



Nickel-iron alloy nanoparticle encapsulated in mesoporous nitrogen-doped carbon nanosphere as a counter electrode material for dye-sensitized solar cells



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ABSTRACT

NiFe alloy nanoparticle encapsulated in mesoporous nitrogen-doped carbon sphere (MNCS) was synthesized by thermal pyrolysis of nickel hexacyanoferrate (NiHCF) precursor at 500 °C in argon atmosphere without additional metal catalyst and/or carbon source. NiHCF with three-dimensional open tunnels allowed the formation of MNCS featuring bimodal pore size distribution after pyrolysis. The tiny mesopores (<4 nm) in carbon shell originated from the coordination complex of NiHCF, while the unique large mesopores (>20 nm) in sphere resulted from the calcination. After partial removal of uncovered NiFe nanoparticles, the remaining NiFe nanoparticles were encapsulated in carbon shells, forming the NiFe@MNCS core-shell nanostructures. The NiFe@MNCS turned out to have superior electrocatalytic performance for I^-/I_3^- couple than the MNCS only. With protective carbon shell, the corrosion of NiFe nanoparticles in I^-/I_3^- redox electrolyte could be considerably mitigated, leading to an improved long-term stability. Although the NiFe@MNCS electrode revealed slightly higher diffusion impedance, it showed a lower charge-transfer resistance than Pt. Thus, the power conversion efficiency of dye-sensitized solar cell (DSSC) achieved by employing the NiFe@MNCS counter could attain 7.6%, similar to that of DSSC using Pt (7.8%).

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1. Introduction

Dye-sensitized solar cell (DSSC) has gained substantial research attention among researchers owing to their potential application in clean energy conversion. Several factors such as counter electrode (CE), photoanode, electrolyte, and dye contribute to the overall photovoltaic performance of DSSC. Among them, CE is one of the most important factors and accordingly plays a vital role in improving the photovoltaic characteristics of DSSCs [1]. As the CE materials for DSSCs using the traditional I_3^-/I^- electrolyte, the charge-transfer resistance for the electrochemical reduction of I_3^- needs to be as low as possible. Besides, the CE materials have to possess chemical and electrochemical compatibility with the electrolyte. The most conventional CE material for DSSC application using I_3^-/I^- electrolyte is the nanostructured Pt material, primarily due to its high electrical conductivity, chemical/electrochemical

stability, and electrocatalytic ability [2–4]. Nevertheless, the Pt-based material is rare in the earth and very expensive compared to other non-noble metals, leading to a significant increase in the cell cost and limiting the potential large-scale application. Thus, many efforts have been made aiming to replace the Pt-based catalysts for DSSC application. Alloying of Pt with non-noble metals has been developed as a cost-effective counter electrode for DSSCs [5–7]. Metal selenide alloys turn out to have superior catalytic activity and charge-transfer ability toward I_3^-/I^- redox couple [8].

Several catalyst materials like non-noble metal oxides, metal alloys, carbon-based materials, conducting polymers, carbides, nitrides, sulfides, and phosphides have been characterized as promising alternatives to Pt catalyst for DSSCs [8–15]. Among the alternatives, carbon-based materials have the advantages of low cost, good chemical/electrochemical stability, large surface area, and suitable electrical conductivity, rendering them promising electrocatalytic ability for I_3^-/I^- redox couple [16–21]. Effect of carbon morphology and structure on the efficacy of DSSC devices has been widely investigated, involving nanotube, mesoporous, graphene, and hierarchical structures [22–24]. One of the most

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straightforward methods to boost the electrocatalytic activity of carbon materials is the incorporation of foreign elements like nitrogen, phosphorus, sulfur, and oxygen into the carbon lattice due to the improvement in local electronic structure of carbon materials after doping. Among the foreign elements, the nitrogen with similar atomic size to carbon serves as a perfect hetero-element for carbon [25]. The nitrogen-doped carbon materials involving carbon aerogel, mesoporous carbon, graphene, carbon nanotube, and carbon nanoparticle have been characterized as prospective catalyst candidates for DSSCs [18,26–28]. Recently, the metal-sulfides/carbon hybrids have been characterized as the promising CE materials owing to their unique nanostructure that offers a promising synergistic effect on electrocatalytic performance for the I_3^-/I^- redox reaction [29–32]. Our previous work has shown that the nitrogen-doped hollow carbon nanosphere exhibits lower electrocatalytic ability than the nitrogen-doped nanotube [33]. The combination of carbon materials with foreign metals and/or metal oxides may circumvent the poor electrocatalytic ability of the carbon materials for I_3^-/I^- couple [18,34–38].

