-roll printing, spray coating, inkjet printing, *etc*. However, the low PCE stability (<1000 h), toxicity (contains lead) and high material cost are intrinsically limiting future prospect of PSCs, requiring magnificent amount of investment in laboratory-scale research as well as decades of learning curve in industry-scale installation and deployment. Therefore, c-Si and GaAs, which have been through the process of perfection in material quality and maturation in production line [8], have the highest technology readiness level, with superiorities over perovskite materials in terms of long-term durability, low toxicity, abundant raw material supply and manufacturability for cells and modules.

The current module cost of c-Si could be further reduced by improving the photoactive material feedstock utilization and using cost-effective and eco-friendly top electrode materials, which accounts for *ca*. 60% of the total module cost [2]. In a PHJ solar cell, the top electrode layer is required to have high electrical conductivity and optical transparency simultaneously, with appropriate electronic band structure and Fermi level position matching the used photoactive layer. These requirements are usually realized by a double-layer design comprising of a transparent conductive film (TCF) and a selective hole/electron transport layer, as shown in Fig. 1b. The conventional materials for TCFs are noble metal grids (such as silver and gold) and rare-earth metal oxides (such as indium-doped tin oxide, ITO). However, the elemental scarcity and high cost potentially prevent their use at scale. For the selective hole/electron transport layer, the commonly used materials are conductive organic materials such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and lithium bis(trifluoromethylsulphonyl)imide-doped 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD:LiTFSI). PEDOT:PSS and spiro-OMeTAD:LiTFSI are inhomogeneous dispersions which suffer from instability and degradation of electrical conductivity [9]. Additionally, PEDOT:PSS is highly acidic (pH~1) which may corrode ITO and other components in PHJ solar cells. Therefore, it is highly desirable to develop new materials for the top electrode layers of the PHJ solar cells.

Graphene and single-walled carbon nanotubes (SWNTs) are atomic-thin sp^2 hybridized nanocarbon materials. The strong covalent π bonds in graphene and SWNTs enable ballistic electron and phonon transport, excellent mechanical strength and flexibility, as well as good chemical inertness and stability. The excellent physical properties of graphene and carbon nanotubes makes them fundamentally suitable for PHJ solar cells. As shown in Fig. 1c, a prototype nanocarbon-based PHJ solar cell is constructed by a photoactive layer sandwiched by a thin nanocarbon film as emitter and a rear metal electrode. The nanocarbon film serves as both the transparent conductive layer and the hole collecting layer, which could effectively simplify the PHJ structure. The Fermi level of the nanocarbon film could be shifted through doping, even for metallic SWNTs and graphene which behaves metallic. Therefore, the quantum nature of the nanocarbon materials determines that the nanocarbon-Si junction is a planar heterojunction (PHJ) rather than a Schottky-barrier junction (*i.e.* metal-semiconductor junction). The strongest advantage of a PHJ over a *p*–*n* homojunction is the minimized charge carrier recombination loss at the surfaces of Si wafer, which is embodied by recent record efficiencies of 25.1% [3] and 26.3% [8] for c-Si PHJ solar cells.

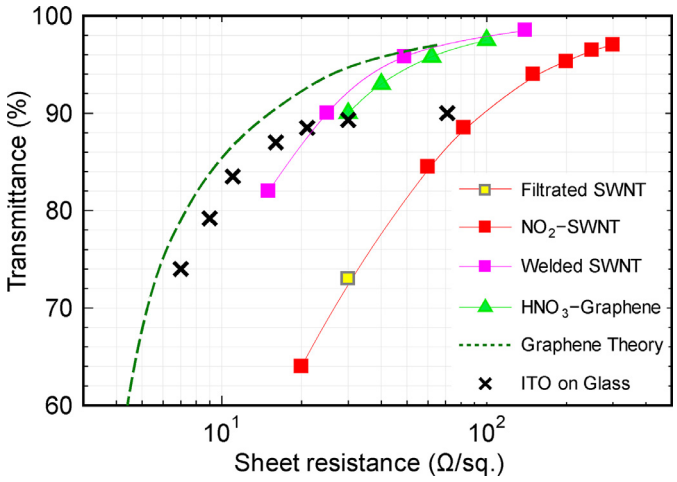

Fig. 2. Comparison of optoelectronic property (sheet resistance versus optical transparency) of different transparent electrode materials based on: HNO_3-doped filtrated SWNT [17], NO_2-doped SWNT film [18], welded SWNT film with HNO_3 doping [11], HNO_3-doped graphene (theoretical and experimental values) [19] and ITO on glass substrate [20].

Graphene and CNT films offer excellent optoelectronic properties for applications in PHJ solar cells. As shown in Fig. 2, using advanced synthesis method [10,11] and appropriate chemical functionalization, SWNT and graphene films are very conductive especially at transparency (optical transmission at 550 nm wavelength) higher than 90%, which is difficult to achieve for metal-oxide based electrode materials. Moreover, the mechanical flexure and strong light-matter interaction of nanocarbon materials could be utilized to fabricate flexible thin-film PHJ solar cells. CNTs and graphene can have Young's modulus and tensile strength as high