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Review

Graphene for energy harvesting/storage devices and printed electronics

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ABSTRACT

Graphene-based materials are intriguing from the perspective of fundamental science and technology because they are non-toxic, chemically and thermally tolerant, and mechanically robust. Graphene exhibits superior electrical conductivity, high surface area and a broad electrochemical window that may be particularly advantageous for their applications in energy storage devices. In addition, graphene can be prepared in the form of a colloidal suspension with adjustable solubility and thus is suitable for printing applications and offers both transparency and good conductivity at the same time. In this review, applications of graphene in solar cells, batteries, supercapacitors and fuel cells are summarized with the latest developments. Furthermore, graphene as a conductive ink for printed electronics is also discussed.

Contents

1. Introduction

Graphene is a material which consists of a 2D layer of sp^2 hybridized carbon atoms bonded together and the shape that results from it is a “honeycomb” lattice, notable for its high regularity. It is attracting growing interest from the scientific community (Dresselhaus & Araujo, 2010) due to the recent advancements that have led to the award of the Nobel Prize in Physics in 2010 (Novoselov et al., 2004). Among the possible fields of applications, the use of graphene in energy harvesting and storage devices is particularly interesting due to the number of extremely promising and practical potential uses (Geim & Novoselov, 2007). Graphene exhibits superior electrical conductivity, a high charge carrier mobility ($20\,m^2/(V\,s)$), fascinating transport phenomena such as the quantum Hall effect, high surface areas of over $2600\,m^2/g$ and a broad electrochemical window (Dresselhaus & Araujo, 2010). These features make graphene particularly advantageous for applications in energy technologies. In addition, graphene can be transferred to substrates for transparent electronic applications allowing the fabrication of transparent or semi-transparent energy harvesting and storage devices.

Graphene can be prepared in a number of ways: (i) Mechanical exfoliation from highly oriented pyrolytic graphite (HOPG), which is also indicated as scotch tape peeling. This method is still widely used in many laboratories to obtain pristine perfectly structured graphene layers for basic scientific research and for making

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Abbreviations: CVD, chemical vapour deposition; EDLC, electrochemical double layer capacitor; FTO, fluorine tin oxide; GO, graphene oxide; HOPG, highly ordered pyrolytic graphite; ITO, indium tin oxide; PCE, power conversion efficiency.

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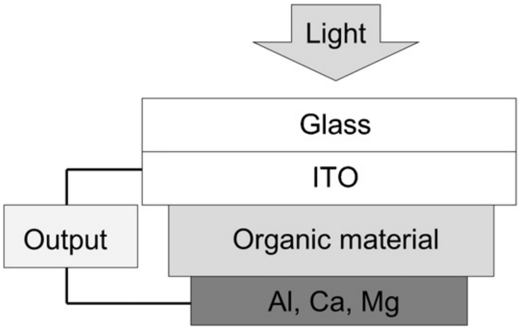

Fig. 1. Mechanism of organic photovoltaic (OPV) cell.
Adapted from Spanggaard and Krebs (2004).

proof-of-concept devices. However, it is not suitable for mass production. (ii) Thermal decomposition of SiC wafer under ultrahigh vacuum conditions (Emtsev et al., 2009). Graphene samples from this method are composed of a multitude of domains, most of them submicrometre in scale, and are not spatially uniform in number or size over larger length scales. (iii) Epitaxial growth through chemical vapour deposition (CVD) on metal substrates. CVD has the potential to enable large scale graphene production for electronic applications such as thin film transistors, solar cells and touch panels which require large area graphene sheets in the order of tens of centimetres but always involve transfer of graphene to a desired substrate. Similar as thermal decomposition of SiC method, CVD is an expensive process. (iv) Exfoliation of graphite in solvents (Zhu, Murali, Cai, et al., 2010).

Graphene oxide (GO) can be obtained through a modification of Hummer's method (Hummers & Offeman, 1958) and the subsequent reduction with $NaBH_4$ or hydrazine can lead to pristine graphene. Due to the toxicity of the reducing agents, green pathways using reducing sugars are also under investigation (Zhu, Guo, Fang, & Dong, 2010). These methods offer the scope to cheaply produce large quantities of graphene. Particularly, chemical reduction of GO is a simple process and sheets as large as 50 μm have been made and then they can be modified chemically. Among the chemical methods, recently developed electrochemical exfoliation is regarded as a green method that allows easy tenability of the obtained products by varying the applied potential. Moreover, in this method, graphene can be prepared in the form of a colloidal suspension with adjustable solubility, suitable for printed electronics applications in an industrial scale. In this review, applications of graphene in solar cells, batteries, supercapacitors and fuel cells are summarized with the latest developments. Furthermore, graphene as a conductive ink for printed electronics is also discussed.

