



Reduced graphene oxide catalysts for efficient regeneration of cobalt-based redox electrolytes in dye-sensitized solar cells



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ABSTRACT

Efficient and low cost reduced graphene oxide (rGOV) is prepared by chemical reduction of graphene oxide (GO) using vitamin C. Detailed characterization by XRD, SEM and Raman techniques confirm the successful reduction of GO. Thin films of rGOV with various thickness are deposited by spin coating on FTO glass substrates and are used as counter electrodes (CEs) in dye-sensitized solar cells (DSCs) incorporating the organic sensitizer D35 dye and the $\text{Co}(\text{bpy})_3^{3+}/\text{Co}(\text{bpy})_3^{2+}$ redox couple. These devices present high photocurrent density (J_{sc}) and open-circuit voltage (V_{oc}) values resulting in enhanced photovoltaic performance in comparison with the Pt catalyst. The novel rGOV electrodes constitute an excellent, low-cost and environmentally friendly alternative solution to the costly platinum-based cathodes.

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1. Introduction

Dye-sensitized solar cells (DSCs) have been of significant interest during the last two decades due to their low cost, ease of fabrication, and high energy conversion efficiency [1,2]. A typical DSC consists of a photoanode comprising a TiO_2 nanoparticulate film sensitized by a dye monolayer, a redox electrolyte which has the role of regenerating the oxidized dye, and a counter electrode (CE) where the oxidized species of the redox electrolyte are being reduced. All of the above referred components play an important role on the performance and stability of a DSC device.

In order to decrease the cost and increase the efficiency of DSCs (η), high up research has been focused on the optimization of DSCs by tuning the TiO_2 film (photoanode) morphology [3], producing new dyes [4], introducing novel redox mediators [5] as well as exploring new materials for cathode electrodes [6]. Among all materials that have been explored, platinum remains the most widespread choice for CE, owing to its excellent electro-catalytic activity and the very high electrical conductivity, which are both essential properties for a very efficient CE, leading to DSCs with

increased fill factor (FF) values and, consequently, high power conversion efficiency.

Nevertheless, platinum's high cost, scarcity as a noble metal as well as low chemical inertness has provided a trigger towards suitable replacements of the platinum cathodic electrode using as alternative, low cost, corrosion resistant, outstanding catalysts and conductors. The most promising candidates for this substitution are the carbon-based materials, such as carbon nanotubes [7], carbon black [6], graphite [8] and reduced graphene oxide, as well as graphene [9–14].

Graphene is the particularly challenging two-dimensional sp^2 -hybridized carbon material with ultrahigh transmittance, excellent electron mobility and conductivity, mechanical and thermal properties, chemical inertness, and high electrocatalytic activity [15]. However, the high production cost of pure graphene remains an obstacle towards its wide use. In order to reduce the cost of the as prepared devices, that would promote their large scale production, several functionalization options have been employed [15–20]. One of the most developed methods: to produce graphene-based materials in high yields and low-cost, consists of the initial strong oxidation of graphite to graphite oxide, followed by exfoliation of graphite oxide to graphene oxide (GO) which can be subsequently reduced resulting in reduced graphene oxide (rGO).

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It has been observed that the choice of the reduction process strongly affects the properties of the resulting rGO materials [21–24]. In particular, the chemical reduction of GO is reputed as one of the most efficient, economic and large-scale production processes of this material [25]. Hydrazine or hydrazine derivatives are the most commonly applied reducing agents, but they are explosive and highly toxic and usually lead to materials presenting low solubility and strong agglomeration. Consequently the use of mild and environmental friendly reductants is necessary and several microorganisms and biomolecules have been used as substitutional agents, like *Shewanella* [26], *Escherichia coli* [27], bovine serum albumin [28], glucose [29], amino acids [30] and L-ascorbic acid (commonly known as vitamin C) [31].

The graphene-derived materials have good optical, electrical, and electrocatalytic properties, which make them suitable for applications in electronics (supercapacitors, biomedical sensors), optics, (field emitters, photoelectrochemical devices) and energy-harvesting devices, including their incorporation with great success in solar cells [32–42]. As aforementioned, there are essential parameters which are related to the performance of a DSC and which are directly correlated to the proper function of the CE. Among them, the appropriate selection of the electrolyte and consequently the sensitizer are some of major relevance. Although electrolytes containing iodide/triiodide (I^-/I_3^-) are the most widespread, this redox couple has low redox potential (ca. 0.35 V vs. SHE), which limits the accessible open-circuit voltage (V_{oc}) of the DSC. In addition, the triiodide itself absorbs light, which hinders the optimum absorbance and, thus affecting the sensitizing ability of the dye. In order to overcome the above disadvantages of I^-/I_3^- redox couple, various systems with more positive redox potentials were inquired, with most prominent the $Co(bpy)_3^{3+}/Co(bpy)_3^{2+}$ (bpy is 2,2'-bipyridine) redox couple (0.56 V vs. SHE), which results in DSCs with favorable V_{oc} higher than 0.9 V.

