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PEG-assisted Synthesis of Homogeneous Carbon Nanotubes-MoS_2-Carbon as a Counter Electrode for Dye-sensitized Solar Cells

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ABSTRACT

Carbon nanotubes-MoS_2-carbon (CNTs-MoS_2-carbon) was synthesized via a method of wet impregnation and calcination with the assistance of surface-active polyethylene glycol 400 (PEG400). Characterizations of TEM, Raman spectra, XRD, XPS, BET and TG-DSC revealed that CNTs were homogenously coated with ultra-thin layers of MoS_2. It was demonstrated that the unique structure is attributed to the wetting and emulsification capacity of PEG400. The CNTs-MoS_2-carbon was used as counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). Analyses of electrochemistry indicate that the CEs modified by CNTs-MoS_2-carbon have high activity and stability in the electro-reduction from I_3^- to I^- due to the low charge transfer resistance. DSSCs based on CNTs-MoS_2-carbon CEs were demonstrated to have a power conversion efficiency of 7.23%, which is higher than Pt CEs (6.19%).

1. Introduction

Hexagonal molybdenum sulfide (MoS_2) has a lamellar structure similar to graphene. The unit cell of MoS_2 consists of three atom layers, i.e., molybdenum atoms are sandwiched between two layers of sulfur atoms. Because of the weak Van der Waals interactions between the sheets of sulfide atoms, MoS_2 can be exfoliated into thin pieces which results in brilliant lubricity, catalytic and optical adjustability. MoS_2 has been used as lubricant, [1,2] hydrogen evolution reactions,[3–5] anode materials for lithium ion batteries,[6–8] photoluminescence,[9] and transistors.[10] The weakness of MoS_2 is its low conductivity due to the nature of semiconductor. To expand the use of MoS_2 in the field of electrochemistry, e.g. as an electrochemical catalyst, coupling of MoS_2 with other conductors was always preferred. Carbon nanotubes (CNTs) have been well proven to be good conductors. There have been some reports on the preparation of CNTs-MoS_2 composites to enhance the conductivity of MoS_2. Methods including hydrothermal reaction,[11–13] solvothermal decomposition,[14,15] and electro-deposition [16] can been found to prepare CNTs-MoS_2. However, these methods are not valid to get samples with uniformly coated layers of MoS_2. For example, precursors (molybdate, sulfide or ammonium tetrathiomolybdate) underwent a fast kinetics in the hydrothermal decomposition, and huge particles of MoS_2 were always produced. Moreover, solvothermal method can cause the environmental pollution because of the vast use of organic solvents (such as oleylamine and N, N-dimethylformamide). Wet impregnation of CNTs in $(NH_4)_2MoS_4$ aqueous solution was a promising way to prepare homogeneous CNTs-MoS_2. [17] But our experiments indicated this method still has some drawbacks, for example, MoS_2 particles are always found to grow detached from the surface of CNTs. It is a challenge to get uniformly dispersed precursors e.g. $(NH_4)_2MoS_4$ on the surface of the hydrophobic CNTs. Non-ionic surfactant can reduce the surface tension and thus overcome this difficulty because of its wetting capability that can promote the emulsification of the precursor. In this research, we prepared a homogeneous composite of CNTs-MoS_2-carbon with ultra-thin coating layers of MoS_2 via a wet impregnation-calcination method. The environmental friendly surfactant, polyethylene glycol 400 (PEG400), was demonstrated to play key roles in the formation of the uniform layers of MoS_2.

Dye sensitized solar cells (DSSCs) have attracted great attention due to their facile preparative procedures, low coats and high photo-to-electro efficiency. [18,19] However, DSSCs based on traditional Pt counter electrodes have a major drawback because platinum is expensive and tends to be poisoned due to the formation of PtI_4 in the redox process of

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I_3^-/I^-. [18] To replace Pt in CEs efforts have conducted to find alternatives in DSSCs, and the materials include carbon,[20,21] conducting polymers,[22,23] transition metal sulfides, [18,24–28] nitrides,[29] and CNTs in form of thin films. [30] Amongst these materials CNTs has the highest conductivity and can be the most promising materials for CEs used in DSSC.[19] However the CNTs still required to be modified by nitrides [31] and carbides [32–34] in order to improve the catalytic activity. In this paper, the prepared homogeneous CNTs-MoS_2-carbon was employed as CEs in DSSCs, The CEs was found to possess low charge transfer resistance, and excellent efficiency in photo-to-electron conversion was achieved.

2. Experimental

2.1. Synthesis of CNTs-MoS_2-carbon

The precursor ($(NH_4)_2MoS_4$) of MoS_2 used in this research was synthesized as follows: Ammonium molybdate (2.6 g) was dissolved in distilled water (50 ml), then the solution of $(NH_4)_2S$ (6–12wt%, 40 ml) was added. The mixture was kept at temperature of 60 °C for 1 hr. After cooling the mixture was recrystallized, and the products $(NH_4)_2MoS_4$ in form of red crystals were obtained after filtration and washing. The CNTs were carboxylated by refluxing in the boiling mixture of $HNO_3 + H_2SO_4$ (1:3, v/v) for 3.5 hrs followed by washing with distilled water till to the pH of 7.0. The PEG400 (20 ml) and $(NH_4)_2MoS_4$ (1.0 g, 0.0038 mol) were dissolved in 40 ml water in a round-bottom flask, and the acid-washed CNTs were then added to the mixed solution. The mixture was treated ultrasonically for ~1 h, and composite (CNTs-PEG-$(NH_4)_2MoS_4$) were separated by centrifugation and washing. The sample was dried at 60 °C and annealed at 850 °C for 2 hrs in a flow of H_2. The sample was termed as CNTs-MoS_2-carbon. In a control experiment, the preparation of the hybrid (CNTs-MoS_2) without PEG follows the same procedures as the above-mentioned except that no PEG400 was added.

