



Morphological Influence of Polypyrrole Nanoparticles on the Performance of Dye–Sensitized Solar Cells



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ABSTRACT

Polypyrrole (PPy) with various morphologies were synthesized by chemical oxidative polymerization and further used as the counter electrode (CE) in dye–sensitized solar cells (DSSCs). The conventional anionic surfactant, docusate sodium salt (AOT), cationic surfactant, cetylmethyl ammonium bromide (CTAB), and the newly developed polymeric dispersant, poly(oxyethylene)–imide (POEM), were employed in the PPy synthesis. Scanning electron microscopy images (SEM) revealed diversified morphologies of the synthesized PPy nanoparticles with irregular sheet (IS), hierarchical nanosphere (HNS), and nanosphere (NS), corresponded to the choice of the commercial surfactants AOT and CTAB, as well as the home–made POEM, respectively. Fourier transform spectroscopy (FT–IR) and X–ray diffraction (XRD) analysis were used to confirm the PPy structures and crystalline properties. When fabricated into films and used as CE in DSSCs, the PPy–HNS demonstrated the superior cell efficiency of $6.71 \pm 0.16\%$ to those of PPy–IS ($5.46 \pm 0.31\%$) and PPy–NS ($6.31 \pm 0.24\%$), respectively. The excellent electrocatalytic ability of PPy–HNS was essentially attributed to its high electrochemical surface area (A_e), which was quantitatively calculated through a rotating disk electrode system by using the Koutecky–Levich equation. Brunauer–Emmett–Teller (BET) surface area measurement, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) were also used to substantiate the explanation for the DSSC performances.

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1 Introduction

Dye–sensitized solar cells (DSSCs) are important power sources, as they are expected to provide a partial answer to many environmental and energy problems. In addition, these types of cells have many advantages, such as low material cost, easy fabrication, and reasonably high efficiency for energy conversion [1–3]. Various efforts have been made to enhance the overall performance of DSSCs, such as modifying the morphology of nanocrystalline semiconductor [4–6] and the molecular structures of organic sensitizers [7,8] as well as using low–volatility electrolytes [9–12] and new counter electrode (CE) materials [13–24]. In DSSCs, the CE is one of the most important and indispensable components. The reactions at the CE rely on the type of redox

couple in the electrolyte. Traditionally, the I^-/I_3^- couple has been adopted as the redox mediator.

CE of DSSC is usually made of platinum (Pt), which has high conductivity, stability and catalytic activity for the reduction of I_3^- ions. However, Pt is an extremely rare metal and is thus a factor to be considered for cost–effective fabrication of a DSSC, although it shows a high catalytic activity for the reduction of I_3^- ions and an excellent electronic conductivity. Replacement of Pt with other cheaper catalytic materials is required for the reducing the production cost of the DSSCs, especially when the production is in mass scale. Several carbonaceous materials, e.g., activated carbon [13], carbon fiber [14], graphitic/grapheme [15], multi–walled carbon nanotube (MWCNT) [16], and single–walled carbon nanotube (SWCNT) [17] have become potential materials to substitute Pt. The inorganic transition metallic compounds, e.g., NiS [18], MoS_2/C [19], and CoS/CNT [20], have also been proposed to replace the Pt for the CEs of DSSCs, because of their low cost, high conductivity and good catalytic ability for the reduction of I_3^- ions. Meanwhile, conducting polymers are also considered as one of the alternatives for Pt for the CEs of DSSCs; The conducting

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polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) [21], polyaniline (PANI) [22], and polypyrrole (PPy) [23–28], are promising CE materials used in DSSC, because of their unique properties, such as inexpensive material, good conductivity, stability and catalytic activity for the reduction of I_3^- ions [21–28].

Among all the conducting polymers, PPy is of special interest due to its remarkable conductivity and electrochemical catalytic properties [29] for the application in field emission display device [30], sensors [31], and DSSCs [23–28]. Gong et al. [23], incorporated reduced graphene oxide into PPy matrix and used it as the CE of DSSCs to obtain a cell efficiency of 8.14%. Jeon et al. [24], synthesized PPy nanospheres by chemical polymerization and applied them to the CE of DSSCs, which achieved a cell efficiency of 7.73%. Wu et al. [25], also constructed PPy nanospheres for the use of the CE in DSSCs, and they obtained a cell efficiency of 7.66%. Makris et al. [26], fabricated a PPy-based CE for the quasi-solid-state DSSC by electrochemical deposition, and obtained a cell efficiency of 4.60%. Some reports indicated that the morphologies and the structures of PPy can be tuned by incorporating the surfactant or polymer-based stabilizer in the synthesized processes and being applied as the CE in DSSCs [27]. Peng et al. [28], have reported a composite film of PPy nanorod network and carbon black nanoparticles as the catalytic layer on the CE in DSSC, and achieved a cell efficiency (η) of 7.2%, this was due to the good catalytic property of PPy for reducing I_3^- and the higher surface active area from its nanorod network structure. Recently, we reported the synthesis of a novel amphiphilic polymer, i.e., poly(oxyethylene)-imide (POEM), which can function as the surfactant (or stabilizer) to well control the morphologies and sizes of metal nanoparticles [32]. Accordingly, the POEM seems a promising surfactant (or stabilizer) for synthesizing the PPy nanoparticles containing different nanostructures.