2. Application of graphenes in energy harvesting and storage

2.1. Solar cells

As the economies of scale cut down the production costs, rapid growth of the photovoltaic (PV) industry induces the depletion of the raw materials involved in the production of solar panels. This is particularly true for indium, which is used in the form of indium tin oxide (ITO) as a transparent conducting oxide (TCO) in several electronic applications. Organic photovoltaic (OPV) devices are made of an organic layer sandwiched between two charge collecting electrodes, one of which must be transparent, e.g., ITO or fluorine tin oxide (FTO); while the other is usually aluminium, sometimes coated with LiF or MgO (Spanggaard & Krebs, 2004). As shown in Fig. 1, the organic layer provides exciton dissociation to generate a potential and consequently electrical energy.

OPVs have the advantage over classical solar harvesting devices in that (i) they are flexible and semitransparent; (ii) they can be manufactured in a continuous printing process by coating large areas; (iii) they can be integrated in different devices; and (iv) they are cost effective and environmental friendly. The main challenges are efficiency, lifetime and competitive substitutes for ITO (Brabec, 2004). Graphene was found to be an alternate to ITO in OPVs due to its unique characteristics: single-layer graphene transmits nearly 98% of the total incident light (Nair et al., 2008), while each additional layer contributes approximately 2.3% to the overall opacity. Sheet resistance of a film is expressed as number of Ohms (Ω) of resistance per square of material. Sheet resistance of graphene used in different devices reported is ∼6 kΩ/sq (Blake et al., 2008; Lemme, Echtermeyer, Baus, & Kurz, 2007; Tan et al., 2007), whereas ITO has a transmittance of ca. 90% and a resistance of ∼20 Ω/sq. The main challenge is how to obtain high quality graphene sheets with less defects or without defects in order to further decrease its sheet resistance. Kalita, Matsushima, Uchida, Wakita, and Umeno (2010) recently synthesized graphene sheets from camphor for use in solar cell applications. Pyrolysis of camphor at 900 °C in argon allows the detachment of methyl carbons from the chemical structure, leaving a transparent graphene-structured carbon films (TGFs) with different thicknesses and with overall resistivity lower than that of ITO. Generally speaking, sheet resistance of graphene from chemical reduction of GO is in range of 1–100 kΩ/sq with transmittance below 80% (Eda, Fanchini, & Chhowalla, 2008; Wang, Zhi, & Mullen, 2008) or from 31 kΩ/sq to 18 MΩ/sq at 95% transmittance (Wu et al., 2008; Zhu, Cai, Piner, Velamakanni, & Ruoff, 2009), while in contrast, sheet resistance of graphene from the electrochemical exfoliation of graphite is in range of 0.015–0.21 kΩ/sq at 96% transparency (Su et al., 2011; Wang, Manga, Bao, & Loh, 2011).

Park, Rowehl, Kim, Bulovic, and Kong (2010) grew graphene sheets by CVD to replace ITO as the negative electrode, with a power conversion efficiency (PCE) comparable to devices containing ITO (1.63% for doped graphene vs. 1.77% for the latter). However, the hydrophobicity of graphene creates some difficulty in adhesion to the organic layer, that is, a mixture of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), is needed to act as a hole-transporting layer. The use of $AuCl_3$ nanoparticles as doping agent proves to be effective in increasing the wettability between the two surfaces, thus improving the device performances. $AuCl_3$ nanoparticles tend to reduce the sheet resistance of the graphene electrodes (Kim et al., 2010), though the success rate is still very low (∼10%), probably due to the variability in the $AuCl_3$ particle sizes, which range from 10 to 100 nm.

A vacuum filtration method was used by Wang, Geng, Zheng, and Kim (2010) to produce transparent conducting (TC) graphene films from chemically reduced graphene colloids. The films were then transferred onto quartz substrates for annealing and graphitization at high temperatures (400 °C and 1100 °C respectively). A sheet resistance lower than 2 kΩ/sq and a transparency well over 80% were achieved at a typical wavelength of 550 nm. As indicated in another work by Liu, He, et al. (2010) graphene could be used not only to substitute ITO but also to enhance electron transport and exciton dissociation in the hetero-junction of a solar cell. They questioned the use of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the standard electron acceptor, and combined solution-processable functionalized graphene (SPFGraphene) and functionalized multiwalled carbon nanotubes (f-MWCNTs) to produce a new active layer that was then sandwiched between PEDOT:PSS and LiF. The best result obtained was a PCE of 1.05% (Liu et al., 2008).