



In-situ Grown Hybrid Nanocarbon Composite for Dye Sensitized Solar Cells



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ABSTRACT

Herein, a facile *in-situ* grown nanocarbon composite including one dimensional (1D) carbon nanotubes (CNTs) and two dimensional (2D) graphene nanosheets on FTO conductive glass substrates is used directly as a transparent counter electrode (CE) for dye sensitized solar cells (DSSCs) without any post-treatments. In the novel nano-composite, the CNTs without aggregations are not woven into each other, which is beneficial for the transport of carriers. Additionally, the 2D graphene between CNTs and the FTO conductive glass substrates is thought as the platform for accelerating the ballistic transport. It is found that the hybrid CNTs/graphene nano-composite exhibits relative high electrocatalytic activity for the reduction of triiodide. Besides, the design of bifacial DSSC with the hybrid transparent CNTs/graphene CE improves the utilization ratio of incident light. As a consequence, the bifacial DSSC with the optimized hybrid CNTs/graphene exhibits energy conversion efficiency (η) of 5.16% and 4.30%, corresponding to front- and rear-side illumination, respectively.

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1. Introduction

Dye sensitized solar cells (DSSCs) have aroused extensive attentions due to the easy fabrication, low cost and relatively high efficiency to convert solar energy into electricity. Typically, a DSSC comprises a dye-sensitized nanocrystalline titanium dioxide (TiO_2) photoanode, electrolyte solution that commonly use a dissolved I^-/I_3^- redox couple, and a counter electrode (CE) [1–7]. The role of a CE is to transfer the electrons that arrive from the external circuit back to the I^-/I_3^- redox couple in the electrolyte, and to catalyze the reduction of the I_3^- into I^- . Typically, platinum (Pt) is used as the catalytic layer material for the CE despite its extremely high expense [8,9]. Although the properties of sputtered Pt CEs on rigid and flexible substrates have been systematically discussed, sputtering of Pt CEs leads to an inevitable waste of expensive metal during the fabrication process and the electrode is opaque which makes back-side illumination of the cells impossible. In order to reduce the cost of the DSSC to cater its prospective large

scaled applications in the future, alternative inexpensive catalytic materials have been explored for making the DSSC CE. Previous studies have revealed that carbonaceous materials including graphite, carbon black, carbon nanotubes and graphene, can exhibit comparable electrocatalytic performance to Pt for the reduction of I_3^- ions [8]. It is noteworthy that carbonaceous materials also show other advantages such as abundant, low-cost and high resistivity against corrosion in I^-/I_3^- electrolyte [9–11]. Therefore, the replacement of Pt with low-cost carbonaceous materials as optically transparent CEs could facilitate the commercialization of DSSCs in the future [8,12,13]. Among these carbon materials, particularly, one dimensional (1D) carbon nanotubes (CNTs) and two dimensional (2D) graphene attract considerable interest for electrocatalytic applications in DSSCs due to their high electrochemical stability, low resistivity and high catalytic activity [3–5,11–16]. Besides, compared with the Pt catalytic layer, these carbon materials with high optically transparency could be used as the transparent CE for DSSCs. Therefore, using CNTs to replace Pt can endow the CEs with the following advantages: nanometer-scale transfer channels for carriers, large specific surface areas, low costs, high catalytic activities and light weight. In addition, graphene is a 2D material with a one-atom-thick layer of sp^2 -bonded carbon atoms in a

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honeycomb lattice with many superior properties such as excellent electrical conductivity, large theoretical specific surface area and high optically transparency [17,18].

Recently, S. Hwang et al. reported the electrocatalytic properties of CNTs with different diameters as a CE to fabricate DSSCs with high conversion efficiency. However, the CNTs were grown on the opaque Si substrate, which restricts the further increase of conversion efficiency for the bifacial DSSC with the CNTs CE [6]. B.K. Koo et al. demonstrated that the CNTs CE for DSSC was prepared by using doctor blade method for coating the CNTs paste on FTO glass. However, the CNTs film showed severely tangled structure of CNTs combined with Carboxyl Methyl Cellulose (CMC) solution, which reduced the defective active sites for the reduction of I_3^- [19]. CNTs CEs by using screen printing and chemical vapor deposition (CVD) techniques have been prepared by B.S. Kim et al. [20]. The CNTs of printed CEs were randomly oriented and woven into each other, whereas the CNTs of CVD CEs grew directly on the conductive glass surface. The superiority of CVD CNTs could be attributed to the high conductivity arising from the well-aligned arrangement. Generally speaking, during the typical process for fabricating CNTs CE, CNTs paste was required for adhesion between transparent conductive oxide substrate using doctor-blade, drop-casting, and spin coating, which will cause the poor bonding strength between the CNTs and the substrate, resulting in a poor electron transport. So, these methods were inconvenient to prepare the high-quality CNTs CEs [19]. On the other hand, in the application of nanoelectronics, semiconducting CNTs are usually used as the channel material. Due to the 1D transport and long mean free path (in the order of a few hundred nanometers), particular, the CNTs without aggregations can offer scattering-free ballistic transport and enable the possibility of ballistic transport for short channel devices, resulting in low power dissipation [7,8]. Besides, vertical hollow carbon nanostructures filled by metal or metal-oxide have been fabricated on ITO-covered glass over large areas without any addition of catalytic particles via chemical vapor deposition (CVD) by A. Goldoni et al. [21]. Due to the peculiar growth method, the substrate itself acting as a built-in bottom contact for the vertical one-dimensional architecture was used for improving electrochemical performances in Li-ion batteries. Therefore, a crucial step for the CNTs as the CE is the formation of a high-quality CNTs film with strong bonding on the conducting substrate. To overcome these problems, TiO_2 was attempted to improve the bonding strength. However, it was found that adding too much TiO_2 could weaken the catalytic activity of the CNTs CE due to the bad conductivity of TiO_2 . An excessively thin CNTs film could lead to insufficient catalytic activity while an excessively thick carbon film could crack and detach from the substrate [22]. This separation could be attributed to interfacial stress between the CNTs films and the substrate as well as the internal stress of the CNTs film body itself. Furthermore, if even single CNT was to become detached from the electrode and bridges the narrow gap between the CE and working electrodes, the cell would be shorted and the cell rendered useless [23]. For long-term stability, the mechanically anchored CNTs grown directly on the CE substrate will be superior. We have therefore chosen to pursue this idea. Fortunately, the weak bonding between the carbonaceous materials and the substrate could be resolved by *in-situ* techniques [24–26]. To the best of our knowledge, no researches on *in-situ* growth of binary carbonaceous materials including 1D CNTs and 2D graphene simultaneously on conductive substrates as the transparent CEs for DSSCs have been reported so far.

