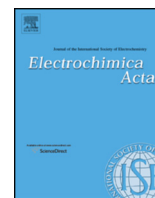




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Charge and energy transfer interplay in hybrid sensitized solar cells mediated by graphene quantum dots



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ABSTRACT

We explored the role of graphene quantum dots (GQDs) as co-sensitizers in hybrid dye sensitized solar cell (DSSC) architectures, focusing on various concurring mechanisms, such as: charge transfer, energy transfer and recombination rate, towards light harvesting improvement. GQDs were prepared by the hydrothermal method that allows the tuning of electronic levels and optical properties by employing appropriate precursors and synthesis conditions. The aim was to realize a type II alignment for TiO₂/GQD/dye hybrid configuration, using standard N3 Ru-dye in order to improve charge transfer. When GQDs were used as co-sensitizers together with N3 Ru-dye, an improvement in power conversion efficiency was achieved, as shown by electrical measurements. The experimental analysis indicates that this improvement arises from the interplay of various mechanisms mediated by GQDs: (i) enhancement of charge separation and collection due to the cascaded alignment of the energy levels; (ii) energy transfer from GQDs to N3 Ru-dye due to the overlap between GQD photoluminescence and N3 Ru-dye absorption spectra; and (iii) reduction of the electron recombination to the redox couple due to the inhibition of the back electron transfer to the electrolyte by the GQDs.

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1. Introduction

In solar technologies it is generally accepted that the dye-sensitized solar cells (DSSC) together with organic photovoltaics represent the third-generation of energy harvesting devices, bringing mainly the advantage of simplicity in their fabrication procedures, done practically under ambient conditions. One of the main drawbacks is related to the charge loss during the transport of photogenerated electrons in photoanodes.

The unique properties of carbon based nanomaterials (e.g. morphological, electrical, optical, and mechanical ones) made them a legitimate opportunity for enhancing the performances of both energy-conversion and storage devices [1]. Accordingly, intensive efforts were devoted to explore their feasibility as cheaper and eco-friendly materials to replace the components of conventional DSSC, like in the case of alternative counter electrode

instead of platinum ones, whose high cost, rarity or risk of corrosion by the redox species are known, and therefore, the significant improvements brought by using carbon nanotubes (CNT) [2], graphene nanosheets [3] or carbon nanoparticles [4] were demonstrated. On the other hand, the incorporation of carbon-based nanomaterials in the photoanode seems to be considered very promising in terms of reducing the photo-electrons' loss and improving its electrical conductivity [5,6]. However, the low surface contact between 1D (e.g. CNT) or 2D (e.g. graphene) nanomaterials with nanostructured TiO₂ film is seen as the main impediment for enhancing the device performance.

In the recent years, the graphene quantum dots (GQDs) have generated interest both in the fundamental science [7,8] and for potential applications in chemical sensing and bioimaging [9,10] or even as channels for field effect transistors [11] devices. Regarding the energy storage and conversion devices, the GQDs have been defined as an emerging material for energy-related applications and beyond [12] due to their extraordinary optical and electrical properties. Hence, their huge potential for memory devices [13], supercapacitors [14], fuel cells [15], photovoltaic devices [16,17], light-emitting diodes [18] was revealed. Furthermore, different

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architectures of solar cells based on QDs have been proposed, where they form heterojunctions with crystalline silicon or silicon nanowires [19,20] and organic bulk heterojunction [21] on one hand, or they were embedded in polymers to replace the standard TiO₂ photoanode [22] or Pt counter electrode [23] in DSSCs on the other hand.

In ultraviolet spectral range, GQDs have extinction coefficients ranging from 10 to 200 · 10³ M⁻¹ cm⁻¹ [24], larger than that of common fluorophores, and comparable to those of semiconductor quantum dots (QDs) [25]. Due to this fact, GQDs can be physically included in a photoanode to act as a sensitizer in quantum dot-sensitized solar cells (QDSSC), but only very low efficiencies have been reported to this point, albeit different GQDs synthesis methods or different architectures of TiO₂ electrode were proposed [26–29]. The explanation for the rather low efficiencies of the GQDs sensitized solar cells resides in the limited spectral range of absorption as well as in their low quantum yield compared with the standard fluorophores or semiconducting QDs.

A method to circumvent these issues is to use hybrid sensitizers containing both GQD and conventional dyes such that their absorption spectra cover the useful range of the solar spectrum. Several studies reporting on the interaction between semiconductor quantum dots and different organic dyes were published [30,31], but few data are available for GQDs – dye interaction [32,33]. The proposed explanation for the improved efficiency of hybrid solar cells co-sensitized with GQD and N719 Ru-dye is the injection of hot electrons from GQD into TiO₂ photoanode [32] or the up-conversion properties of GQD [33]. However, for GQD's sizes of several nanometers the photon flux challenge is not met [34] making unlikely for the solar radiation to cause multiphoton processes and generate hot electron populations. It is clear that a deeper understanding of the competition between various mechanisms such as charge transfer and energy transfer in hybrid systems is necessary in order to better exploit the special optoelectronic properties of GQDs.

