Diamond & Related Materials 89 (2018) 286–292

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Photocurrent generation of biohybrid systems based on bacterial reaction centers and graphene electrodes

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ARTICLE INFO

Keywords:
Bio-photovoltaics
Reaction centers
Single layer graphene
Multilayer graphene
Hybrid system
Charge transfer

ABSTRACT

The direct conversion of sunlight into chemical energy *via* photosynthesis is a unique capability of plants and some bacterial species. Aimed at mimicking this energy conversion process, the combination of inorganic substrates and organic photoactive proteins into an artificial biohybrid system is of a great interest for artificial bio-photovoltaic applications. It also allows to better understand charge transfer processes involved in the photosynthetic chain. In this work, single layer graphene (SLG) and multilayer graphene (MLG) electrodes are used as a platform for the immobilization of reaction centers (RCs) from purple bacteria *Rhodobacter sphaeroides*, a protein complex responsible for the generation of photo-excited charges. Electrochemical experiments with graphene electrodes and redox molecules reveal fundamental differences in the charge transfer processes for SLG and MLG films. We demonstrate that both graphene-based materials enable the immobilization of RCs without loss of functionality, attested by a photocurrent generation under illumination with IR-light at a wavelength of 870 nm. Furthermore, we report on the dependence of the generated photocurrent on the applied bias voltage, as well as on the presence of charge mediators in the surrounding electrolyte. This work demonstrates that SLG and MLG are a suitable platform for RC immobilization and subsequent photocurrent generation, suggesting a promising potential for graphene-based materials in bio-photovoltaics.

1. Introduction

A unique property of the photosynthesis process in green plants and some bacteria is the ability to convert solar energy into excited charge carriers with a high efficiency [1]. The fundamental biological components responsible for the energy conversion are the photosystems I, II (PS I and PS II) and the smallest photochemical unit, the so-called reaction center (RC). Aiming at developing a more profound understanding of the processes governing charge transfer between organic and inorganic systems, significant effort has been devoted to biohybrid systems based on inorganic electrodes and bacterial light-harvesting systems. A most recent overview about biohybrid photovoltaic systems can be found in [2]. In particular, previous investigations include the immobilization of photoactive proteins onto bare [3–6] and linker-modified gold electrodes [7–14]. It was shown that the use of modified gold electrodes for RCs binding lead to a more efficient photocurrent generation. Hereby, the RCs are oriented with their P-side to the substrate, supporting the charge transfer. In addition, it was shown that a rough *e.g.* silver surface compared to a smooth surface enhances the photocurrent generation due to a possibly higher protein loading [15]. Nevertheless, biohybrid systems based on metal electrodes have drawbacks, *e.g.* considering the transparency of the electrode. Alternatively, fluorine-doped tin oxide glass [16], indium tin oxide [17,18], titanium dioxide [19,20], carbon nanotubes [21], diamond [22] and graphene electrodes [23–25] have recently been explored as electrodes for light-harvesting systems. More particularly, biohybrid systems were realized by the formation of PS I multilayer either directly immobilized on transparent graphene [23] and reduced graphene oxide electrodes [24,26] or on π-system modified graphene electrodes [25]. Functionalized diamond electrodes with RCs [22], despite the differences in the mediators used, show a faster photoresponse when switching on and off the illumination, compared to transparent graphene electrodes with PS

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https://doi.org/10.1016/j.diamond.2018.09.005
Received 3 July 2018; Received in revised form 12 August 2018; Accepted 5 September 2018
Available online 06 September 2018

I [23]. However, higher photocurrent was generated upon light exposure of transparent graphene electrodes modified with PS I [24] and mercapto reduced graphene oxide electrodes modified with RCs [27] than for functionalized diamond electrodes [22]. The generation of photocurrent in bio-photovoltaics based on light-harvesting systems and inorganic substrates is furthermore enabled trough the presence of mediators in the surrounding electrolyte. Previous studies have shown that the use of two different charge transfer mediators in the electrolyte can enhance the photocurrent generation. One example are carbon-based electrodes in the presence of different quinones combined with cytochrome *c* [22,27] or ferrocene derivates [22,28]. Besides their good electrochemical performance, graphene and graphene oxide electrodes have the benefit of flexibility, transparency and scalability [29–31], which makes them a promising alternative to gold electrodes. Recently, RCs immobilized on transparent graphene oxide electrodes were used as biohybrid systems for photocurrent generation *via* light exposure in the presence of quinone and cytochrome *c* [27]. In this work, higher photocurrent densities than for modified diamond electrodes [22] were generated. In this context, the suitability of single layer (SLG) and multilayer graphene (MLG) electrodes as substrates for charge transfer processes and the effect of the RCs immobilization on the electrodes are demonstrated in the present work. Further, since the charge transfer mediators have a high impact on the photocurrent generation of the biohybrid systems, the influence of ubiquinone Q_0 and aminomethylferrocene (AmMeFc) as charge transfer mediators on the dominant charge transfer process, shown in Fig. 1(a), are investigated. In particular, the charge transfer in both graphene electrodes and their interaction with the redox molecule AmMeFc is explored by electrochemical studies. Furthermore, photocurrent generation during IR-light exposure is studied for modified graphene electrodes in the presence of Q_0 and AmMeFc. Additionally, we report on the dependence of photocurrent generation during illumination on the voltage applied across the biohybrid device, as well as on the long-time light exposure stability.

