



# Photoelectrocatalytic oxidation of ascorbic acid and electrocatalytic reduction of dioxygen by polyaniline films for renewable energy conversion



Junchen Liu, Shuojian Lu, Xinghui Liang, Qiting Gan, Yi Wang, Hong Li \*

Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

## ARTICLE INFO

### Article history:

Received 13 July 2015

Received in revised form 10 January 2016

Accepted 11 January 2016

Available online 12 January 2016

### Keywords:

Polyaniline

Ascorbic acid

Spectroelectrochemical analysis

Photoelectrochemical fuel cell

## ABSTRACT

A honeycomb-structured polyaniline (PANI) film is used to simultaneously promote the photoelectrocatalytic oxidation of ascorbic acid (AA) and electrocatalytic reduction of dioxygen ( $O_2$ ). The in situ spectroelectrochemical evidences suggest that the PANI film controlled between  $-0.20$  and  $0.70$  V shows four transformable redox forms, among which emeraldine base (EB) and leucoemeraldine base (LEB) can mediate the oxidation of AA and the reduction of  $O_2$ , respectively. The EB-based electrode exhibits good linear spectral absorbance and/or photovoltaic responses to AA between  $0.01$  and  $1.0$   $mmol\ L^{-1}$  with high sensitivity and good reproducibility. The LEB-based electrode shows a good linear potentiometric response to  $O_2$  permeation flux rate between  $10$  and  $60$   $mL\ min^{-1}$ . Furthermore, the CdS nanoparticles and carbon felt (CF) are used to support the PANI film for the preparation of PANI/CdS anode and PANI/CF cathode. The assembled photoelectrochemical fuel cell driven by visible light shows an open-circuit photovoltage of  $0.614$  V, short-circuit photocurrent density of  $125.55\ \mu A\ cm^{-2}$ , maximum power density of  $19.05\ \mu W\ cm^{-2}$  at  $0.492$  V, fill factor of  $0.24$  and photoenergy conversion efficiency of  $10.58\%$ . The present study provides a new approach for the utilization of renewable energy sources.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Considerable efforts are made to discover effective techniques for the conversion and utilization of renewable energy resources because of rising energy demands and long term depletion of fossil fuels [1,2]. The semiconductor-based photovoltaic device [3], dye-sensitized solar cell [4,5], photocatalytic solar cell [6] and biofuel cell [7] have been used to realize the conversion efficiency of abundant solar energy and biomass energy [8,9]. A photoelectrochemical fuel cell, which is regarded as a combination of fuel cell technologies with photoelectrocatalysis, shows advantages for renewable energy conversion [10–12]. In this system, the fuel is oxidized on a photoanode, which consists of traditional semiconductors (e.g.  $TiO_2$ , CdS, ZnO and  $SnO_2$ ) and photosensitizers [13–16]. There are two kinds of commonly used photosensitizers. One is composed of small molecules with a rigid substantially planar conjugated aromatic structure, such as ruthenium polypyridyl complex, porphyrin and metal porphyrin, and the other is the electronically conducting polymer [17–20]. Polyaniline (PANI) has been served as a redox-active  $\pi$ -conjugated polymer to enhance the electron separation efficiency of semiconductor-based photoanodes and to simultaneously suppress their photocorrosion in a dye-sensitized solar cell [21–23]. Despite the fact that there are many researches on nanostructured PANI/metal oxide composites used as

anode of microbial fuel cells or cathode of dye-sensitized solar cells [24–26], it would be of value to know whether PANI could be used to decorate a photoanode for its applications in photoelectrochemical fuel cells.

As a high-performance photoelectrochemical fuel cell, it needs to use an effective anodic electrocatalyst, which usually consists of noble metals or metal oxides, enzymes and/or microbes [27]. PANI belongs to a class of organic conductive polymers prepared by chemical or electrochemical oxidation of aniline monomers [28,29]. It has been chosen as one of the most promising electrocatalysts due to its several advantages including low cost, high visible light-harvesting efficiency, stability and biocompatibility [30–32]. However, some of the fuels are difficult to be electrocatalytically oxidized by PANI [33–35]. Ascorbic acid (AA) is a biologically important compound with antioxidant properties, and has been suggested as a promising fuel [36,37]. In comparison with methanol fuel, AA soluble in acidic aqueous solutions may be electrochemically oxidized using either Pt-group metals or PANI-based polymers as the catalysts [38–41]. Additionally, a PANI-based polymer film has been used as cathodic catalysts to displace Pt-group metals to promote the reduction of dioxygen ( $O_2$ ) for fuel cell applications [42–44]. To sum it up, a number of researchers have reported the synthesis, characterization and electrocatalytic performance of PANI by means of various electrochemical techniques [45–47], there are no reports on the PANI-based bifunctional electrocatalysis for photoelectrochemical fuel cells.

