



Dispersion of graphene in organic solvents and their use for improving efficiency of dye- and quantum dot-sensitized solar cells



Archontoula Nikolakopoulou^{a,b}, Dimitrios Tasis^b, Lamprini Sygellou^b,
Panagiotis Lianos^{a,b,*}

^a Department of Chemical Engineering., University of Patras, 26500 Patras, Greece

^b FORTH/ICE-HT, P.O. Box 1414, 26504 Patras, Greece

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ABSTRACT

Pristine graphene was directly suspended in a variety of organic media, which are used either as electrolyte solvents or deposition media in sensitized solar cells. Dispersion occurred directly through sonication-assisted exfoliation of graphite powder, without adopting the oxidative approach involving intermediate formation of graphene oxide and its subsequent reduction. The concentration of the thus dispersed graphene was relatively low, in the order of a few tens of micrograms per ml, but it was very effective in increasing the efficiency of sensitized solar cells. Dispersed graphene was first deposited on solid substrates and was extensively characterized by TEM, SEM, XPS and Raman spectroscopy. Also dispersed graphene has been introduced in liquid-electrolyte and gel-electrolyte dye-sensitized solar cells by means of sulfolane/3-methoxypropionitrile mixtures and in quantum dot sensitized solid-state solar cells by means of chlorobenzene-based suspensions. Increase of cell efficiency in the presence of the above tiny quantities of graphene was very large, particularly in the case of solid state cells where more than 3-fold increase of efficiency was observed.

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1. Introduction

Graphene is a two-dimensional hexagonal honeycomb-like carbon nanostructure with excellent mechanical, thermal, optical and electronic properties [1,2]. The principal electronic characteristic of graphene is its extensive conjugated system, which offers extended delocalization of the π -electronic cloud. Indeed electron mobility in graphene is about $10^4 \text{ cm}^2\text{V}^{-1}$ [3]. Electronic applications of graphene are thus envisaged for a large range of products including batteries, superconductors and mesoscopic solar cells. In particular for sensitized solar cells, graphene has been used as additive with the purpose to increase efficiency in all three major components of these cells, i.e. in the oxide semiconductors of the photoanode [3], in the electrolyte filling the cells [4–7] and as electrocatalyst at the counter electrode [8–10].

Concerning the processing methods used towards the synthesis of mono- and few layer carbon nanostructures and subsequent incorporation in solar cells, graphene may be produced at high quantities by chemical vapor deposition (CVD).

High quality graphene is transferred through spin coating of a polymer solution and etching of the catalytic substrate. An alternative solid-state route involves the mechanical exfoliation of graphite through the “scotch-tape” approach. The main disadvantage of this approach is the low yield of monolayer graphene production as well as its laborious nature. Recent efforts have shown that graphene platelets may be isolated and manipulated in the liquid phase, in aqueous or organic media. Since pristine graphene is hardly dispersible in any solvent medium, it is mostly utilized in its oxygenated form, the so-called graphene oxide. Due to the oxidative conditions taking place during the synthesis of graphene oxide, the π -conjugation is locally broken, producing a relatively large population of defect sites at the basal plane consisting of carbon atoms with sp^3 hybridization. These characteristics define graphene oxide as an insulator material. The defect sites carry a variety of oxygen-containing functionalities such as $-OH$, $-COOH$ and epoxide groups, which allow dispersability of graphene oxide sheets in aqueous media. In order to restore the electronic properties of graphene oxide, researchers have adopted various reduction/deoxygenation protocols for obtaining reduced graphene oxide [8]. The latter may hardly approach the electronic and structural properties of pristine graphene nanostructure. This means that reduction process leads to a partial recovery of sp^2

* Corresponding author.

E-mail address: lianos@upatras.gr (P. Lianos).

hybridization, leading to formation of a semiconducting material with varying band gap, depending on the extent of reduction. With this in mind, in the present work, we adopted a simple procedure to avoid the graphene oxide/reduced graphene oxide route and directly incorporate pristine graphene flakes in sensitized solar cells in order to assess the effect of these carbon nanostructures on their efficiency. We have suspended trace quantities of graphene by exfoliation of graphite in specific organic media, which are used either to prepare electrolyte for solar cells or are used during the process of component deposition in solid state solar cells. In this way, graphene was introduced into the cells. The effect of added graphene was thus assessed in three types of sensitized solar cells: liquid electrolyte Dye-Sensitized Solar Cells (DSSCs), quasi solid-state dye-sensitized solar cells (QSS-DSSCs) and quantum-dot-sensitized solid-state Hybrid organic-inorganic Solar Cells (HSCs).

2. Experimental

2.1. Materials

Unless otherwise indicated, reagents were obtained from Aldrich and were used as received. Graphite with an average particle size of 500 μm and a purity of >95% was supplied from NGS Naturgraphit GmbH (batch: large flakes). Regioregular Poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals and the sensitizer dye N719 from Solaronix. Commercial nanocrystalline titania Degussa P25 (specific surface area 50 m^2/g) was used in all cell constructions and Millipore water was used in all experiments. PEDOT:PSS solution (Orgacon Type EL-P 3040 ink for screen printing) was an AGFA product and $\text{SnO}_2:\text{F}$ transparent conductive electrodes (FTO, Resistance 8 Ω/square) were purchased from Pilkington.

