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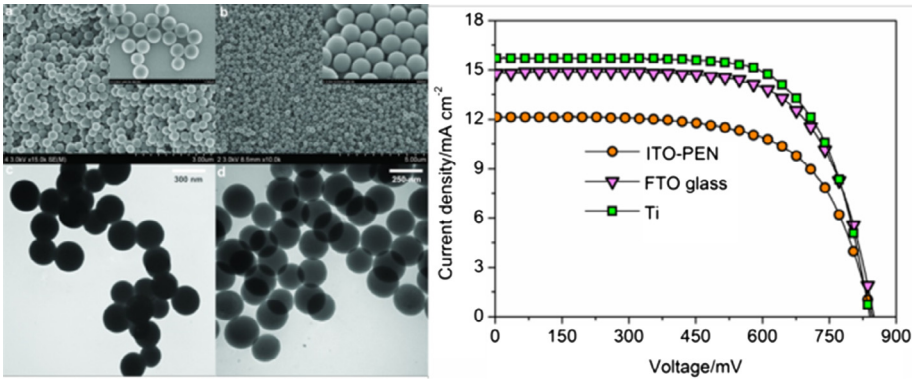
Highly effective carbon sphere counter electrodes based on different substrates for dye-sensitized solar cell

Qianji Han, Hongrui Wang, Yali Liu, Yajing Yan, Mingxing Wu *

College of Chemistry and Material Science, Key Laboratory of Inorganic Nano-materials of Hebei Province, Hebei Normal University, No. 20 Rd. East of 2nd Ring South, Yuhua District, Shijiazhuang City, Hebei 050024, China

GRAPHICAL ABSTRACT



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ABSTRACT

A monodisperse carbon sphere with high uniformity, high catalytic activity and conductivity are successfully synthesized. Versatile counter electrodes using this carbon sphere catalyst on different substrates of fluorine-doped tin oxide (FTO) glass, indium-doped tin oxide polyethylenena phthalate (ITO-PEN), and Ti foil are fabricated for dye-sensitized solar cell (DSC). The impacts of substrates on the catalytic activities of the carbon sphere counter electrodes have been also evaluated by electrochemical analysis technologies, such as cyclic voltammetry, electrochemical impedance spectroscopy and Tafel polarization curves. With cobalt electrolyte, the DSC using carbon sphere counter electrodes based on FTO glass, ITO-PEN, and Ti substrates yield high power conversion efficiency values of 8.57%, 6.66%, and 9.10%, respectively. The catalytic activities of the prepared carbon sphere counter electrodes on different substrates are determined by the apparent activation energy for the cobalt redox couple regeneration on these electrodes.

1. Introduction

How to transfer the clean and abundant solar energy to the convenient electric energy cleanly and effectively has a direct bearing on human destiny and the sustainable development of both environment and the mankind. Among so many photoelectric devices, the dye-sensitized solar cell (DSC) is widely studied because of the merits of simple assembly process, flexibility, transparency, and high power conversion efficiency (PCE) under lower irradiation. Generally, DSC consists three parts: photoanode, electrolyte (containing redox couple) and counter electrode (CE).

* Corresponding author.
E-mail address: mingxing.wu@hebtu.edu.cn (M. Wu).

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Generally, as a critical part, the CE is fabricated with a catalytic material deposited on a conductive substrate. The catalytic material works as a catalyst toward the redox couple regeneration, while the conductive substrate is used to collect the photoelectrons from the external circuit.

Up to now, the common used CE catalytic material is still Pt [1,2]. However Pt is expensive with limited reserves, therefore it cannot be widely used in commercial application. To overcome this issue, several Pt-free CE catalytic materials, such as carbon materials [3,4], polymers [5,6], and metal compounds [7,8] have been explored to replace the expensive Pt. Among them, the carbon materials have the advantages of low cost, high catalytic activity, high conductivity, high thermal stability and corrosion resistance, and the authors consider that carbon materials are potential CE catalysts to replace Pt in commercial application. To data, so many kinds of carbon materials have been applied in DSC, such as activated carbon [9], carbon black [10], carbon nanofibers [11], ordered mesoporous carbon and so forth [12–14]. Recently, we applied a novel kind of carbon sphere (CS) CE on fluorine-doped tin oxide (FTO) glass and found that the CS CE show great potential to replace the expensive Pt [15]. In addition, this kind of CS can be also used in gas absorption, drug delivery, lithium ion batteries, and fuel cells due to the merits of uniformity, conductivity, and thermal stability, and large surface area/volume ratios [16–21].