In this study, we successfully synthesize three kinds of PPy nanoparticles containing different morphologies via a simple surfactant-assisted solution process. By incorporation of the anionic-type surfactant (docusate sodium salt, AOT), the cationic-type surfactant (acetylmethyl ammonium bromide, CTAB), and our home-made amphiphilic-type polymer (POEM), the synthesized PPy nanoparticles resulted in different architectures of irregular sheet (IS), hierarchical nanosphere (HNS), and nanosphere (NS), respectively. The DSSCs using the CEs with PPy-IS, PPy-HNS and PPy-NS exhibited cell efficiencies of 5.46 ± 0.31 , 6.71 ± 0.16 , and $6.31 \pm 0.24\%$, respectively. The main novelty of our study is to report the morphological variance of the PPy nanoparticles via using different types of surfactants (anionic-type, cationic-type and amphiphilic-type), and the DSSC performance and electrocatalytic activities of the corresponding PPy CEs are also investigated. Another novelty is to introduce, for the first time, our home-made amphiphilic-type polymer (POEM) as the surfactant for PPy synthesis; it is illustrated that POEM is suitable for the synthesis of conducting polymer-based nanoparticles. Among all PPy CEs, the PPy-HNS CE renders its DSSC the highest efficiency of $6.71 \pm 0.16\%$, which is 90% compared to that of the cell with Pt CE. The PPy-HNS CE also suggests a low-cost and high efficient substitution of Pt CE. Moreover, the simple surfactant-assisted solution process of PPy nanoparticles is beneficial to large-scale production and marketing of DSSCs in the future.

2. Experimental

2.1. Materials

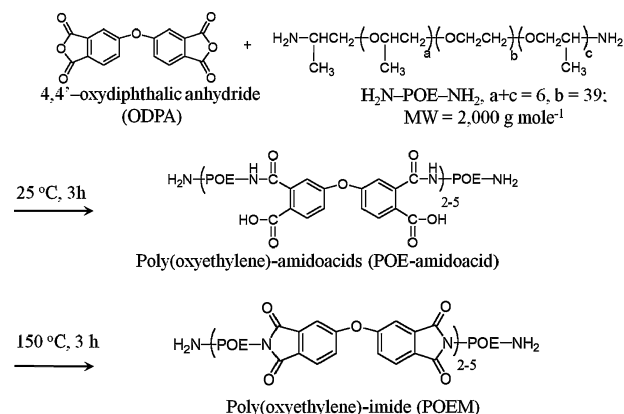
Poly(oxyethylene)-diamine or poly(oxypropylene-oxyethylene-oxypropylene) segmented polyether of bis(2-amino-propyl ether) (POE2000, 2,000 MW) was a solid and water-soluble compound (waxy solid, melting point 37–40 °C, amine content

0.95 meq g^{-1} with a formula of 39 oxyethylene and 6 oxypropylene units). Monomer, 4,4'-oxydiphthalic anhydride (ODPA, 97% purified by sublimation), titanium (IV) tetra-iso-propoxide (TTIP > 98%), acetonitrile (ACN, 99.99%), isopropyl alcohol (IPA, 99.5%), cetylmethylammonium bromide (CTAB, 99%), and docusate sodium salt (AOT, 99%) were obtained from Aldrich Chemical Co. Tetrahydrofuran (THF, 95%) and ethyl alcohol (99.5%) were purchased from Teida Chemicals. Pyrrole (Py, 98%), lithium iodide (LiI, chemical grade), iodine (I_2 , chemical grade), and poly(ethylene glycol) (PEG, 20,000 MW) were obtained from Merck Chemical Co. 4-Tert-butylpyridine (TBP, 96%) was obtained from Acros Chemicals. Ferric chloride ($FeCl_3$, 99.5%), dimethyl sulfoxide (DMSO, 99.7%) and 3-methoxypropionitrile (MPN, 99%) were obtained from Riedel-deHaën (Fluka). Hydrochloric acid (HCl, 37%) and 2-methoxyethanol (99.95%) were obtained from Sigma-Aldrich.

The TiO_2 colloidal solution was prepared by a sol-gel method. TTIP (69.10 g, 0.24 mole) was added to 430 ml of 0.1 M nitric acid aqueous solution with continuous stirring and heating at 85 °C for 8 h. When the resultant colloid was cooled down to room temperature, it was transferred to an autoclave (Parr 4540, USA); the temperature of the autoclave was maintained at 240 °C for 12 h. The prepared TiO_2 colloid was concentrated to 10 wt%; the obtained TiO_2 had particles of about 20 nm in diameter. Large-sized TiO_2 (PT-501 A, 99.74%, $15 m^2 g^{-1}$ surface area, 100 nm diameter) was purchased from Ya Chung Industrial Co. Ltd. Taiwan, for using as scattering particles in the TiO_2 photoanode.

2.2. Synthesis of PPy nanoparticles and preparation of the PPy films

A home-made surfactant, poly(oxyethylene)-imide (POEM), was prepared by a standard synthesizing procedure according to our previous report [12]. The number-average molecular weight (M_n) was measured by gel permeation chromatography technique (GPC; Waters apparatus 515HPLC pump; 717 auto sampler; 2410 refractive index detector; the waters style gel columns set: HR2 and HR4E were used with a 1.0 ml/min flow rate of THF, calibrated by polystyrene standards (Showa Denko, Shodex Standard SM-105)) to obtain $M_n = 13,000$ and $PDI = 2.13$. Scheme 1 represents the synthesis of poly(oxyethylene)-imide (POEM) by two-step process of forming POE-amidoacids and POEM at elevated temperature [12]. Py was purified by distillation under reduced pressure and stored in a refrigerator at about 4–8 °C before use. Three kinds of monomeric solutions were separately prepared by mixing the 0.06 mole (4.03 g) purified-Py monomer with 0.02 mole of different surfactants (AOT, CTAB or POEM) in 200 ml aqueous solution under stirring for 1 h. The 0.12 mole of $FeCl_3$ oxidant



Scheme 1. Synthesis of poly(oxyethylene)-imide (POEM) by two-step process of forming POE-amidoacids and POEM at elevated temperature.

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