2.2. Dispersion of graphene in various organic media

We have tested four media for graphene dispersion: sulfolane, chlorobenzene, 3-methoxypropionitrile and an equal weight mixture of sulfolane with 3-methoxypropionitrile. The choice of these solvents was dictated by the fact that mixtures of sulfolane with 3-methoxypropionitrile are used as electrolyte solvent in DSSCs and QSS-DSSCs while chlorobenzene is the standard volatile solvent employed in the deposition of the hole-transporting material in HSCs (see below). Pristine graphite flakes were added into the corresponding medium (starting concentration 2 mg/ml) and bath sonicated for a total period of 60 min (2 \times 30 min). During sonication, graphene sheets were exfoliated from the graphite flakes and dispersed in the organic medium. The suspensions were then left to settle overnight. Next day, we observed that graphene suspension in sulfolane precipitated in great extent and the supernatant part of the solvent was transparent. On the contrary, the suspensions in chlorobenzene, 3-methoxypropionitrile and in the sulfolane/3-methoxypropionitrile mixture were black-colored. In order to discard the graphite flakes, the suspensions were gradually centrifuged, by using the following protocol: 10 min at 500 rpm, 10 min at 1000 rpm and 20 min at 2000 rpm. The sulfolane suspension totally precipitated after centrifugation at 1000 rpm, showing that exfoliation of graphite was not successful in this medium. In the rest of the dispersion media, gradual centrifugation led to gradual precipitation of multilayer graphite flakes finally leaving in dispersion mono- as well as few-layer graphenes. In the case of sulfolane/3-methoxypropionitrile 1:1 mixture, due to the presence of the second component, graphene was again exfoliated and kept in suspension.

2.3. Fabrication of liquid electrolyte and quasi-solid state dye-sensitized solar cells

The following procedures, similar to a previous publication [8] were undertaken in order to construct photoanode electrodes: A FTO glass electrode was cut in the appropriate dimensions and was carefully cleaned first with soap and then by sonication in isopropanol, water and acetone. A thin layer of compact titania was first sprayed over a FTO electrode using 0.2 mol L^{-1} diisopropoxytitanium bis(acetylacetonate) solution in ethanol and then it was calcined at 500 $^\circ\text{C}$. On this thin bottom layer, a titania paste made of P25 nanoparticles was applied by doctor blading. The film was calcined again up to 550 $^\circ\text{C}$ at a rate of 20 $^\circ\text{C}/\text{min}$. The final thickness of the film, as measured by SEM, was approximately 10 μm . Then, the film was treated with a 0.04 mol L^{-1} aqueous solution of TiCl_4 for 30 min at 70 $^\circ\text{C}$, followed by calcination up to 500 $^\circ\text{C}$. The geometrical area of the film was 1 cm^2 (1 $\text{cm} \times$ 1 cm). As soon as the final film was taken out of the oven, it was dipped in an acetonitrile:tert-butanol (50:50v.) solution containing 5 mmol L^{-1} of the dye N719 and was left overnight. The film was then heavily colored with attached dye. It was rinsed with acetonitrile, dried in a N_2 stream and heated for a few minutes at 100 $^\circ\text{C}$.

In the case of quasi solid-state solar cells, the electrolyte was a gel based on a Ureasil precursor, same as for Refs. [8] and [11] where its synthesis was reported. 1.2 g of sulfolane and 1.2 g of 3-methoxypropionitrile were mixed under stirring with 0.7 g of the above Ureasil precursor, 0.35 ml of acetic acid (AcOH), 0.12 g LiI and 0.12 g 1-methyl-3-propylimidazolium iodide. When the solution was clear, we added 0.06 g I_2 . Thus the molar ratio of I^- to I_2 was approximately 6:1. Finally, we added about 0.5 mol L^{-1} tert-butylpyridine and 0.1 mol L^{-1} guanidinium thiocyanate, which are known to raise the open-circuit voltage and the short-circuit current in DSSCs, respectively. The solution was stirred for several hours before application. During this period, a slow solvolysis took place developing silica bonds between precursor chains and leading to condensation and gel formation [8,11]. In the case of liquid electrolyte DSSCs, we used the same electrolyte without adding Ureasil and AcOH, which facilitates gel formation. In each category of solar cells, reference devices were directly compared with the ones, in which the electrolyte contains suspended graphene sheets.

In both aforementioned cases, the counter electrode was made by twice spin coating a solution of 0.02 mol L^{-1} chloroplatinic acid hexahydrate in isopropanol and subsequent calcination at 550 $^\circ\text{C}$.

Cells were assembled in the standard configuration. One drop of the sol, was placed on the top of the N719@nc-TiO₂ film. A Pt-functionalized counter electrode was applied on the top and held together with a metal clip. It was left like this for a few hours. During this time, the sol becomes a solid gel and acts as adhesive resin steadily holding the two electrodes together. No encapsulation or sealing of the cells has been done in that case and all measurements were performed under ambient conditions. This construction was applied for the study of QSS-DSSCs. In the absence of Ureasil, that is, in the case of liquid electrolytes, we used a thermoplastic surlyn-type material of around 50 μm thickness as a gasket to hold anode and counter electrodes together, while the electrolyte was introduced by drilling two holes in the counter electrode. Wire connection was made by using auto-adhesive copper ribbons. As already said, two cells were made in each case, one containing electrolyte made of pure solvents for comparison and one made of solvents containing dispersed graphene.

2.4. Fabrication of solid-state hybrid solar cells

Solid-state solar cells of inverted structure were made by using nanocrystalline titania photoanodes and P3HT as hole transporter. Photoanode electrodes were made as described in section 2.3 using

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