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Review

Graphene and its derivatives for solar cells application

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ABSTRACT

Graphene has played the role of game-changer for conductive transparent devices indebted to its unique two dimensional (2D) structures and gained an exceptional opportunity to be employed in energy industry. In the past two decades graphene has been merged with the concept of photovoltaic (PV) material and exhibited a significant role as a transparent electrode, hole/electron transport material and interfacial buffer layer in solar cell devices. This review covers the different methods of graphene fabrication and broadly discusses the recent advances in graphene-based solar cells, including bulk heterojunction (BHJ) organic, dye-sensitized and perovskite solar cell deices. The power conversion efficiency surpassed 20.3% for graphene-based perovskite solar cells and hit the efficiency of 10% for BHJ organic solar cells. Except the part of charge extracting and transport to the electrodes, graphene has another unique role of device protection against environmental degradation via its packed 2D network structure and provides long-term environmental stability for PV devices. We highlighted a comparative study on the role of graphene and its derivatives in photovoltaic devices. After all, the potential issues and the perspective for future research in graphene-based materials for PV applications are presented.

1. Introduction

For decades, emerge of new devices and technologies to generate, store and effectively utilize solar energy has been an encouragement to explore new ways for production of clean energy. Sun is a rich, safe, cheap and clean source of energy that can be directly converted to electricity without producing pollution and environmental problems. Photovoltaic materials and devices facilitate the conversion of sunlight to electricity through photoelectric effect. According to European Photovoltaic Industry Association (EPIA) till now over 50% of countries use solar power and totally 420 GW of photovoltaic systems have been installed in 2017, which is capable of producing 160 TW h per year of electricity [1].

Owing to unique optical and electrical properties graphene is a highly considerable material for industrial applications and basic studies. Graphene-based materials have been widely investigated in photovoltaic (PV) technology due to properties such as high optical transparency, high carrier mobility, zero-band gap and high mechanical strength. Graphene oxide (GO, an oxidized single or multi-layered graphene) and reduced graphene oxide (rGO) are practically the most studied graphene derivatives. The nature of oxidation process leaves different types of functional groups such as hydroxyl, epoxy/ether, and carbonyl and carboxylic acid in GO, which provide hydrophilic characteristic to GO and rGO that facilitate their stability in protic and polar solvents, resulting in simple fabrication of graphene-based structures. Furthermore, the oxygen moieties bring further functionalization possibility on GO with other materials such as organic, inorganic and small molecules to fabricate novel and new compositions. Despite the outstanding properties of the graphene, its application divides into different categories in PV devices depending on its optical response. For example, In the case of graphene sheets (GSs) no detectable photoluminescence (PL) occurs and it is inattentive to applied conditions. By contrast, zero dimensional (0D) graphene quantum dots (GQDs) are fluorescent nanomaterial with extraordinary properties due to their remarkable quantum confinement and edge effects (energy traps) which can play an important role in the PL of GQDs. Research on graphene-based devices has an impressive growth with outstanding rate and it is crucial to compile the innovative contribution of graphene-based materials in photovoltaic devices as one of the top emerging technologies.

Herein, firstly we describe the fabrication techniques of graphene-based materials, pointing at the benefits and drawbacks of the methods in terms of availability, scalability, crystal structures, and intrinsic properties. Then the advances of graphene-based materials in PV devices such as organic Solar cells (OSCs), dye-sensitized solar cells (DSSCs), perovskite solar cells (PSCs) are systematically reviewed with their working principles, cell configuration and current issues of each energy device. Furthermore, the PV devices performances are examined

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by introducing graphene and its derivatives as electrodes, active layers and transport layers. [2,3] The relationship between the graphene-based nanostructure and the resulted devices performance is described through representing the references by focusing on new developments in which the results compete with commercially existing materials. The essential roles of graphene-based materials in PV devices are highlighted by reviewing the most compelling results. At the end, the current issues and possible directions for further research work on graphene-based materials in energy conversion applications are provided.

