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Application of non-covalent functionalized carbon nanotubes for the counter electrode of dye-sensitized solar cells

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were functionalized noncovalently by lysozyme (LZ), cetyl pyridinium chloride (CPC), deoxycholate sodium (NaDC) and polyethylene glycol octylphenol ether (Triton X-100), respectively in this study. Four different kinds of functionalized MWCNTs were employed into dye-sensitized solar cell (DSSC) as the Pt-free counter electrode (CE). The correlation between the dispersion of MWCNTs and electrochemical active area of CE and the photovoltaic characteristic of DSSC were investigated. Among these four DSSCs, the one with Triton X-100 functionalized MWCNTs showed the best energy conversion efficiency of 2.69% which is 11.16% higher than the DSSC using pristine MWCNTs CE (2.42%), yet the efficiency is lower than the DSSC using Pt CE. While the DSSC with CPC, NaDC and LZ functionalized MWCNTs as the CE showed inferior the photovoltaic conversion efficiency than the DSSC using pristine MWCNTs CE. On analysis of the photovoltaic performance of DSSC and the dispersion of MWCNTs and electrochemical active area of CE, it is found that the high efficiency of the DSSC is associated with the good dispersion of MWCNTs and large electrochemical active area of the counter electrode material.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention since their discovery in the early 1990s [1], owing to their low cost, environmental friendliness, good performance in weak light conditions, and simple manufacturing processes [2–8]. The counter electrode (CE) of DSSCs is one of the key components in DSSCs. Platinum (Pt) has been considered as standard CE material because of its superior electrochemical catalytic activity, good corrosion resistance, small resistance, large electrochemical active area and high reflecting properties [7–10]. However, in practice, Pt CE is expensive and impractical for the large-scale device fabrication. Therefore, several alternatives [11–15] have been explored to replace Pt as the counter electrode for DSSCs.

Carbon nanotubes (CNTs) are an allotrope of carbon with long, hollow cylindrical nanostructure and formed by rolling graphene layers. Owing to the special structure, CNTs possess large specific surface area, good chemical stability, excellent electronic properties, and remarkable electrocatalytic activities. Therefore, CNTs have been used as the CE in DSSCs instead of Pt, and some good results have been obtained [16–18]. However, CNTs have a very high tendency to form agglomerates because of the high aspect ratio of CNTs, strong van der Waals forces and π–π stacking between CNTs, thus reducing the electrochemical properties of CNTs for DSSCs. Hence solving the problem on breaking the CNT agglomerates and dispersion of CNTs is looming ahead. Many methods have been applied to disperse CNTs at present [19–22].

Someone studied the functionalized CNTs applied in the DSSCs. In 2012, Lin's group [23] functionalized MWCNTs using an acid mixture solution and fabricated counter electrode with electrophoretic deposition for DSSCs. The photovoltaic conversion efficiency of the cell is as high as 2.16%. Song et al. [24] prepared a MoN-CNT composite using carboxylic groups-functionalized CNTs and assembled the DSSC with MoN-CNT composite CE. The DSSC showed an energy conversion efficiency of 6.74%, which is much higher than that of the DSSC using pure MoN nanoparticles (5.57%). Zhang's group [25] reported a simple, solution-based method of preparing FTO-free counter electrode based on Pt nanoparticles/CNT composite films and achieved an efficiency of 3.76%. All of these results demonstrated that functionalized CNTs are beneficial to improve the efficiency of DSSCs. These works used covalent functionalized MWCNTs. Covalent functionalization of MWCNTs is

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to achieve the covalent bonds between the modified group and CNTs by changing the sp2 hybridization of carbon atoms or damaging π-electron conjugated system between CNTs [26,27]. The disadvantage of this method is the structural of MWCNTs damaged and may bring negative influences on the properties of carbon nanotubes. Hence, non-covalent modification methods have been developed and caught great attentions [19,20,28,29].

Non-covalent modification methods create π-π stacking between CNTs and the other organic molecules, these methods preserve the original structure of CNTs. However, little works has been done on the non-covalent functionalized MWCNTs used for DSSCs yet. Therefore, it is interesting to study the effect of dispersion of non-covalently functionalized MWCNTs on the DSSCs to reduce the cost of solar cell and enhance the overall performance of it. Generally, CNTs can be non-covalently functionalized by macromolecules, such as surfactants, polymers, biomacromolecules, etc. Macromolecules play an important role in dispersion of carbon nanotubes: Macromolecules adsorbed on CNTs surface form a molecule film to barrier the reunion of CNTs and increase the space between each CNT, and avoiding to bridge hydroxyl and form the real chemical bonds.

In another hand, surfactants can not only disperse CNTs but also impact on the electric conductivity of CNTs [30]. In this study, we chose four kinds of surfactant as the functionalization medium of CNTs, and compared different categories of the surfactants on dispersion of CNTs. Lysozyme (LZ), a biomacromolecules, is one of the most water-soluble proteins with hydrophobic core was chosen as a natural surfactant [31]. The conjugate of CNTs with chicken egg white lysozyme was found to be stable and soluble in aqueous solutions [31]. Cetyl pyridinium chloride (CPC), one of cationic surfactant, contains a hydrophilic quaternary ammonium group and a 16-carbon methylene chain of hydrophobic moiety [32]. By CPC, the electrochemical response of MWCNTs modified electrodes can be improved. Sodium deoxycholate (NaDC), a kind of cationic surfactant, has a ring skeleton hydrophobic group and a hydrophilic sulfonic group. NaDC have been used as hydrogelators in many places. Triton X-100 is a low cost nonionic surfactant. It can be regarded as a "green" alternative surfactant. It has a bulk tert-octylphenyl hydrophobic group and a hydrophilic polyethylene oxide group [33].

