



# Co–N doped reduced graphene oxide used as efficient electrocatalyst for dye-sensitized solar cells



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## ABSTRACT

An efficient electrocatalyst for Pt-free  $I^-/I_3^-$  reduction has been synthesized by high temperature treatment of graphene oxide-cobalt phthalocyanine mixtures. The graphitic material was characterized by various techniques and was found to consist of reduced graphene oxide carrying  $CoN_3$  entities, obtained by thermal decomposition of cobalt phthalocyanine. This material had an ionization potential equal to  $4.9 \pm 0.1$  eV and thus it was judged appropriate to act as reduction electrocatalyst for the  $I^-/I_3^-$  redox electrolyte. It was subsequently deposited as thin film on FTO electrodes, which were employed as counter electrodes for dye-sensitized solar cells. Its capacity to reduce  $I^-/I_3^-$  redox electrolyte was verified by electrochemistry. When it was finally employed for the construction of solar cells, it demonstrated full capacity to substitute standard Pt electrocatalyst verifying that the construction of Pt-free dye-sensitized solar cells is feasible.

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## 1. Introduction

A serious constraint that limits the possibility of commercialization of Dye-sensitized Solar Cells (DSSCs) is the employment of rare and expensive Pt as electrocatalyst for the reduction of  $I^-/I_3^-$  redox couple. For this reason, there is a strong effort for the search of alternative electrocatalysts. In this respect, carbonaceous materials, have been early recognized as possible Pt substitutes [1] and have presently become the center of focus [2–5], with graphene claiming a lion's share. The popularity of graphene stems from its favorable properties. It is a 2-dimensional honeycomb-like structure, being the thinnest 2D material (atomic layer). It possesses a high carrier mobility of more than  $200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [4,6,7], high specific surface area ( $2600 \text{ m}^2 \text{ g}^{-1}$ ) [4] and high optical transparency (97,7%) [4,8]. Thus, the excellent conductivity of graphene, which results in decreased charge transfer resistance, makes it a good candidate for DSSC counter electrodes [4]. There is, however, a difficulty in studying graphene as counter electrode material, which is related with the process of graphene deposition on electrodes. In most cases,

solution processed graphene deposition involves the utilization of graphene oxide (GO). After deposition, GO is deoxygenated either chemically or thermally, producing reduced graphene oxide (RGO). The latter is a semiconductor and thus may approach, but never exactly reach, the qualities of pristine graphene. Reduction of GO depends on the process used and it may vary from one procedure to the other or from one laboratory to the other. Under these conditions and because of the diversity of the published data, reduction of GO has created a very extensive and ever growing literature [2–5,9,10]. Inspection of this literature reveals that, in reality, graphene or RGO by themselves cannot be sufficient substitutes of Pt but they should be combined or doped with appropriate co-catalysts. In this respect, they provide an excellent support for co-catalysts and a vast ground for doping either with metals or non-metals as well as with their combinations [5,11–17].

When graphene-based materials are used as electrocatalysts, it is important to balance conductivity with electrocatalytic activity [13] since the latter seems to be associated with the existence of defect sites. In other words, pristine graphene is a very good conductor but a poor electrocatalyst because it has no active sites, while RGO has lower conductivity but possesses oxygen-containing functional groups that makes it a better electrocatalyst. Doping of graphene lattice with heteroatoms (for example, N or P [13–16]) can introduce electrocatalytic active sites. Furthermore, introduction of (non-precious) metal centers can further enhance electrocatalytic capacity. In this respect, there exists a substantial research effort for

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the development of carbon-based electrocatalysts doped with metal-nitrogen centers, mainly for oxygen reduction applications in fuel cells [18,19]. Having these data in mind, in this work we managed to synthesize a material by high temperature treatment of graphene oxide mixed with cobalt phthalocyanine (CoPc). This material is composed of RGO doped with CoN<sub>3</sub> functionalities. In order to underline the synthesis procedure, the obtained material is abbreviated as RGO-CoPc. This material was then employed as electrocatalyst in DSSCs and revealed itself as a valuable substitute of Pt for the reduction of I<sup>-</sup>/I<sub>3</sub><sup>-</sup>.

## 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). Commercial nanocrystalline titania Degussa P25 (specific surface area 50 m<sup>2</sup>/g) was used in all cell constructions and Millipore water was used in all experiments. SnO<sub>2</sub>:F transparent conductive electrodes (FTO, Resistance 8 Ω/square) were purchased from Pilkington.

