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Facile synthesis of hierarchical nanostructured polypyrrole and its application in the counter electrode of dye-sensitized solar cells

Guiqiang Wang *, Weinan Dong, Chao Yan, Shuo Hou, Wei Zhang

School of New Energy, Bohai University, Jinzhou 121013, China

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ABSTRACT

Hierarchical nanostructured polypyrrole (HNPPy) of spherical polypyrrole (PPy) nanoparticles anchored on the surface of PPy nanofiber network is prepared by a facile process and incorporated into dye-sensitized solar cells (DSCs) as Pt-free counter electrode. This unique hierarchical nanostructure can provide the fast electron-transport pathway and abundant electrocatalytic active sites simultaneously. Electrochemical impedance spectroscopy analysis demonstrates that the electrocatalytic activity of HNPPy electrode for the I_3^- reduction is higher than that of PPy nanoparticles (PPyNPs) electrode and comparable to that of Pt electrode. As a consequence, the DSC fabricated with HNPPy counter electrode achieves a high conversion efficiency of 6.78%, which is close to the efficiency using Pt counter electrode.

1. Introduction

Recently, the third-generation photovoltaic devices have been widely studied as the emerging technologies, leading to great advances in the efficiency and stability [1]. Dye-sensitized solar cells (DSCs) are the remarkable third-generation photovoltaic devices due to their attractive features of low cost and high conversion efficiency [2,3]. As a key component of DSCs, the counter electrode gathers the electrons and catalyzes the reduction reaction of I_3^- in the electrolyte, thus affects the photovoltaic performance of DSCs greatly. Platinum (Pt) is a preferred counter electrode material so far for high-efficiency DSCs [4,5]. However, the high price and unstability in the corrosive I^-/I_3^- electrolyte of Pt incentivize the great efforts to develop cost-effective alternatives to Pt for the counter electrode in DSCs [6].

Recently, polypyrrole (PPy) has attracted more and more interests as the potential candidate for Pt counter electrode in DSCs due to its high stability, good electrochemical performance, and facile preparation. PPy nanoparticles (PPyNPs) counter electrodes have displayed good photovoltaic performance [7–10]. Nevertheless, the high electron-transport resistance of PPyNPs deriving from the abundant particle boundaries severely restricts the further improvement of the photovoltaic performance. This limitation impelled to construct the PPyNPs/multi-walled carbon nanotubes composite [11,12], which combined both the excellent electrocatalytic performance and high electron-transport efficiency in one material and then greatly enhanced the photovoltaic performance of the corresponding device.

In this work, hierarchical nanostructured polypyrrole (HNPPy) of spherical PPyNPs anchored on the surface of PPy nanofibers network was prepared by a facile process and incorporated into DSCs as Pt-free counter electrode. HNPPy can provide both the fast electron-transport pathway and the abundant electrocatalytic active sites. As a result, the as-prepared HNPPy counter electrode exhibited superior performance to PPyNPs as the counter electrode of DSCs.

2. Experimental

HNPPy was prepared by a facile process. Briefly, 1 g of pyrrole was dissolved in 60 ml of 1 M HCl solution by stirring. Then 10 mg of V_2O_5 nanofibers was dispersed in the above solution. The mixture was stirred for 4 h at room temperature. Then, 5 ml of 3 mM $FeCl_3{\cdot}6H_2O$ aqueous solution was added drop by drop. After reaction at room temperature for 1 h, the obtained PPy precipitate was filtered and washed with double distilled water and ethanol. For comparison, PPyNPs were also prepared by using similar procedure without V_2O_5 nanofibers.

100 mg of the obtained PPy sample was dispersed in the mixed solution consisting of 10 ml of n-butanol and 15 μl of tetrabutyl titanate by grinding and sonication. The PPy dispersion was deposited onto fluorine-doped tin oxide (FTO) glass by a spraying

* Corresponding author.
E-mail address: wgqiang@bhu.edu.cn (G. Wang).

