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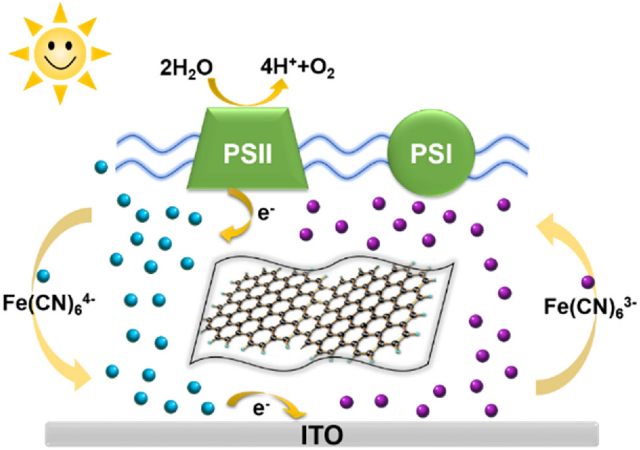
Co-assembly of thylakoid and graphene oxide as a photoelectrochemical composite film for enhanced mediated electron transfer

Peng Cai[a,b,c], Guangle Li[b], Yang Yang[d], Xiaoou Su[c], Zhongfeng Zhang[a,*]

[a] Tobacco Research Institute of Chinese Academy of Agricultural Sciences, Qingdao 266101, China
[b] Beijing National Laboratory for Molecule Sciences, CAS Key Lab of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[c] Institute of Quality Standard and Testing Technology for Agricultural Products, Chinese Academy of Agricultural Sciences, Beijing 100081, China
[d] CAS Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, National Center for Nanoscience and Technology, Beijing 100190, China

GRAPHICAL ABSTRACT



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ABSTRACT

Nature provides us the most effective way of harnessing solar energy, that is photosynthesis. The investigation of natural photosynthetic components integrated electrodes for the construction of photoelectrochemical cells has attracted more and more attention. However, the efficiency of assembled systems still be plagued by the complex and unclear electron transfer process. In this research, thylakoid membrane was integrated with graphene materials for the construction of photoelectrochemical cells and photocurrent of mediated electron transfer was investigated. Moreover, the main route of electron transfer within the composite film modified electrode was discussed. The functional groups and structural support of graphene oxide could increase local mediator concentration and accelerate diffusional mass transport, thus enhancing the photocurrent density.

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[*] Corresponding author.
E-mail address: zhangzhongfeng@caas.cn (Z. Zhang).

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1. Introduction

Photosynthesis is known to be the most important reaction on the earth which has evolved for billions of years. It happens in the thylakoid membrane (TM) of higher plant, algae and cyanobacteria. The highly effective mechanism of photosynthesis to split water under visible light provides a wonderful blueprint for the construction of artificial solar energy conversion systems. Apart from the enormous efforts devoted to the fabrication of artificial photosynthetic systems based on metal, metal oxide and organometallic compounds [1–4], the immobilization of natural photosynthetic components towards photoelectrochemical cells has attracted more and more attention [5–8]. Different materials have been integrated with photosynthetic components and various immobilization strategies have been developed [9]. However, according to our previous report [10–12], the efficiency of assembled systems still falls far behind that *in vivo* related to the complex electron transfer route, unclear electron transfer mechanism as well as a lack of photostability.

Light-harvesting photosynthetic reaction centers (RCs), i.e., photosystem II (PSII) and photosystem I (PSI) have been commonly used as building blocks for photoelectrode assembly [13,14]. For example, a hybrid photoanode integrating PSII with benzoquinone doped polypyrrole was constructed via a self-assembly approach. Photocurrent was significantly enhanced because of the nanostructured polymer with excellent conductivity and redox property [15]. Wang et al. presented a hybrid photoanode integrating PSII with a hematite film for water oxidation, the electrons generated from PSII multilayers were injected into the valance band of the excited Ti/Fe_2O_3 and significantly enhanced photocurrent was observed [16]. Systems combined PSII with PSI to realize Z-scheme electron transfer *in vitro* have also showed great promise [17,18]. Although isolated RCs possess easier electrochemical accessibility, they are also subjected to relatively complex purification process and instability compared to TM [7]. In addition, the commonly used noble metals for coupling with PSII or PSI restrict the large-scale application of photoelectrochemical cells.

Graphene materials, such as graphene oxide (GO) and reduced graphene oxide (rGO) have been widely used for solar energy conversion systems, but mostly combined with synthetic photocatalyst [3,19]. The unique optical and electrical properties together with low cost and easy to obtain make graphene materials attractive candidates for the integration with natural photosynthetic components. Our previous investigation has demonstrated the superiority of rGO in enhancing direct electron transfer from PSII to the electrode [20]. Furthermore, considering the benefit of diffusional electron acceptor, which can theoretically shuttle electrons from all active proteins to the electrode despite the orientation of PSII [9], it is of great interest to investigate the potential role of graphene materials in mediated electron transfer (MET) process.