### 2.2. Synthesis of graphene oxide

GO was prepared according to the protocol described in the work of Kovtyukhova et al. [20], similarly to a previous publication [11]. It consists of two steps, the first step being the pre-oxidation of graphite flakes and the second step following the standard Hummer's method for GO production. Graphite powder (15 g) was put into an 80 °C solution containing concentrated H<sub>2</sub>SO<sub>4</sub> (60 ml), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (7.8 g), and P<sub>2</sub>O<sub>5</sub> (8.4 g). After reaching 80 °C again, the mixture was left to cool down to room temperature over a period of 6 h. The mixture was then carefully diluted with 300 ml of distilled water, filtered through 0.4 μm PTFE membrane (Millipore), and washed on the filter until the pH of the rinsing water became neutral. The product was dried in vacuum at 60 °C for 24 h. This pre-oxidized graphite was then subjected to oxidation by Hummer's method. The pre-oxidized graphite powder (15 g) was put into cold (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub> (500 ml). KMnO<sub>4</sub> (60 g) was gradually added with stirring and cooling, so that the temperature of the mixture was not allowed to reach 20 °C. The mixture was then stirred at 35 °C for 2 h and distilled water (900 ml) was added. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (2.5 L) and 30% H<sub>2</sub>O<sub>2</sub> solution (50 ml), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with 1:10 HCl solution (5 L) in order to remove metal ions. The GO product was suspended in distilled water to give a viscous 2% dispersion, which was subjected to dialysis for seven days to completely remove metal ions and acids. The resulting GO dispersion was used to prepare exfoliated GO. Exfoliation was achieved by dilution of the GO dispersion with deionized water, followed by 60 min bath sonication.

### 2.3. Doping of GO with Co-Phthalocyanine

30 ml of GO suspension in water (10 mg/ml) were placed in a beaker and were mixed with 60 ml of THF solution, containing 170 mg of cobalt(II)phthalocyanine (CoPc). The organic solution was added drop-wise under continuous stirring of the GO aqueous suspension. The mixture was placed onto a metal plate and heated for approximately 10 h, until complete evaporation of solvents. During that time, the temperature of the metal plate was kept

constant at about 70 °C and stirring was maintained until the last possible moment. The solid residue was isolated from the beaker and placed in an oven for 6 h at 90 °C. Subsequently, the blend was transferred to a porcelain combustion boat, which was inserted in a horizontal tube furnace. It was heated from room temperature up to 700 °C with a ramp rate of 10 °C/min *under inert atmosphere*, and was left at the elevated temperature for 1 h. After that period, the heat was turned off and the oven was allowed to cool to 50 °C over a period of approx. 4 h, before the combustion boat was removed. The black-colored powder was washed with THF by transferring it to a beaker containing ~30 ml of the solvent, under stirring conditions. The organic solution turned blue-colored, due to dissolution of unpyrolyzed phthalocyanine or byproducts derived by thermal decomposition of the organic substance. The colored suspension was then filtered over a PTFE membrane (0.45 μm pore size) under vacuum and the doped graphitic material was washed with excess of THF. The solid was left to dry in an oven at 80 °C for 5 h and was kept into a sealed container. The obtained material was RGO doped with CoPc fragments and it is hereafter abbreviated as RGO-CoPc.

### 2.4. Construction of the counter electrodes by deposition of RGO-CoPc

RGO/CoPc was dispersed (5 mg/ml) in isopropanol/water (2:1) mixture by sonication for 2 h. The mixture was spin-coated (1500 rpm for 30 s) as thin film on FTO electrodes. The procedure was repeated twice. Finally, the samples were annealed at 350 °C for 30 min to complete the counter electrode fabrication. The active surface was 0.4 × 0.4 cm<sup>2</sup>.

A counter electrode was also constructed by depositing standard Pt electrocatalyst for comparison. For this purpose, a solution of 0.02 M hexachloroplatinic acid in isopropanol was twice spin-coated (1000 rpm) on an FTO electrode and was annealed at 500 °C. The active surface was again 0.4 × 0.4 cm<sup>2</sup>.

### 2.5. Construction of nc-TiO<sub>2</sub> films on FTO electrodes and dye-adsorption (photoanode electrode)

FTO-coated glass substrates were cut in the desired dimensions (1.5 cm × 2 cm) and washed with mild detergent, distilled water and subsequently with ethanol and acetone in an ultrasonic bath, finally dried under air stream. A compact thin layer of TiO<sub>2</sub> was sprayed by aerosol spray pyrolysis using a solution of 0.2 M diisopropoxytitaniumbis(acetylacetonate) in ethanol and the samples were then heated for 1 h at 500 °C. Subsequently, a mesoporous TiO<sub>2</sub> layer composed of titania paste made of P25 nanoparticles was deposited by doctor blading on the above compact layer and calcined for 15 min at 500 °C. The last step was repeated two more times to obtain a film about 10 μm thick. Finally, a layer of TiCl<sub>4</sub> was deposited by dipping the patterned electrode in a solution of 0.04 M TiCl<sub>4</sub> in H<sub>2</sub>O for 30 min and annealed at 500 °C. The active area of the film matched that of the counter electrode, i.e. it was 0.4 cm × 0.4 cm. Then the integrated photoanode electrode was dipped in the solution of the dye (0.5 mM N719 dye in ethanol and 5 mM chenodeoxycholic acid) for 24 h. After completion of dye and additive adsorption, the samples were rinsed with ethanol, dried in a N<sub>2</sub> stream and used as photoanodes in DSSC.

### 2.6. Synthesis of the liquid electrolyte containing the redox couple I<sup>-</sup>/I<sub>3</sub><sup>-</sup>

The liquid electrolyte was synthesized by the standard procedure: 0.5 M 1-methyl-3-propylimidazolium iodide, 0.1 M lithium iodide, 0.05 M iodide and 0.5 M tert-butylpyridine were mixed

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