Very little information is available for the nitrogen-doped carbon sphere with embedded metal/alloy particles as the CE catalyst [18,34,35]. In general, the nitrogen-doped carbon materials are prepared through thermal pyrolysis employing the nitrogen-enriched chemicals and catalyst precursor [39]. In this work, the mesoporous nitrogen-doped carbon sphere (MNCS) encapsulating the NiFe alloy nanoparticle is proposed as a prospective CE material for DSSC using a simple one-pot pyrolysis method followed by acid treatment. MNCS-NiFe material with unique NiFe@MNCS core-shell structure could be obtained by thermal pyrolysis of nickel hexacyanoferrate (NiHCF) without the need for additional metal catalyst and/or carbon source as illustrated in Fig. 1. NiHCF featuring 3D (three-dimensional) open-framework tunnels enables the formation of mesoporous nitrogen-doped carbon shell with bimodal pore size distribution during pyrolysis. The improvement of Pt corrosion in I_3^-/I^- electrolyte has become one of the key issues in developing advanced DSSCs [6,40]. In this work, the carbon shell could protect the NiFe core against corrosion in I_3^-/I^- redox electrolyte. The effect of NiFe alloy on the electrocatalytic activity for I_3^-/I^- redox couple is investigated. As expected, the cyclic voltammetry, electrochemical impedance spectroscopy (EIS), and photocurrent-voltage ($J-V$) curve demonstrate that the obtained NiFe@MNCS catalyst is an effective CE material to replace the expensive Pt catalyst.

2. Experimental

2.1. Material preparation

NiHCF colloids were synthesized by adding 50 mL of 0.04 M $Ni(NO_3)_2$ dropwise into 50 mL of 0.02 M $K_3Fe(CN)_6$ solution at 70 °C under continuous stirring [41,42]. After cooling down to the ambient temperature (about 27 °C), the turbid solution containing NiHCF colloids was stirred at that temperature for 6 h, then centrifuged and cleaned with de-ionized (DI) water several times. MNCS-NiFe material was obtained by calcining NiHCF powder in a horizontal quartz tube furnace at 500 °C for 5 h under an argon flow. MNCS-NiFe material was treated with 1 M HCl for 24 h to remove the NiFe particles that were not fully encapsulated in carbon spheres, forming the NiFe@MNCS core-shell structure. For comparison, most of the NiFe particles in MNCS-NiFe material were dissolved by boiling concentrated HNO_3 solution under reflux condition for 1 h, forming MNCS material. After acid treatment, the powder was centrifuged and washed with DI water several times until the pH value reached about 7, and then dried at 60 °C for 12 h.

2.2. Electrode preparation

MNCS and MNCS-NiFe materials were coated on fluorine-doped tin oxide (FTO) glass by means of EPD (electrophoretic deposition) method at ambient temperature in a two-compartment cell. EPD was fulfilled under an electric field of -40 V cm^{-1} between working (FTO) and auxiliary (Pt) electrodes in a colloidal suspension comprising 50 mg of MNCS or MNCS-NiFe powder, magnesium nitrate hexahydrate (0.1 mM) as a charging agent, and isopropyl alcohol (50 mL). To obtain the required amount of deposits on FTO, the EPD durations were 50 and 100 s for MNCS-NiFe and MNCS, respectively. After EPD, the FTO with attached active material (MNCS or MNCS-NiFe) was heated at 450 °C for 1 h under the nitrogen flow through the tube furnace. In comparison with the MNCS and MNCS-NiFe electrodes, FTO with attached Pt nanoclusters was fabricated employing a two-step dip coating process, the detailed procedure was described in literature [43]. TiO_2 photoanode (about 15 μm thick) was fabricated by screen-printing the commercial TiO_2 paste onto FTO and then heated at 450 °C in air for 1 h [44]. The TiO_2 electrode was immersed in a dye solution (N719) at ambient temperature for 12 h to adsorb dye on the surface of TiO_2 nanoparticles.

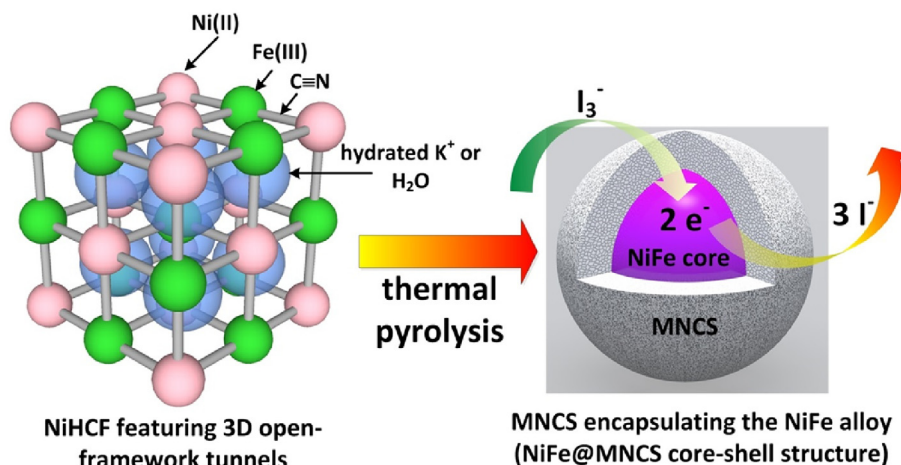


Fig. 1. Schematic illustration of NiFe@MNCS core-shell structure obtained through pyrolysis of NiHCF precursor without the need for additional metal catalyst and/or carbon source as a prospective catalyst material for DSSC.

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