Herein, we report a facile construction of hybrid photoanodes integrating TM with GO or rGO via a self-assembly approach. The MET photocurrent of the composite film modified electrodes in the presence of electron mediator was investigated. It has been experimentally demonstrated that GO-TM film exhibited the most superior photoelectrochemical activity. Moreover, the main route of electron transfer within the modified electrode was discussed.

2. Experimental

2.1. Materials and methods

Polyallylamine hydrochloride (PAH), average Mw ~58000, 2-morpholinoethanesulfonic acid (MES), bovine serum albumin (BSA), graphite powder, 325 mesh, potassium ferrocyanide trihydrate, paraquat dichloride hydrate and 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU) were purchased from commercial suppliers and used without any purification.

The suspensions of TM, GO and rGO were characterized by UV–vis absorption spectra (Hitachi U-3010). The functional groups of GO and rGO were investigated by FTIR (Bruker EQUINOX 55/S). The morphology of TM, GO, rGO, TM film, GO-TM film and rGO-TM film was observed by SEM (Hitachi S4800) and AFM (Bruker Dimension FastScan). TEM (JEOL JEM-2011) was also used for the morphology observation of GO and rGO. The cyclic voltammetry of $K_4Fe(CN)_6$ with the concentration of 1.5 mM was carried out by using an electrochemical workstation (CHI 660D) with the initial potential of −0.2 V and the scan rate of 50 mV s^{-1} in the electrolyte buffer solution (pH = 6.5, 20 mM MES, 50 mM KCl, 5 mM $MgCl_2$, and 3 mM $CaCl_2$) at 25 °C.

2.2. Synthesis of GO

GO was synthesized from natural graphite according to a modified Hummers method [20]. Typically, 3.0 g graphite powder was added into 70 mL of concentrated H_2SO_4 (98%) and stirred for 5 min. The mixture was then transferred into an ice bath and 1.5 g $NaNO_3$ was added. With vigorously stirring, 9.0 g $KMnO_4$ was added very slowly (about 0.5 g min^{-1}) to keep the temperature below 10 °C. After stirred for 2 h, the mixture was put at room temperature and kept stirring for another 5 days. Then, 140 mL of deionized (DI) water was added to the mixture and stirred for 15 min. Afterwards the mixture solution was further diluted by 500 mL of DI water under vigorous stirring. 20 mL of H_2O_2 (30%, wt) was then added to the mixture and the colour of the solution changed from dark brown to brilliant yellow with bubbling. The mixture was centrifuged and washed with 1:10 HCl/water solution (250 mL) and DI water by centrifugation until the pH of the suspensions was between 6.0 and 7.0. Finally, the product was dialyzed for 1 week to remove impurity atoms and then freeze-dried until further use.

2.3. Synthesis of rGO

For the reduction of GO with PAH, 0.25 mg mL^{-1} GO sheets were dispersed in water and ultra-sonicated for 30 min. The resultant aqueous GO dispersion (40 mL) was mixed with 40 mL of 4 mg mL^{-1} PAH aqueous solution, and the mixed solution was then stirred at 60 °C for 12 h. After cooled to room temperature, 120 μL of hydrazine monohydrate (85%) solution was added to the resulting dispersion. After being vigorously shaken, the reaction system was put in an oil bath at 95 °C for 12 h. After reaction, extra PAH and hydrazine hydrate were removed by repeated centrifugation at 14,000 rpm for 10 min and washed three times. And the obtained rGO was re-dispersed in DI water for further use.

2.4. Purification of TM

TM were isolated and purified from chloroplasts of spinach, according to reported method with modifications [20]. In brief, 100 g of spinach leaves were homogenized in blender together with 200 mL of buffer A (20 mM Tricine-NaOH pH 7.8, 0.35 M NaCl, 1 mM $MgCl_2$, 1 mM $MnCl_2$, 2 mM EDTA, 0.2% BSA). The mixture was filtered with eight layers of cotton gauze and the obtained filtrate was centrifuged at 200 g for 2 min. Then, chloroplasts were collected by centrifuging the supernatant at 1000 g for 7 min. The obtained chloroplasts were resuspended in a hypotonic buffer B (20 mM Tricine-NaOH pH 7.8, 10 mM $MgCl_2$, 0.2% BSA). After stirring for 15 min, buffer C (40 mM Tricine-NaOH pH 7.8, 0.7 M NaCl, 2 mM $MgCl_2$, 2 mM $MnCl_2$, 4 mM EDTA, 0.4% BSA) with the same volume of buffer B was added and the chlorophyll concentration of obtained TM was determined according to the following equation:

$$c_{\mathrm{chlorophyll}}\ (\mu\mathrm{g\ mL^{-1}}) = 8.02 \times (\mathrm{Abs}_{663} - \mathrm{Abs}_{720}) + 20.21 \times (\mathrm{Abs}_{645} - \mathrm{Abs}_{720})$$