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Graphene as transparent front contact for dye sensitized solar cells

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ABSTRACT

A transparent conductive graphene film is investigated as front contact in dye-sensitized solar cells (DSSCs), as an alternative to traditional transparent conducting oxides (TCO). The film is composed of poly-crystalline few-layers graphene, covering homogeneously an area of 1 cm^2, deposited by chemical vapour deposition (CVD) technique on larger area Cu catalyst substrate and transferred on glass. DSSC photoanode is then fabricated, according to consolidated procedure, by sequential casting of TiO_2 films through tape casting technique, followed by annealing at 500 °C, and sensitization with N719 dye. An outstanding value of photoconversion efficiency as high as 2% is recorded for the best cell, under one sun irradiation (AM 1.5 G, 100 mW cm^{-2}), which is the highest ever reported for this kind of devices using graphene as front conducting film. Compared to previous results in the literature, the application of a large area continuous graphene film, guaranteed by the CVD deposition, definitely outperforms graphene layers composed by smaller graphene platelets (at micrometer scale). Morphological and electrical characterizations of graphene are reported and the functional performances of the best cell are compared with those obtained from classical DSSC exploiting fluorine-doped tin oxide. Obtained results encourage further investigation of graphene homogeneous thin film as viable alternative to standard TCOs for application in advanced devices, requiring high temperature processing or flexible substrates, incompatible with standard TCO films.

1. Introduction

Transparent conductive electrodes (TCEs) are essential components of several different optoelectronics devices, like solar cells, liquid crystal displays or touch panels. Currently adopted TCEs are essentially based on doped semiconductor materials, such as fluorine-doped tin oxide (FTO), aluminum zinc oxide (AZO), and the most common, although expensive, indium-doped tin oxide (ITO) [1]. Despite their widespread use, all these materials exhibit several drawbacks. Fabrication costs are for instance high, because of the scarcity of some constituents like indium in ITO. The materials are unable to sustain high temperature processes and are sensible to acid and alkaline environments [2–4]. Furthermore, there are issues as for electrical performances (e.g. FTO presents leakage currents due to its structural defects) [5,6], and all these materials are brittle and therefore unsuitable for flexible electronics applications [7]. All these open issues are determining an increasing interest for alternative materials exploitable in industrial electronic applications.

In order to overcome these limitations, several different materials have been recently explored, such as metal-based nanostructures (metallic nanowires and metal grids) [8], carbon nanotubes (CNTs) [9–11] and graphene membranes [12,13]. All these potential replacements are matching the basic requirements for TCEs, namely sheet resistance of the order of 100 Ω/□ or below, together with transmittance higher than 90% in the visible range. Moreover, graphene membranes are able to maintain these properties under severe bending and/or stretching, making this material an ideal solution, in particular, for flexible optoelectronic applications [14].

CNTs and graphene films have been already applied as transparent conducting layers in front and back contacts for a series of technologically relevant applications, such as light emitting diodes

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(LED) [15–17] biosensors [18–21], memories [22,23] and transistors [24–26]. They are also used in composite systems to increase electron conduction, while not significantly affecting the transparency of the layer [27], such as in all-organic [28,29], hybrid [30] or dye sensitized solar cells [31–33].

Dye- and quantum dot-sensitized solar cells (DSSCs and QDSSCs, respectively) are a promising alternative to the commercially available solid-state p–n junction photovoltaic devices because of their low fabrication cost, the use of more environmentally friendly materials and the possibility of simple fabrication scale-up [34,35]. At present, the highest DSSC photoconversion efficiency (PCE) is slightly above 13%, which makes these devices suitable for commercial exploitation [36]. In addition, the possibility to use flexible substrates [37], the relatively high PCE under diffused light illumination [38] and their colorful semitransparent behavior make these devices appealing candidates for several applications, like portable electronics, building-integrated photovoltaics and off-grid power sources.

Classical DSSC (QDSSC) architecture envisages the use of a mesoporous film (10 to 20 μm thick) of a wide band gap semiconductor metal oxide as anode. Mesoporous photoanode is sensitized by a light harvester (molecules or semiconductor nanocrystals), which is able to generate an exciton under sunlight irradiation. Then, exciton separation occurs at the interface between the dye (or QD) and the metal oxide, and electron injection occurs from dye (QD) to the semiconductor. Light harvester element is regenerated through an electrolyte acting as a mediator for hole exchange between the dye (QD) and the cathode.

Main efforts of the scientific community working in the field are focused on the enhancement of device PCE, as well as on seeking for alternative materials to further reduce the overall costs of fabrication processes.

