

Advanced Nanocarbons (Graphene, Nanodiamond and Beyond) as the Electrode Materials in Dye-Sensitized Solar Cells

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Abstract

The dye sensitized solar cell (DSC) also called the Graetzel cell [1] is an efficient, low-cost photovoltaic device achieving competitive parameters on the lab-scale, but its wide-scale commercialization still requires improvements. The cathode (counterelectrode) in DSC is usually a platinized F-doped SnO₂ (FTO) which, however, contributes by about >20-60% to the cost of the DSC-module. The search for cheaper cathode materials points at nanocarbons and graphene-based materials. [2,3] Graphene, graphene oxide (GO) and reduced graphene oxide find applications in solar cells as (i) active light-absorbing component, (ii) current collector, (iii) photoanode additive or (iv) catalytic counter electrode [3,4]. Graphene nanoplatelets (GNP) in the form of optically transparent films on FTO are useful counterelectrode material to replace Pt. [4,5] They exhibit good electrocatalytic activity towards I-based mediators particularly in ionic liquid medium. The triiodide/iodide couple can be also interchanged with Co(III/II)-based redox mediators. [6,7] The obvious motivation consists in enhancing the voltage of DSC, as well as in the decrease of the electrolyte optical absorbance to visible light. [8]

GNP exhibits high electrocatalytic activity for Co(III/II) based mediators [9,10], sometimes even outperforming the activity of Pt [10]. The exchange current densities scaled linearly with the electrode optical absorbance, and they were by 1-2 orders of magnitude larger than those for the I-based systems. Dye-sensitized solar cells achieved energy conversion efficiencies between 8 to 10 % for both GNP and Pt-based cathodes. However, the cell with GNP cathode is superior to that with Pt cathode particularly in fill factors and in the efficiency at higher illumination intensities. Graphene oxide showed almost no activity as DSC cathode, resembling the properties of basal plane pyrolytic graphite. However, the activity of GO improved dramatically upon reduction with hydrazine and/or heat treatment. The reduced GO/GNP composite films are favored by excellent adhesion to FTO and by higher stability against aging [11]. The state-of-art champion device with 13% efficiency used Co(bipy)₃ redox mediator and FTO-supported graphene nanoplatelets as the cathode catalyst. [12] Recently, the efficiency was boosted over 14% in a DSC device, using FTO-gold supported graphene nanoplatelets cathode and acetonitrile solution of Co(phen)₃^{3+/2+} redox mediator. [13]

To avoid expensive FTO in the cathode, an alternative material, which also works well with the I₃⁻/I⁻ redox mediator, is the woven fabric consisting of transparent PEN fibers in warp and electrochemically platinized tungsten wires in weft. [14] (Patented by Sefar AG: Peter Chabreck et al., European Patent Specification EP 2 347 449 B1, published 25.03.2015.) This electrode outperforms the platinized FTO in serial ohmic resistance, R_s (1.5 vs. 8.2 Ωcm²), charge-transfer resistance for triiodide reduction (0.59 Ωcm² vs. 0.76 Ωcm²) and offers comparable or better optical transparency in the visible and particularly in the near-IR spectral region (≈80%). The Pt-W/PEN cathode exhibits good stability during electrochemical load with the maximum (diffusion-limited) current both in cathodic and anodic directions, and during long term (≈months) storage at open circuit. The practical dye-sensitized solar cells with either Pt-W/PEN or Pt-FTO cathodes show similar performance, confirming that the former is a promising alternative for replacement of conductive glass in the DSC cathodes.

Spectral sensitization of diamond surface by organic dyes has been pioneered in 2008 by Zhong et al. [15] who anchored covalently dicyanovinyl-bithiophene and C₆₀-bithiophene through Suzuki coupling to H-terminated BDD. They observed photocurrents of ca. 120 nA/cm² under white light illumination (150 W halogen lamp) in aqueous electrolyte solution with dimethylviologen acting as the electron carrier. Later on, photocurrents of ca. 4-6 μA/cm² were observed in similar systems under 1 sun illumination. [16] Sensitization of BDD by manganese phthalocyanine [17,18] and Ru(SCN)₂(pbca)₂ (pbca = 2,2'-bipyridine, 4,4'-dicarboxylate) (commonly coded N3 dye) [19] provided rather low photocurrents, typically of the order of 1-10 nA/cm² under ca. 1 sun illumination. Yeap et al. [20] modified the diamond surface with thiophene derivatives through a combination of diazonium electrografting and Suzuki cross-coupling and observed photocurrents of ca. 150 nA/cm² under white light illumination (15 mW/cm² intensity). Krysova et al. [21] reported on non-covalent anchoring of 4-(bis-{4-[5-(2,2-dicyano-vinyl)-

thiophene-2-yl]-phenyl)-amino)-benzoic acid (coded P1) dye. In a two-step procedure, polyethyleneimine (PEI) was adsorbed on H-terminated BDD, and subsequently modified with P1. This dye is known to be successful for the sensitization of p-NiO. [22,23] Interestingly, the same P1 dye is applicable also for the sensitization of n-TiO₂ [23] which is reminiscent of the activity of N3 dye in both systems. [19] The P1-sensitized diamond electrode exhibited stable cathodic photocurrents under visible light illumination in aqueous electrolyte solution with dimethylviologen electron mediator. [21] The found photocurrents were about 100-150 nA/cm² at the white light intensity of 18 mW/cm². In spite of the simplicity of the surface sensitization protocol, the photoelectrochemical performance was similar or better compared to that of other sensitized diamond electrodes which were reported in previous studies. [15-21]

To enhance the roughness factor of the photocathode, a diamond foam was used instead of compact dense diamond films made by the standard chemical-vapor deposition (CVD). [24] The former was prepared via silica templating route and chemically modified with two donor-acceptor type molecular dyes. They were covalently anchored to the diamond surface through a phenyl linker. Chemical modification of the diamond surface was performed through a combination of diazonium electrografting and Suzuki cross-coupling reactions. Cathodic photocurrents under solar light illumination are about 3-times larger on foam electrodes compared to those on flat diamond. Illumination of the sensitized foam electrodes with chopped light at 1 sun intensity causes an increase of the cathodic photocurrent density to ca. 15-22 μ A/cm². Photocurrent densities scale linearly with light intensity (between 0.1 a 1 sun), and they represent the largest values reported so far for dye-sensitized diamond electrodes.

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