In the current work, we first concentrate on the bifunctional electrocatalysis of PANI towards the oxidation of AA and the reduction

\* Corresponding author.  
E-mail address: [lihong@scnu.edu.cn](mailto:lihong@scnu.edu.cn) (H. Li).

of O<sub>2</sub>. The PANI film controlled between  $-0.20$  V and  $0.70$  V yields four transformable forms, among which emeraldine base (EB) and leucoemeraldine base (LEB) show high bifunctional electrocatalytic responses for the potentiometric determination of AA and O<sub>2</sub>. Because PANI is sensitive to the visible light irradiation, another great attempt is made to assemble a high-performance photoelectrochemical AA/O<sub>2</sub> fuel cell driven by visible light using CdS nanoparticles and carbon felt (CF) to support the PANI films as photoanode and cathode. It is anticipated that the present study will be of interest to readers in the fields of photoelectrocatalysis and renewable energy source.

## 2. Experimental section

### 2.1. Materials

Unless otherwise noted,  $0.5 \text{ mol L}^{-1}$  sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) was used as an electrolyte solution, which was prepared with doubly distilled water. The fresh aniline monomer from Damao Chemical Reagent Factory (Tianjing, China), ascorbic acid (AA) from Qiyun Biotechnique Co. (Guangzhou, China), cadmium chloride (CdCl<sub>2</sub>), sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) and other reagents were used as received.

### 2.2. Preparation of PANI/indium tin oxide (ITO) and PANI/carbon felt (CF) electrodes

An ITO glass sheet (coating  $90 \text{ nm}$ , resistance  $20 \Omega \text{ sq}^{-1}$ , Nanbo Co., Shenzhen, China) or CF sheet was employed as the working electrode, while a platinum sheet was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Aniline was polymerized onto the surface of ITO or CF ( $0.8 \text{ cm}^2$ ) by repetitive cyclic voltammetry of 15 cycles between  $-0.20$  and  $0.90$  V with  $0.05 \text{ V s}^{-1}$  in  $0.5 \text{ mol L}^{-1}$  H<sub>2</sub>SO<sub>4</sub>/ $0.2 \text{ mol L}^{-1}$  aniline [48]. The resulting electrode was kept at a constant temperature of  $40 \text{ }^\circ\text{C}$  for 12 h. Prior to each measurement, set the PANI-modified electrode in electrolyte solutions to perform cyclic voltammetric measurement of 10 cycles between  $-0.20$  and  $0.70$  V at  $0.01 \text{ V s}^{-1}$  in order to obtain an identical PANI surface.

### 2.3. Preparation of PANI/CdS/ITO electrode

Following a previously published procedure [49], the CdS/ITO electrode was first prepared by 100 cycles of cyclic potential scanning between  $-0.3$  and  $-0.9$  V (vs. SCE) at  $0.05 \text{ V s}^{-1}$  scan rate in a homemade three-electrode cell filled with  $0.01 \text{ mol L}^{-1}$  CdCl<sub>2</sub>/ $0.1 \text{ mol L}^{-1}$  Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (pH 2.0). The CdS/ITO electrode was kept at a constant temperature of  $40 \text{ }^\circ\text{C}$  for 2 h, and its effective surface area of  $0.82 \text{ cm}^2$  was determined by cyclic voltammograms of  $1.0 \text{ mmol L}^{-1}$  K<sub>4</sub>[Fe(CN)<sub>6</sub>] in  $1.0 \text{ mol L}^{-1}$  KCl with the diffusion coefficient of  $6.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [50]. The PANI film was electrodeposited onto the CdS/ITO electrode by 10 cycles of cyclic potential scanning between  $-0.20$  and  $0.90$  V (vs. SCE) at  $0.05 \text{ V s}^{-1}$  in  $0.01 \text{ mol L}^{-1}$  H<sub>2</sub>SO<sub>4</sub>/ $0.2 \text{ mol L}^{-1}$  aniline.

### 2.4. Preparation of PANI<sub>LEB</sub>, PANI<sub>ES</sub> and PANI<sub>EB</sub> films

While potentiostatically controlling the PANI-decorated electrode at  $-0.20$  V,  $0.35$  V and  $0.70$  V (vs. Ag/AgCl) for 60 s in  $0.5 \text{ mol L}^{-1}$  H<sub>2</sub>SO<sub>4</sub>, respectively, the PANI<sub>LES</sub> (leucoemeraldine salt)/PANI<sub>LEB</sub> (leucoemeraldine base), PANI<sub>ES</sub> (emeraldine salt) and PANI<sub>EB</sub> (emeraldine base) films were formed [45,51].