An advantage of GQDs is the possibility to engineer their electronic properties such as gap and energy levels, by appropriate surface functionalization. In this way, when employed together with a conventional dye, one can obtain a charge transfer type II band alignment or an energy transfer type I band alignment. It is important to mention that the energy transfer process from GQD to dye can also occur in type II band alignment when there is a strong overlap between the PL emission spectra of GQD and the absorption spectrum of the dye [31].

Another salient feature of the GQD which is of interest for the sensitized solar cells is the capability of GQDs to store charge. As we observed in various types of electrical and photoelectrical measurements like, for instance, in time rising and decay photoconductivity measurements of GQDs embedded in polymers, the GQDs have a lifetime of tens of seconds [13]. This suggests an inhibited recombination mechanism in these systems. Starting from this finding, it would be of interest to investigate whether in other physical systems such as DSSC the presence of GQDs in the TiO₂ layer will, eventually, act as inhibitors for recombination improving in this way the charge collection.

In this article we explore the GQD influence on the electrical parameters of hybrid sensitized solar cells that is both the dye and the GQDs are sensitizers. Firstly, by a simple one-step microwave assisted synthesis method we obtained GQD presenting an improved quantum yield as well as the desired bandgap and energy levels, appropriate for a type II band alignment for a hybrid GQD and standard Ru-dye sensitized solar cell, N3. Moreover, the as-prepared GQDs have a self-passivated surface, bearing amino functional groups, as shown by the XPS survey that improved their attachment capabilities on the titanium oxide surface. Secondly, in order to ascertain whether the GQDs played a role in improving the

conversion efficiency, we realized and characterized a proof-of-concept solar cell using standard commercial DSSC components. We did not focus on optimization studies, in terms of dye and GQD impregnation times on TiO₂ or additional treatments, our only interest being to investigate mechanisms underlying functionality of hybrid GQD based DSSC.

The effects of GQDs on the hybrid DSSC performances were investigated by means of current-voltage (I–V) measurements under dark and illumination conditions, incident photon to current conversion efficiency (IPCE) and open-circuit voltage decay (OCVD). We demonstrate that the presence of GQDs leads to a consistent improvement of the photocurrent and power conversion efficiency with respect to a conventional N3 based DSSC as shown by I–V measurements. The light harvesting observed for the hybrid structure of GQDs and dye was determined by a simultaneous fulfilment of several requirements: (i) extension of the spectral absorption range; (ii) energy transfer between GQDs and N3 dye; (iii) existence of a multistep cascade energy levels of the TiO₂-GQD-N3 dye system; (iv) efficient spatial separation of the electrons and holes; (v) facilitation of the electron injection from dye to TiO₂ and GQD; and (vi) longer recombination time.

2. Experimental section

2.1. Materials and reagents

D-(+)-Glucosamine hydrochloride, 2-Amino-2-(hydroxymethyl)-1,3-propanediol (Tris), ethanol and acetonitrile (ACN) were supplied by Sigma-Aldrich. Tetrabutylammonium perchlorate (TBAP) was provided by Molekula GmbH. Test cell spare parts, electrolyte and dye were bought from Solaronix. Commercially available drilled Pt electrodes prepared by screen-printing a platinum precursor on a TCO22-7 FTO coated glass (reference number: 74,201), gaskets (74,301), sealing (74,401), caps (74,501), Iodolyte AN-50 (31,121) and Ruthenizer 535 (N3) (21,552) were supplied without any modification. Customized transparent titania electrodes consisted of a barrier layer, a 10 μm TiO₂ mesoporous layer and a 4 μm reflective layer were used in our experiments.

2.2. Synthesis of luminescent graphene quantum dots (GQDs), modification of TiO₂ electrodes and cell preparation

The luminescent graphene quantum dots (GQDs) were synthesized by a microwave assisted single step hydrothermal route. A microwave acid digestion vessel (4781 type) provided by Parr Instrument Company and a commercial microwave oven were used during synthesis. In a typical procedure, 1.0 g of D-(+)-Glucosamine hydrochloride and 6.9 g of 2-Amino-2-(hydroxymethyl)-1,3-propanediol were solubilised in distilled water (10 mL). The solubilisation process was accelerated using a laboratory ultrasounds bath (Elmasonic X-tra basic 300) for 25 minutes. The entire volume was introduced in the reaction vessel and during 60 seconds, 700 W were applied; the reaction mixture was allowed to cool down at room temperature for 45 minutes. The reaction mixture was further centrifuged at 20.000 rpm, at 10 °C, using a Beckman Coulter Avanti J-30I centrifuge. The supernatant was collected and used for further experiments or stored at 4 °C. Functionalization of titania electrodes was achieved: (1) by liquid impregnation, using the graphene quantum dots supernatant solution, during 2 hours immersion time; (2) by immersion in a 5 · 10⁻⁴ M Ruthenizer 535 (N3) alcoholic solution for 2 hours staining time; (3) TiO₂ electrodes were first immersed during 2 hours in the GQDs supernatant solution and thereafter soaked for another 2 more hours in 5 · 10⁻⁴ M Ruthenizer 535 solution. After soaking in GQDs supernatant solution, the electrodes were rinsed with water and dried under a gentle flow of nitrogen and after immersion in Ruthenizer 535 solution the

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