Carbon materials (CNTs or graphene) can be applied in DSSCs (QDSSCs) thanks to their excellent electrical properties. Specifically, they can be used inside the photoanode as either bridge from the oxide to the FTO [32] or to increase the charge exchange from counter electrode to the electrolyte [39]. A very recent review on this topic illustrates the potential held by graphene as a transparent conducting material for DSSCs [40].

However, a few investigations have been carried out especially devoted to substitute ITO/FTO with low cost and still effective layers, such as carbon-based nanomaterials, as front contacts in DSSCs or similar devices.

Recent studies [41–44] demonstrate the possibility to integrate graphene in hybrid and organic solar cells processed at room temperature. However, no one succeeded in integrating graphene in photoanodes treated in oxidizing atmosphere at relatively high temperature (500 °C) while preserving high conductivity, transparency and adhesion to the substrate, which is strictly required for integration in DSSCs. Most significant result in the field date 2008: Wang and co-workers [45] applied a film composed of reduced graphene oxide (RGO) micro-platelets as front contact in a solid-state DSSC. Authors were able to fabricate an operating device, but functional properties resulted to be very low (PCE 0.26%) due to low electrical conductivity of the film. In fact, the use of micro-platelets imposes electron transport to take place through the highly defected edges of the sheets and/or through hopping from platelet to platelet, each of these paths introducing significant resistance and eventually limiting the transport process, as possibly indicated by the fill factor value of 0.36, which is quite low in the panorama of DSSCs.

A potentially optimized solution is represented by the application of continuous, homogeneous and highly crystalline layer of graphene with controlled thickness. In such a way, ballistic transport through the entire graphene sheet is guaranteed [46], without any hopping process through different sheets (as illustrated in Scheme 1, depicting the different charge transport properties using micro-platelets and a continuous film). In addition, as graphene optical properties can be precisely tailored by tuning the number of deposited graphene sheets [47], the control of layer thickness results in a simultaneous control of transmittance and conductivity, in a more straightforward way than in the case of packed platelets, where the random arrangement of the platelets can be hardly controlled. In that case, indeed, control of film thickness is rather critical and, in addition, overlapping edges of the platelets negatively affect light transmission without any benefit on charge transport.

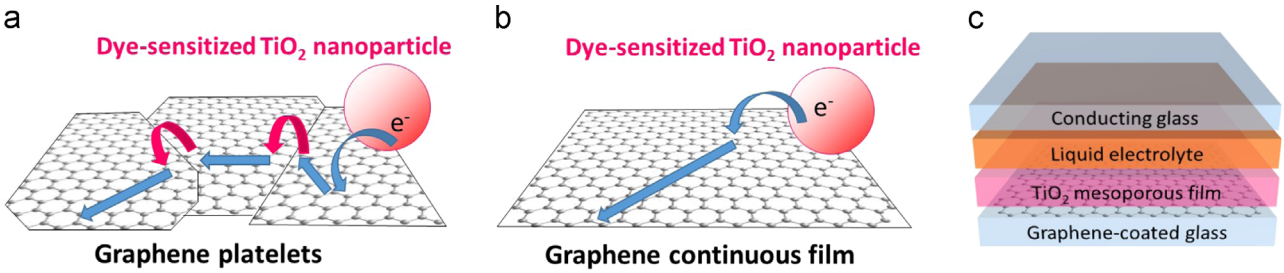
Chemical vapour deposition (CVD) can be used to produce high quality continuous graphene films, with low defect concentration and controllable optical and electrical properties [48–50]. These features make CVD growth the ideal technological platform for integration of graphene continuous films in dye sensitized solar cells, in which the control of the physical and chemical properties of the transparent conducting front contact over large area is critical for the proper operation of the final device.

In the present study, we applied this strategy for the fabrication of DSSCs, exploiting a homogeneous graphene film as front contact, while using the simplest cell architecture (thin transparent TiO_2 nanoparticles film, without any pre- or post-deposition $TiCl_4$ treatment), in order to provide the proof of concept of an enhanced charge transport through graphene.

2. Materials and methods

2.1. Deposition of graphene film onto the glass

Graphene was grown by CVD using copper as a catalytic substrate and methane carbon feedstock [51]. Copper foil (99.98% pure, 25 μm thick, Sigma-Aldrich), was annealed under hydrogen flow at 1000 °C, then it was exposed to methane gas for the deposition of graphene. The resulting carbon film covers the whole copper foil surface, with an average thickness of 1–4 graphene



Scheme 1. Schematics of different graphene films based on (a) overlapping micro-platelets and (b) continuous film. Electron injection from TiO_2 to graphene and different electron conduction paths are highlighted: presence of platelet discontinuity inhibits electron transport (purple arrows) resulting in increased resistivity. (c) Scheme of a dye sensitized solar cell based on graphene-coated front contact.

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