The substrate is also a key part of a CE, and the most common used one is the FTO glass [22]. However FTO glass is expensive with low conductivity and poor flexibility and several cheaper metal foil substrates with high conductivity have been developed [23]. Moreover, the metal foil can be used as flexible substrate. To embody the merits of both transparency and flexibility of DSC, transparent plastic substrates are required, such as indium-doped tin oxide polyethyleneterephtalate (ITO-PET) or polyethylenena-phtalate (ITO-PEN). The merits of flexibility and lightweight make the plastic and metal foil substrate fit for roll-to-roll type production in commercial application. We can say that the substrates of the DSC determines the application fields to some extent and compare the catalytic performance of the CE based on different substrate is crucial for practical application. However, very few special comparison researches on the CE substrates at the same conditions can be found. In this work, the potential CS CE is prepared on different substrates in DSC and the impact of the substrates on the catalytic activities is also investigated through the electrochemical tools of the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Tafel polarization curves. The electrochemical results show that the CS CE on Ti foil behaves better than those on FTO glass as well as ITO-PEN substrates. The DSC using CS CE on Ti foil presents the highest PCE of 9.10%, stemming from the lowest apparent activation energy of the cobalt redox couple regeneration on this kind of electrode.

2. Experimental

2.1. Preparation of carbon sphere

The carbon sphere (CS) was synthesized according to our previous work [15]. First, resorcinol (220 mg) was dissolved in deionized water (400 mL) under stirring at 25 °C, and added F127 (100 mg) and formaldehyde (300 μL, 37%), achieving a clear solution. Then put 1,2-diaminohexane (60 mg, DAH) into the above solution, and the clear solution became white colloidal. Next, heat the solution to 80 °C and keep 12 h under string and a polymer (phenolic resin, PR) precursor was collected by centrifugation with water. Finally, CS was obtained by pyrolysis of the polymer precursor at 800 °C for 2 h under a N_2 atmosphere.

2.2. Cell fabrication

CS powder (20 mg) was dispersed in 5 mL of isopropanol under ultrasonic dispersion for 30 min, producing a CS suspension. The prepared CS suspension was then sprayed onto the substrate of FTO glass, ITO-PEN, or Ti foil. The FTO glass or Ti foil coated with CS film was then sintered under N_2 atmosphere at 400 °C for 30 min, yielding the CS electrode on FTO glass or Ti foil substrate. The ITO-PEN coated with CS film was sintered under N_2 atmosphere at 120 °C for 30 min, generating the CS electrode on ITO-PEN substrate. The thickness of CS film was controlled around 20 μm by spray time. The photoanode is 5 μm-thick layers of TiO_2 particles (Ti-NanoxideD, Solaronix, Switzerland) sensitized with YD2-o-C8 dye. The DSC consists of a photoanode, a CE, and an electrolyte. Symmetrical cell was fabricated with two identical CEs clipping the electrolyte for EIS and Tafel polarization tests. The cells were sealed with a hot melt surlyn film. The cobalt electrolyte is composed of 0.25 M Co (II) tris(bipyridyl) tetracyanoborate, 0.05 M Co(III) tris (bipyridyl) tetracyanoborate, 0.5 M TBP, and 0.1 M LiTFSI in acetonitrile.

2.3. Measurement

IR spectra are conducted with a fourier infrared spectroscope (FTIR-8900SHimadzu, Japan). The morphologies of CS are characterized by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, H-7650, Hitachi, Japan). X-ray diffraction (XRD) measurement is carried out using an automatic X-ray powder diffractometer (D8/advance, Bruke Corporation, Germany). The surface chemical state of the CS is checked by XPS spectrometer (ESCALAB250, Thermo VG, USA). N_2 adsorption–desorption isotherm is carried out using automated surface area analyze (NOVA4000e, Quantachrome, USA), and the surface area is calculated by the Brunauer-Emmett-Teller (BET) method. Raman spectral analysis is conducted using visible excitation at 532 nm with Raman Microscope and Spectrometer (Renishaw inVia Reflex). The photovoltaic performance of the DSC is investigated under simulated AM 1.5 illumination (I = 100 mW cm^{-2}, Peccell, Yokohama, Japan). Cyclic voltammetry (CV) measurements are conducted in a three-electrode system in an argon-purged electrolyte solution at a scan rate of 20 mVs^{-1} using an electrochemical workstation (CHI 660E, Chenhua, Shanghai). Pt wire serves as the counter electrode and AgCl/Ag as the reference electrode. The $Co^{3+/2+}$ electrolyte contains 10 mM Co^{2+}, 1 mM Co^{3+}, and 0.1 M $LiClO_4$ in acetonitrile. EIS experiments are performed using symmetrical cells and the measured frequency ranges from 0.1 Hz to 100 K Hz. The test temperatures are set at −20, −10, 0, and 15 °C. The amplitude of the alternating current is set at 5 mV. Tafel polarization measurements are tested with a symmetrical dummy cell and the scan rate is set at 10 mV s^{-1}.

3. Results and discussion

3.1. Synthesis and characterization of phenolic resin and carbon sphere (PR and CS)

In the preparation of CS section, FTIR spectroscopy was conducted to confirm the formation of the precursor (phenolic resin, PR) and CS. Fig. 1a is the corresponding FTIR spectra. It can be observed that a broad band at 3450 cm^{-1} in the spectra of PR, which corresponds to the stretching vibration of the —OH groups [24]. The two peaks in 1492 cm^{-1} and 1690 cm^{-1} are the vibration of C=C of PR. The vibrational stretching peaks of the aromatic ether appear at 1103 and 1232 cm^{-1}, which are characteristic for the precursor PR. The weak bands at 2850–2970 cm^{-1} refer to the alkyl