In the present work, rGOV was prepared from GO using the environmental friendly reducing agent, vitamin C. GO and the resulting reduced graphene oxide (rGOV) materials have been thoroughly characterized and their structural, morphological and vibrational properties have been explored in detail using XRD, SEM and Raman microscopy, respectively. The same materials have been deposited via the spin-coating technique on transparent conducting FTO glass substrates and were subsequently used as CE in liquid state DSCs. The electrochemical properties and catalytic activity of the prepared electrodes have been explored using voltammetry and spectroscopy methods, while the solar cell photovoltaic performance has been evaluated. The novel electrodes have emerged as a very promising alternative to Pt, since the DSCs incorporating them present higher values of V_{oc} and j_{sc} , which lead to higher power conversion efficiency values. Moreover the combination of the prepared environmental carbonaceous materials with the very promising cobalt complexes based-electrolyte and their use in DSCs, results in increased power conversion efficiency outperforming the corresponding cells using the Pt reference counter electrodes.

2. Experimental section

2.1. Materials

Synthetic graphite (99.9995%), L-ascorbic acid (99% – vitamin C) and hydrochloric acid (37%) were purchased from Sigma-Aldrich. Sulphuric acid (96–98%) was obtained from Riedel-de-Haën, potassium permanganate (99%) from Merck and hydrogen peroxide (30%) was obtained from Fluka.

The D35 organic dye and the $Co(bpy)_3(PF_6)_2/Co(bpy)_3(PF_6)_3$ redox couple used for the preparation of the electrolyte were purchased from Dyenamo AB (Sweden). DSL18NR-T TiO_2 -based

paste was purchased from Dyesol UK and further diluted with a solution of ethyl cellulose/terpineol (6:4 w/w) before deposition. $TiCl_4$ was bought from Fluka. Transparent conductive glass substrates (TEC8, 3.2 mm) were obtained from Sigma Aldrich with sheet resistance $8 \Omega/\square$.

2.2. Synthesis of graphene oxide and reduced graphene oxide by vitamin C

GO was synthesized from synthetic graphite (particle size $\leq 20 \mu m$), by a modified Hummers method [43] described elsewhere [43–45]. In a typical procedure, 120 mL of concentrated sulphuric acid was slowly added to a flask containing both graphite (2.5 g) and $NaNO_3$ (2.5 g), and the mixture was cooled down to $0^\circ C$. Then, 15 g of potassium permanganate was slowly added to the mixture. The suspension was continuously stirred for 2 h at $35^\circ C$. After that, it was cooled in an ice bath and then 750 mL of H_2O_2 (3%) was added slowly. The oxidized material was purified with an hydrochloric acid solution (10 wt.%) and the suspension was then filtered, washed several times with distilled water until the neutrality of the rinsing waters was reached, and dried at $60^\circ C$ for 24 h to obtain graphite oxide. The oxidized material was dispersed in water and sonicated with an ultrasonic processor (UP400S, 24 kHz) for 1 h. Finally, the resulting dispersion was centrifuged for 30 min at 3000 rpm to obtain the GO suspension.

rGOV was prepared by chemical reduction using vitamin C as reducing agent [46] and employing an aqueous dispersion of GO as described in the literature [47]. Briefly, the GO suspension ($1 g L^{-1}$) with the reducing agent (2 mM) was heated at $95^\circ C$ for 3 h under vigorous stirring. The pH of the GO dispersion was adjusted to 9–10 with ammonia solution (25%) to promote the colloidal stability of the GO sheets through electrostatic repulsion.

2.3. Electrode and solar cell fabrication

To fabricate the photoanodes, multilayer titania films were prepared. Initially, in order to avoid the recombination of electrons, a compact layer of 40 mM $TiCl_4$ (30 min at $70^\circ C$ – this procedure was repeated twice) was deposited on transparent FTO conductive glass substrates. After this blocking layer, a transparent thin film of the commercial DSL18-NRT (Dyesol UK) titania paste modified suitably with ethyl cellulose and terpineol was added. The films were dried at $125^\circ C$ (for 6 min) and then, a mesoporous layer of the commercial WER2-O (Dyesol) –mixed with the DSL18-NRT paste was applied by the doctor-blade technique and the films were annealed at $125^\circ C$ (for 5 min), $325^\circ C$ (for 15 min) and $525^\circ C$ (for 30 min). The resulting films were post-treated with 40 mM $TiCl_4$ for 60 min at $70^\circ C$ and were re-annealed at $450^\circ C$ for 60 min. The photoanodes were further sensitized by being immersed overnight into a 0.2 mM [(E)-3-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl) amino) phenyl) thiophen-2-yl) –2 cyanoacrylic acid (D35)-Dyenamo] ethanol solution. A small drop of the redox electrolyte, consisting of 0.2 M $Co(bpy)_3(PF_6)_2$, 0.075 M $Co(bpy)_3(PF_6)_3$, 0.1 M Bis-trifluoromethane-sulfonimide lithium salt (LiTFSI) and 0.5 M 4-tert-butylpyridine (4-TBP, Sigma) in acetonitrile (ACN) was cast on the sensitized photoanode and then sandwiched against the cathode. A 50 μm scotch tape was used as a separator and the active area of the cells was $0.25 cm^2$.

To construct the counter electrodes, the rGOV sample (10 mg) was dispersed in absolute ethanol (1 mL) and sonicated for 15–20 min to obtain a homogeneous suspension. The resulting homogeneous suspension was spin coated (SPIN150-NPP) onto cleaned FTO glass substrates, at 4000 rpm for 60 s. Different volumes of the rGOV suspension ($10 mg mL^{-1}$) were used in order

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