2. Properties and synthesis methods of graphene

A graphene sheet has ~ 0.34 nm thickness and its size varies from several nanometers to centimeters depending of synthesis method. Graphene is the base building block for all graphite derivatives such as fullerene [4], graphene quantum dots [5], carbon nanotubes [6], graphene nano ribbons [7], etc. In graphene, carbon atoms are covalently bonded to each other by three sigma bond and one π-bond. The out-of-plane π-bond is responsible for delocalized electrons and the conductivity of graphene. Graphene has two different architectures on its edges, i.e. zigzag and armchair, which basically co-exist in majority of graphene materials [8,9]. The types of edge have different stability, electronic structure and properties that can be suitable for different applications. Among all the properties of graphene, its electronic property is the most important. Electrical property comes from π-π connections of carbon atoms where the conduction band (π* band) and valance band (π band) meet at six Dirac point, which due to the symmetry only two of them are distinct (K and K'), and the other four are equivalent to them (Fig. 1). It makes the graphene a rare semi-metallic, zero band gap semiconductor material in which the charge carriers exhibit a linear electronic dispersion in the vicinity of the Fermi energy (Dirac point) [9,10]. Charge carriers in graphene are confined to a layer which is only one atom thick and exhibit very high velocities at high fields (4×10^7 cm/s) and very high mobility (120,000 cm^2/Vs) at 240 K, which is the highest ever reported for any semiconductor [11]. The optical and optoelectronic properties of the graphene also attract much attention. A single layer graphene is highly transparent (97.7%) in visible region with very small reflectance (< 0.1%). However, the transparency reduces by increasing the number of the layers. Graphene also can show luminance by splitting to ribbons and quantum dots or doping with the aim of reducing the conductivity of delocalized π- π linkages [12–14]. Optical response of graphene nanoribbons is basically different from GQDs and is controlled by prominent excitonic states. The edge shape and its modification have huge impact on overall properties of graphene ribbons such as binding energy and their luminescence properties.[14] The π-network in graphene also causes thermal conductivity and mechanical strength. The thermal conductivity of the graphene is reported to be $5x10^3$ W/mK, which is higher than diamond and graphite and its young's modulus and intrinsic strength reach up to 1.0 TPa and 130 Gpa, respectively [15,16]. Packed C = C bond network of graphene shows a high resistance to gas permeation and it also has high flexibility and ultra-large specific surface area. The graphene synthesis is based on two general methodologies, i.e. bottom-up and top-down approaches, as shown in Fig. 2. In the top-down method, starting material is graphite and the aim is to intercalate and exfoliate it to graphene sheets through solid state, liquid state or electrochemical exfoliations. Another approach in this category is to exfoliate graphite oxide to graphene oxide (GO) followed by chemical or thermal reduction [17–19]. The bottom-up method is based on making graphene from molecular precursors building blocks by chemical vapor deposition (CVD) or epitaxial growth [18,20,21]. The structure, morphology and properties of the resulted graphene such as number of layers, defect level, electrical and thermal conductivity, solubility and hydrophilic or hydrophobicity depend on the fabrication method.

The direct reduction of the GO has attracted the most attention to produce large quantity graphene by removing all the oxygenated functionality and restoring the π-network. However, the different nature of the functional groups requires both endothermic and exothermic processes which necessitate reduction steps (2 steps or more) [22–25]. Reduction of the epoxide groups of the GO can be conducted by using hydrazine as a reduction agent, but the dehydroxylation and decarboxylation need heat treatment (as an endothermic reaction). Hydrazine de-epoxidation and thermal dehydroxylation have opposite reactions towards heat and thermal treatments. In both processes, the oxygen functionalities attached to the interior of an aromatic domain in GO are removed more easily, both kinetically and thermodynamically (Fig. 3) [25,26] The reduced GO (rGO) and technically is a converted, modified derivative of graphene. rGO is more similar to graphene in physical properties and structure. The degree of π-network restoration mostly depends on the reduction efficiency, which results in graphene with different properties.

CVD method has been developed to produce large area graphene sheets [27]. This technique is based on the pyrolysis of the hydrocarbon precursors on the surface of the transition metal catalyst. In the CVD process, the quality of the graphene (such as layer number, grain size, band gap and doping effect) is manly affected by process parameters such as gas flow, catalyst, precursor, temperature, growth time and gas pressure. The CVD graphene growth based on a heterogeneous catalytic process is carried out in two steps: i) the pyrolysis of the gas precursor to form carbon and ii) the formation of the carbon structure of graphene using the segregated carbon onto the surface of metal catalyst (Fig. 4) [28]. In the first step, the pyrolysis to disassociate carbon atoms must be carried out on the surface of metallic catalysis which absorbs the carbon atoms and prevents the precipitation of carbon clusters. All the steps of decomposition, diffusion and segregation of carbon atoms requires extreme levels of heat (over 2500 °C without a catalyst), and these metal catalysts must be used to reduce the reaction temperature

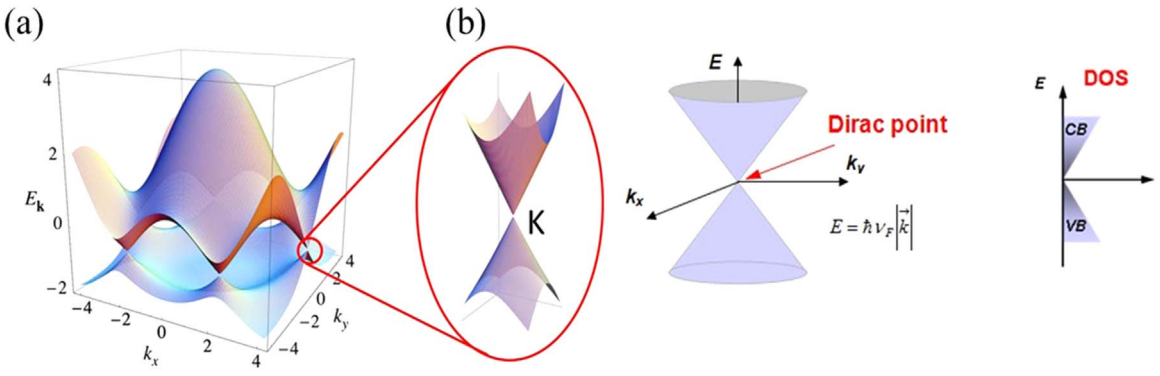

Fig. 1. a) Electronic dispersion in the honeycomb, and b) Lattice structure of graphene, made out of two interpenetrating triangular lattices. The Dirac cones are located at the K and K′ points, reprinted from Ref. [167] with permission from American Physical Society.