### 2.5. Fabrication of potentiometric sensors

A potentiometric sensor was fabricated for the determination of AA and oxygen using PANI<sub>EB</sub>/ITO and PANI<sub>LEB</sub>/CF as indicating electrodes,

and an Ag/AgCl electrode with saturated KCl salt bridge as the reference electrode.

### 2.6. Assembly of visible light-activated fuel cells

The visible light-activated AA/O<sub>2</sub> fuel cell is schematically shown in Fig. 1. The anodic and cathodic compartments were connected with a U-shaped saturated KCl salt bridge. The PANI<sub>LEB</sub>/CdS/ITO and PANI<sub>EB</sub>/CF electrodes were employed as the photoanode and cathode, respectively. The two compartments were filled with electrolyte solutions containing  $0.2 \text{ mol L}^{-1}$  AA and injecting  $60 \text{ mL min}^{-1}$  O<sub>2</sub>, respectively. The tungsten halogen lamp was employed as a stable source of visible light mostly located between 400 and 1100 nm, and its power density irradiated on the photoanode was ca.  $0.18 \text{ mW cm}^{-2}$ .

### 2.7. Experimental methods and conditions

Electronic absorption spectra were measured using a UV-1700 spectrophotometer (Shimadzu, Japan). Voltammetric measurement was performed using a CHI660a electrochemical system (Shanghai, China) in a three-electrode cell. Unless otherwise stated, the modified electrode was employed as the working electrode, while a platinum sheet was used as counter electrode and an Ag/AgCl electrode with saturated KCl salt bridge as the reference electrode. In situ spectroelectrochemical monitoring was performed in a three-electrode quartz cell. A Zeiss Ultra55 field-emission scanning electron microscope (SEM, Germany) was employed to analyze the surface appearance of the PANI-decorated electrodes. All the experiments were carried out at room temperature ( $25\text{--}27 \text{ }^\circ\text{C}$ ).

## 3. Results and discussion

### 3.1. Photoelectrocatalytic activity of PANI towards the oxidation of AA

Cyclic voltammograms (CVs) of PANI/ITO electrode in electrolyte solutions are given in Fig. 2a, showing two pairs of redox peaks (peaks I and II). Compared with CVs in the absence of AA and/or PANI, an oxidative peak enhanced by AA appears in the potential range from  $0.35$  to  $0.70$  V. Combined with the previously reported results from the in situ spectroelectrochemical measurement of PANI/ITO electrode controlled at different applied potentials in an acidic medium [52,53], the cyclic voltammograms are divided into two areas. One corresponds to the redox transformation from PANI<sub>LEB</sub> (and/or PANI<sub>LES</sub>) to PANI<sub>ES</sub> in the potential range between  $0.01$  and  $0.35$  V [54], and the other shows the deprotonation of PANI<sub>ES</sub> to form PANI<sub>EB</sub> between  $0.35$  and  $0.70$  V [55, 56]. The end product of PANI oxidation would be the totally pernigraniline quinoid form, which is non-conducting, allowing us to

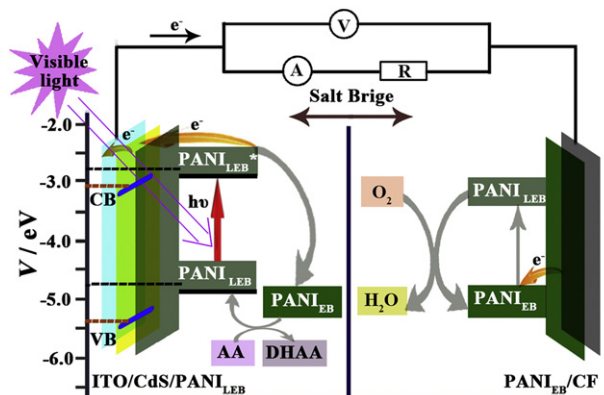


Fig. 1. Schematic configuration and electron transfer processes of a photoelectrochemical AA/O<sub>2</sub> fuel cell employing PANI<sub>LEB</sub>/CdS/ITO photoanode and PANI<sub>EB</sub>/CF cathode.

Download English Version:

<https://daneshyari.com/en/article/218055>

Download Persian Version:

<https://daneshyari.com/article/218055>

[Daneshyari.com](https://daneshyari.com)