In order to use the combination of the merits of the 1D CNTs and 2D graphene nanosheets, one promising strategy for building hybrid carbonaceous nanostructure as CE using *in-situ* growth technique to reduce the aggregations of CNTs for DSSCs was proposed. In the *in-situ* growth process, 1D CNTs and 2D graphene

nanosheets were synthesized by one-step Cu-vapor-assisted chemical vapor deposition (CVD). In the novel carbonaceous nanostructure, the 1D CNTs without aggregations as the main catalytic centers and 2D graphene as the platform and the buffer layer for accelerating the ballistic transport and enhancing the bonding with the conducting substrate were simultaneously achieved. In addition, the hybrid CNTs/graphene CE has relative high optically transparency, which makes back-side illumination of the bifacial DSSCs possible.

2. Experiments

2.1. Synthesis of hybrid CNTs/graphene

FTO (glass coated with $F:SnO_2$, 2 mm of thickness, sheet resistance of 15Ω) with the area of 1 cm^2 were cleaned using an ultrasonic bath in a detergent solution. Hybrid CNTs/graphene was *in-situ* grown on the FTO substrate by one-step Cu-vapor-assisted CVD. During the process of growth, the Cu foil was positioned at the center of a quartz tube and heated to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$, and then maintained for 30 min under a pressure of 10 Torr with a flow of Ar (Ar = 50 sccm). The FTO was positioned at the downstream of gas flow where the temperature was around $610 \pm 10^\circ\text{C}$. Subsequently, the Ar was off, and the CVD growth of CNTs/graphene was triggered by the addition of C_2H_2 (30 sccm). After CVD growth of 120 min, the sample in the quartz tube was cooled to the room temperature at a cooling rate ($30^\circ\text{C}/\text{min}$) under vacuum atmosphere.

2.2. Assembly of DSSCs

The state-of-the-art Pt CE was prepared by the thermal reduction method, in which a Pt precursor ($H_2PtCl_6 \cdot H_2O$) was drop-casted on the FTO glass, followed by thermal treatment at 450°C for 20 min [27,28]. The TiO_2 electrodes were fabricated by a screen-printing method and gradually sintered at 450°C for 10 min after each printing. Then, the TiO_2 photoanodes were immersed in 0.5 mM N719 dye solution in a mixture of acetonitrile and tert-butyl alcohol (volume ratio: 1:1) at room temperature for 24 h to complete the sensitizer uptake, as described in our previous report [15,16]. The dye-sensitized TiO_2 photoanodes were subsequently washed with acetonitrile and further sandwiched with the fabricated hybrid CNTs/graphene and Pt CEs, respectively. The intervening space in the sandwich-type cell was filled with a drop of the electrolyte (0.60 M BMII, 0.03 M I_2 , 0.10 M guanidinium thiocyanate and 0.50 M 4-tert-butylpyridine in the mixture of acetonitrile and valeronitrile (volume ratio: 85:15)). Finally, the electrolyte injection hole was sealed with Surllyn and a microscope cover glass.

2.3. Characterizations

The morphology of the hybrid CNTs/graphene on the FTO substrate was investigated by scanning electron microscopy (SEM, FEI XL30 S-FEG) and transmittance electron microscopy (TEM, JEOL-1400). Transmittance of the hybrid CNTs/graphene CE was obtained by an UV-vis spectrophotometer (Shimadzu UV-2550 spectroscope) in the wavelength range of 400–800 nm. X-rays Photoelectron Spectroscopy (XPS) was performed by using AXIS-NOVA CJ109, Kratos Inc. ranges 0–800 eV for surface composition of the hybrid CNTs/graphene film. The crystal structure was characterized by X-ray diffraction spectroscopy (XRD, Bruker D8 Focus). The electrochemical responses (CV and EIS) were investigated by using an electrochemical station (CH Instruments, CHI660B). The resultant impedance spectra were analyzed using the Zview software. Cyclic voltammetry (CV)

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