



# High-performance counter electrode of carbon nanocubes with embedded cobalt-iron alloy nanoparticles for dye-sensitized solar cells

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## ABSTRACT

High concentration of polyvinylpyrrolidone (PVP) favored the growth of cobalt hexacyanoferrate (CoHCF) nanocubes with sharp corners and small particle size during synthesis. The cobalt-iron (CoFe) alloy nanoparticles were embedded in the carbon matrix through pyrolysis of the CoHCF powder. The presence of PVP in CoHCF also changed the morphology and microstructure of the resultant carbon-CoFe composite. Bare CoHCF formed bamboo-like hollow nanotubes, while CoHCF nanoparticles capped with large and small amounts of PVP tended to form porous nanocubes and aggregated nanoparticles, respectively. Cyclic voltammetry and electrochemical impedance measurements indicated that the carbon-CoFe nanocube electrode exhibited better catalytic performance than the nanotube, nanoparticle, and Pt electrodes, mostly due to its higher surface area and suitable pore size distribution for facilitating the iodide/triiodide couple. Dye-sensitized solar cells (DSSCs) employing the nanocube counter electrode (CE) exhibited a high photovoltaic conversion efficiency of 9.20%, which was greater than those obtained using Pt (8.94%), nanotube (8.48%), and nanoparticle (8.40%) CEs. The enhanced performance of the DSSC using the nanocube CE was due to the low charge-transfer resistance of the porous nanocubes with embedded CoFe nanoparticles compared to the other CEs.

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## 1. Introduction

The dye-sensitized solar cell (DSSC) has attracted considerable research effort due to its prospective benefits in the conversion of solar light to electricity [1]. DSSC is a reliable alternative for silicon-based solar cells due to its low material cost and easy fabrication [1–3]. Typically, DSSC mostly consists of dye-adsorbed TiO<sub>2</sub> photoanode, electrolyte, and a catalytic counter electrode (CE). Fluorine-doped tin oxide (FTO) glass serves as a transparent conducting substrate for the photoanode and CE, enabling the light harvesting without significant losses in the photoanodes. Under illumination, the excited electrons from the dye molecules anchored on the TiO<sub>2</sub> surface are transported through the photoanode and arrive at the CE, assisting in the regeneration of the dyes by catalyzing the generation of iodide from the triiodide in the iodine-based electrolyte. Many interfaces affect the photovoltaic performance of DSSC, among which is the catalytic interface at the

CE. In the iodine-based redox electrolyte, the catalytic CE reduces the triiodide back to iodide at the catalyst-electrolyte interface. Thus, the CEs configuration, morphology, and catalytic ability play key roles in enhancing the DSSC performance. The noble metal Pt materials are commonly adopted as a high-efficiency catalyst for CEs [3]. Thus, the search for the competitive and efficient CE catalysts is the primary challenge for the development of high-performance DSSC for use in large-scale solar power system.

As mentioned above, the CE catalyst for the iodide/triiodide redox couple currently dominated by Pt catalysts is limited by the disadvantages, such as the use of large amounts of the noble Pt material. Recently, research attention has primarily concentrated on the Pt-free catalysts as alternatives for the existing Pt-based catalysts. The use of Pt alloy catalysts has become one of the most straightforward strategies for decreasing the Pt content without the significant sacrifice of catalytic performance [4–9]. PtNi alloy has been found to show comparable charge-transfer capability and superior catalytic activity to Pt, standing out as an alternative CE catalyst [8]. The use of earth-abundant elements in CEs can largely reduce the cost of DSSCs, making them more suitable and efficient for practical application [10]. Pt-free materials, such as

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carbonaceous materials, carbides, phosphides, sulfides, borides, metals, and alloys, have been considered to be promising alternatives for the replacement of the rare and expensive Pt catalyst [11,12]. Among these materials, carbon nanostructures have shown favorable properties, such as appropriate electrochemical activity and high corrosion resistance, which make them potential material for replacing Pt in the CEs of DSSCs [13]. The catalysts prepared by the addition of carbon, nitrogen or phosphorus to transition metals exhibit exciting catalytic performance for application in CEs [14].