2.2. Fabrication of DSSCs

Similar to the procedure used in our previous reports, the photoanode (TiO_2/SiO_2 coated fluorine-doped tin oxide (FTO)) was prepared via a screen printed way.[35,36] The photoanode films were sensitized by immersing in a solution of N719 dye molecules for 24 hrs at room temperature. For the CEs preparation, the synthesized CNTs-MoS_2-carbon, CNTs-MoS_2 or commercial Pt paste (Wuhan Jinke Co., ~5 nm in diameter) were grinded in an agate mortar with absolute ethanol (5 ml), and then sonicated for 30 min to form a stable solution. The mixture solution was then deposited on the FTO glass substrate by a spin coating technique. The photoanode and CEs were clipped together and wrapped with thermoplastic hot-melt Surlyn. The DSSCs were fabricated by injecting the electrolyte (0.03 M I_2, 0.1 M LiI, 0.6 M 1-butyl-3-methylimidazolium dicyanoamide (BMII), 0.1 M guanidinium thiocyanate, 0.5 M butylpyridine in a mixture of acetonitrile + valeronitrile (85/15, v/v). The area of the unit solar cells was 0.25 cm^2.

2.3. Characterizations and measurements

The micro-structure of CNTs-MoS_2-carbon was observed by a high resolution transmission electron microscopy (HRTEM, JEM-2100F type, JEOL). XRD patterns were studied by using a D/MAX 2500 V X-ray instrument. Raman measurements were conducted on a spectrometer (LABRAM-HR, JY) which was excited by an incident laser (λ=532 nm). The XPS experiment using a monochromatic Al Kα radiation was performed with an ESCALAB250 electron spectrometer to ascertain the formation of the coating. The TG-DSC measurements were carried out on a Simultaneous Thermal Analysis (STA449F3) in air gas and pure argon gas atmosphere protection respectively. The specific surface area (BET) was measured using a surface area and pore analyzer (Tristar II 3020 M) by nitrogen absorption. Cyclic voltammograms (CVs) were conducted using a computer-controlled potentiostat (Autolab 320 N), and the electrolyte is acetonitrile with I_3^-/I^-

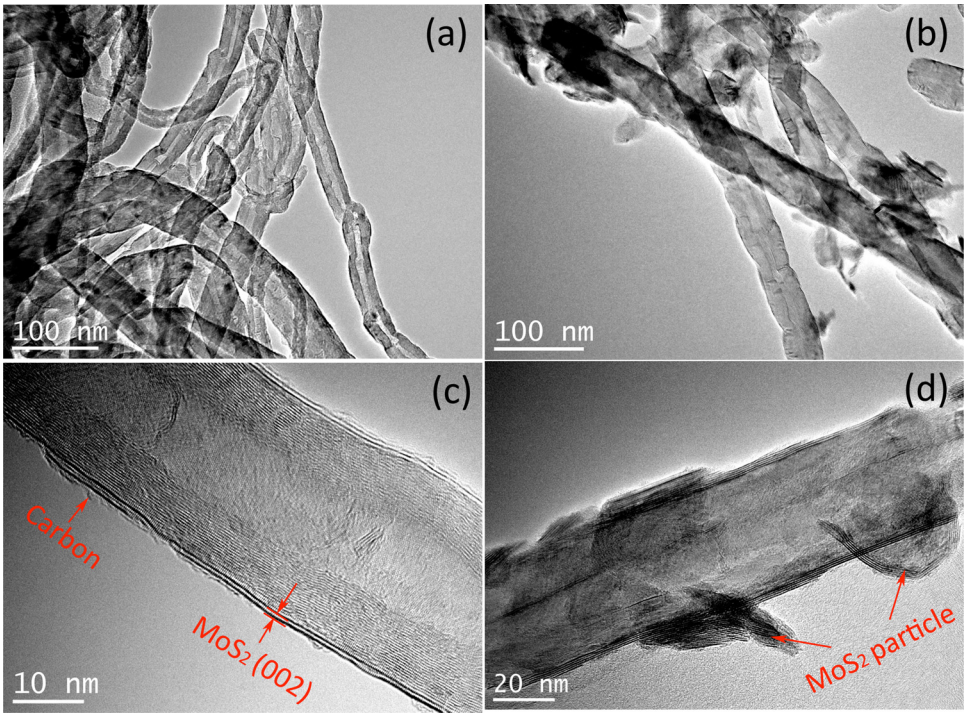

Fig. 1. TEM and HRTEM images of CNTs-MoS_2-carbon (a, c) and CNTs-MoS_2 (b, d)