2. Results and discussion

The well-characterized structure and charge transfer mechanism in RCs from purple bacteria [32–35] make them a suitable protein for biomimetic photocurrent generation studies. The energy levels of the biohybrid system used in this work are depicted in Fig. 1(a). The illumination of the system leads to a charge separation in the RCs, generating a hole in the P-state and an excited electron in the P*-state. The excited electron is transferred *via* the chlorophylls B_A and H_A, and the bound quinone Q_A to the free ubiquinone Q_0. The coenzyme Q_0 is released as ubihydroquinone QH_2 into the environment carrying two excited electrons. The hole in the P-state is filled by a ground state electron, which is ultimately supplied by the graphene electrode. It was found that the use of ferrocene as the supplier of the ground state electron leads to a faster photocurrent response with higher photocurrent values [6,22].

For the preparation of the graphene electrodes, SLG and MLG were

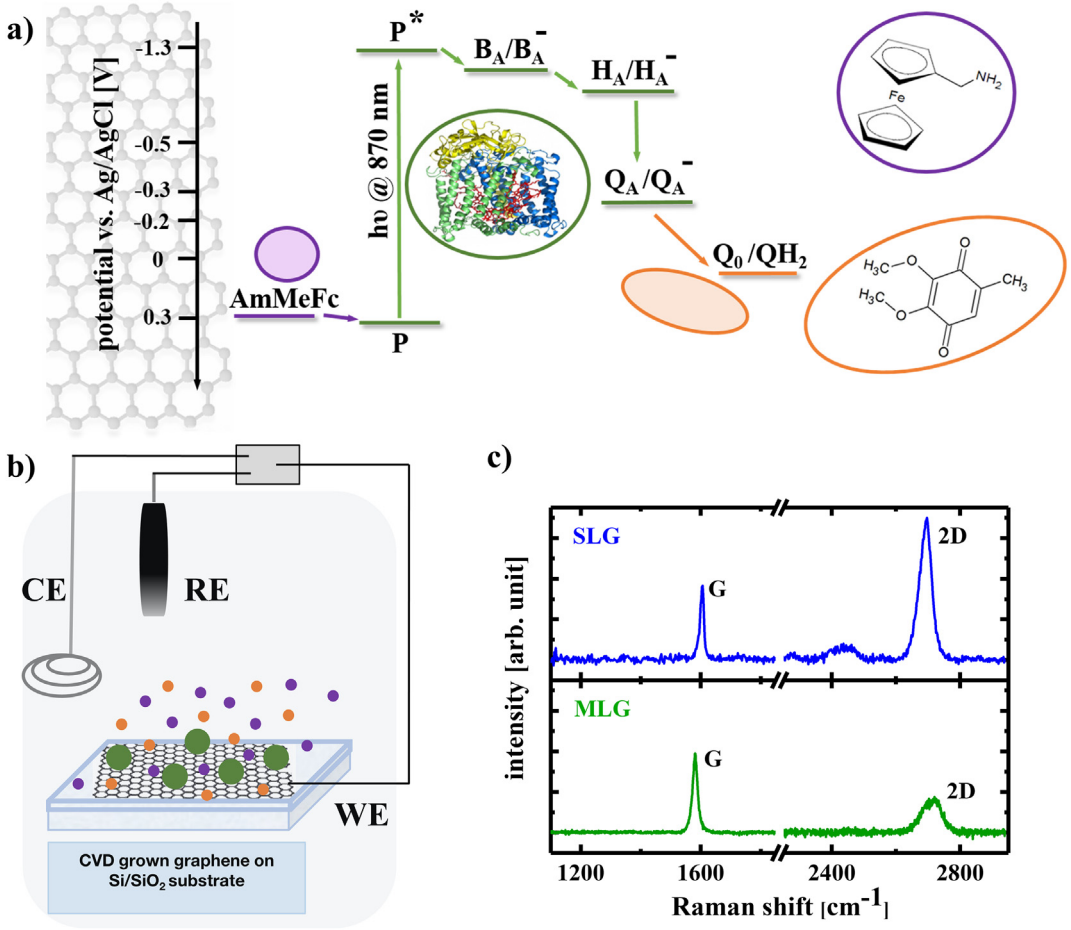

Fig. 1. (a) Energy levels of the biohybrid system based on graphene electrodes with physisorbed bacterial reaction centers (RCs) *vs.* Ag/AgCl. The energy levels for the charge transfer inside the RCs (green) as well as for AmMeFc (violet) and Q_0 (orange) are depicted. (b) Electrochemical setup with a three-electrode configuration: working electrode (graphene electrode), counter electrode (platinum wire) and reference electrode (Ag/AgCl). (c) Raman spectroscopy of single layer graphene (SLG, blue line) and multilayer graphene (MLG, green line) electrodes revealing the characteristic G and 2D bands, of graphene-based materials. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)