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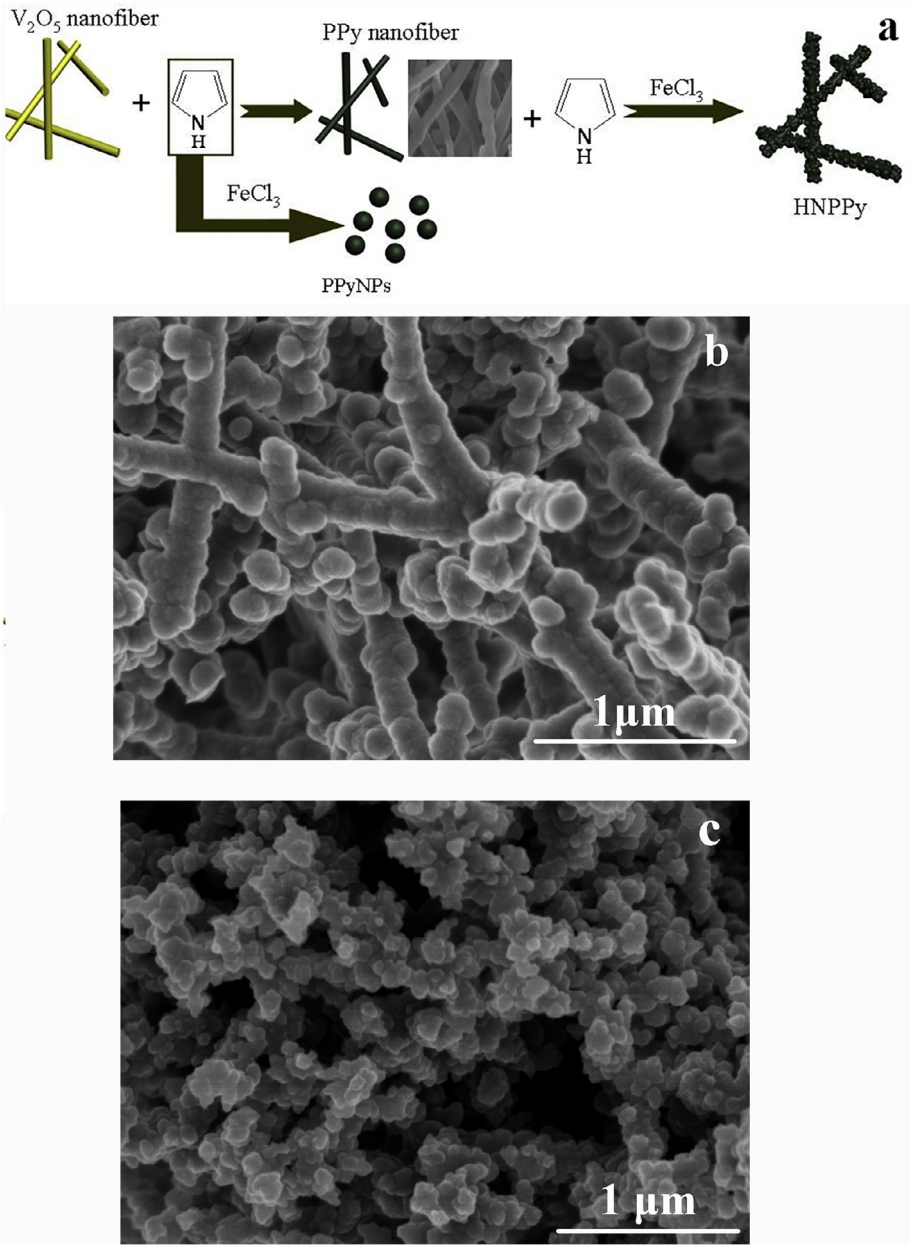

Fig. 1. Schematic illumination of the preparation of HNPPy (a); SEM images of HNPPy (b) and PPyNPs (c).

method. Then, the obtained PPy electrodes were sintered at 150 °C under Ar atmosphere for 20 min.

The dye-sensitized TiO_2 photoanodes were prepared as previous report [13]. A DSC was fabricated by clipping a dye-sensitized photoanode, a drop of electrolyte, and a counter electrode into a sandwich structure. The 3-methoxypropionitrile solution consisting of 0.2 M LiI, 0.5 M 1-hexyl-3-methylimidazolium iodide, 0.05 M I_2, and 0.4 M 4-*tert*-butylpyridine was used as the electrolyte.

The morphology of PPy samples were investigated by a scanning electron microscopy (SEM, Hitachi S-4800). Fourier transform infrared (FTIR) spectra were recorded on a Scimitar 2000 FT-IR spectrometer. X-ray diffraction was performed on a D8 Advance diffractometer (Bruker). The electrocatalytic activity of PPy electrode was investigated by electrochemical impedance spectroscopy (EIS), which was carried out on a Solartron 1287/1255 electrochemical system using symmetric thin-layer cells. The photocurrent density–voltage curves were recorded by a Keithley 2400 source meter under light irradiation of 100 mW cm^{-2} (AM 1.5).

3. Results and discussion

The synthesis procedure of HNPPy is schematically illuminated in Fig. 1a. When V_2O_5 nanofiber mixed with pyrrole, pyrrole monomers were adsorbed and oxidatively polymerized on the surface of V_2O_5 nanofibers. V_2O_5 nanofibers acted as both the template and the initiator, resulting in the production of PPy nanofibers with smooth surface (SEM image in Fig. 1a); meanwhile, V_2O_5 was converted into soluble vanadium salt and then washed away during product washing. When $FeCl_3$ was added, pyrrole monomers were initiated and polymerized on the surface of PPy nanofibers, forming HNPPy. The SEM image of HNPPy (Fig. 1b) displays that the spherical PPy nanoparticles with the size of about 100 nm anchor on the surface of interconnected PPy nanofibers to form a hierarchical architecture. Without the presence of V_2O_5 nanofibers, the polymerization of pyrrole monomers was initiated by $FeCl_3$ and formed PPyNPs (as shown in Fig. 1c). The PPy nanofibers can provide the fast electron-transport pathway, and then greatly improve