In this work, to improve dispersion of MWCNTs we firstly functionalized MWCNTs non-covalently by lysozyme, cetyl pyridinium chloride, deoxycholate sodium and Triton X-100, respectively. Secondly, DSSCs CEs with different functionalized MWCNTs were fabricated to improve the PCE and reduce the cost of DSSCs. The Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) of the counter electrodes were tested. We employed low-cost, volatile, small molecular solvent, methanol, to replace the expensive, high boiling point, and toxic dimethyl formamide (DMF) for the dispersion of MWCNTs to reduce the cost and atmosphere pollution. Finally, we assembled the DSSCs and studied the overall performance of dye-sensitized solar cell with functionalized MWCNTs CE. Lastly, our results revealed the photovoltaic property of DSSCs with different MWCNTs CE is closely related to the dispersion of MWCNTs and the electrochemical active area of counter electrode.

2. Material and methods

2.1. Materials

The MWCNTs used in this study were purchased from XFNANO (Nanjing, China) which were synthesized by thermal chemical vapor deposition (CVD) method. The MWCNTs are with length of 10–30 μm, outer diameter of 10–20 nm, and average surface area of more than 200 m^2/g, and purity of higher than 95%.

2.2. Functionalization of MWCNTs by non-covalent methods

2.2.1. Preparation of LZ functionalized MWCNTs

The lysozyme functionalized MWCNTs were prepared by the following steps: firstly, 200 mg lysozyme was added into 200 ml phosphate buffer solution (PBS) to form uniform lysozyme-PBS solution. Then 200 mg MWCNTs were added into the above solution and sonicated with SONICS VCX800 by 160 W for 30 min. Secondly, the mixture was shaken under 100 rpm at 37 °C for 3 h and centrifuged at the speed of 6000 rpm for 15 min, the precipitate was washed 5 times using 10 ml PBS to clean the unwrapped lysozyme. Eventually, the lysozyme functionalized MWCNTs powder (LZ/MWCNTs) were acquired by drying the precipitate at 60 °C in air for 24 h.

2.2.2. Preparation of CPC, NaDC and Triton X-100 functionalized MWCNTs

The CPC, NaDC and Triton X-100 functionalized MWCNTs was prepared by three steps. Firstly, CPC, NaDC or Triton X-100 solution was prepared by adding CPC (or NaDC or Triton X-100) into 10 ml deionized water. Secondly, MWCNTs were added into 10 ml CPC (or NaDC or Triton X-100) solution, the mass ratio between MWCNTs and CPC (or NaDC or Triton-X-100) is 1:1, and sonicated with SONICS VCX800 at 160 W for 30 min. Afterwards, the mixture was centrifuged at a speed of 5000 rpm for 30 min using a ZONKIA High Speed Refrigerated Centrifuge KDC-140HR (Anhui, China) to collect the upper uniform dispersed suspension. Finally, the Triton X-100 functionalized MWCNTs film (Triton X-100/MWCNTs) was obtained by drying the residual uniform component at 60 °C for 24 h.

2.3. Preparation of CE of DSSC

The FTO glasses (fabricated by NSG Inc Japan, 15 mm × 20 mm × 2.2 mm) were thoroughly cleaned by ultrasonic method for 10 min in deionized water, acetone, and absolute ethyl alcohol, separately.

2.3.1. Preparation of Pt CE

The CE of Pt based referenced DSSC was prepared by thermal decomposition method and the cell is named as Pt-DSSC. H2PtCl6 (5 mM) isopropanol solution was coated on the cleaned FTO glass with a spin coater (Easycoater EZ6) at a speed of 2000 rpm for 30 s. Afterwards the Pt-coated FTO glasses were annealed at 400 °C for 20 min in air.

2.3.2. Preparation of MWCNTs CE

The MWCNTs CE were prepared as follows: 10 mg of MWCNTs were mixed with 4 ml solvent and sonicated at 200 W for 15 min. The solvent for pristine MWCNTs was DMF; the solvent for the functionalized MWCNTs was methanol during the preparation of counter electrode. Subsequently 6 ml of polyethylene glycol 400 (PEG400) was added into the mixture and sonicated for 15 min again. The mixture was centrifuged with a ZONKIA High Speed Refrigerated Centrifuge KDC-140HR (Anhui, China) at a speed of 7000 rpm for 20 min to remove the excess PEG400 and methanol, a black MWCNTs/PEG gel was then obtained. The MWCNTs films were fabricated by doctor blading the MWCNTs/PEG gels on the cleaned FTO glass substrates. Then the MWCNTs film was heated at 250 °C for 30 min, then 300 °C for 60 min in air to remove the PEG400 and methanol.