However, the catalytic activity of Pt-free catalysts appears to depend on their structure, composition, and method of synthesis. In addition, the dissolution of metal-based catalysts in iodine-based electrolytes is an important problem for the development of advanced CEs for DSSCs [7]. The addition of carbon to metallic compounds could mitigate the corrosion problem. While the presence of carbon decreases the DSSC photocurrent, the composite structure could protect the active tin sulfide from dissolution in the corrosive electrolyte [15]. Thus, a combination of metal alloys and tailored carbon nanostructures provides a synergistic effect to enhance the catalytic performance by decreasing the corrosion rate and facilitating the transport through the electrolyte. The use of shape- and composition-controlled catalyst can boost the catalytic performance of CE. In this work, we propose the N-doped mesoporous carbon nanocubes with embedded cobalt-iron (CoFe) alloy nanoparticles prepared by direct thermal pyrolysis of cobalt hexacyanoferrate (CoHCF) nanocubes as a high-performance CE for advanced DSSCs. CoHCF is an analogue of Prussian blue coordination compound which enables the incorporation of nitrogen into the host lattices of graphitic carbon and the encapsulation of CoFe alloy nanoparticles during pyrolysis, generating sufficient active defects for facilitating the redox couples. In this study, the carbon-CoFe composite CEs with nanostructured morphology use the benefits of high surface area and catalytic ability of the carbon matrix to mitigate the corrosion of the CoFe alloy in the iodine-based electrolyte.

## 2. Experimental

### 2.1. Preparation of CoHCF precursors and carbon-CoFe composites

A precipitation process was used to synthesize the CoHCF nanoparticles in the absence and presence of PVP (polyvinylpyrrolidone, K-30) with the average molecular weight of  $40000 \text{ g mol}^{-1}$ . Typically, 400 mL of cobalt acetate (4 mM) was slowly added into 400 mL of potassium hexacyanoferrate (8 mM) under gentle stirring by a stir bar at 160 rpm (revolutions per minute) for 30 min [16]. The turbid suspension containing CoHCF nanoparticles was aged at ambient temperature for 72 h. The precipitate was separated using a centrifuge and later dried at  $60^\circ\text{C}$ . The preparation of the PVP-capped CoHCF powder was similar to that of the bare CoHCF powder, except that PVP (6.4 g or 32.0 g) was added to potassium hexacyanoferrate solution prior to titration. Thermal pyrolysis of the CoHCF powder was carried out in a horizontal tube furnace. The CoHCF powder was placed in a small ceramic crucible and then transferred to the center of a quartz tube. The tube was heated to  $750^\circ\text{C}$  ( $10^\circ\text{C min}^{-1}$ ) and maintained at that temperature for 5 h under constant flow of argon. After pyrolysis, the tube furnace was naturally cooled to ambient temperature. The collected carbon-CoFe material was treated with nitric acid (1 M) under ultrasonic irradiation for 1 h to dissolve the exposed alloy nanoparticles, rinsed with de-ionized water several times until the filtrate reached neutral pH, and dried at  $60^\circ\text{C}$ .

### 2.2. Material characterization and preparation of CEs

The crystal, surface, and internal structures of the CoHCF powder before and after the pyrolysis were investigated using an X-ray diffractometer (Bruker D8) with a Cu  $K\alpha$  target, a scanning electron microscope (SEM, Carl Zeiss Auriga), and a transmission electron microscope (TEM, Jeol JEM-1400), respectively. The elemental composition of the carbon-CoFe composites was determined by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe). Nitrogen adsorption/desorption isotherms (Micromeritics ASAP-2020) were obtained to analyze the BET (Brunauer-Emmett-Teller) surface area and BJH (Barrett-Joyner-Halenda) pore size distribution of the carbon-CoFe powder. After the acid treatment, the samples were coated on FTO using the electrophoretic deposition (EPD) method. EPD was performed by applying an electric field of  $-50 \text{ V cm}^{-1}$  between the FTO (with an exposed area of  $1.5 \times 1.0 \text{ cm}^2$ ) and Pt ( $2 \times 2 \text{ cm}^2$ ) electrodes at room temperature in a quiescent colloidal suspension containing a carbon-CoFe sample (50 mg), magnesium nitrate (0.3 mM), and isopropyl alcohol (50 mL) [17]. The loading amount of the carbon-CoFe composite on FTO was kept at approximately 0.10 mg for each electrode by changing the EPD time. After EPD, the FTO electrode with attached carbon-CoFe particles was heated to  $500^\circ\text{C}$  for 1 h in a horizontal tube furnace under the constant flow of nitrogen. For comparison, a highly catalytic Pt-coated FTO counter-electrode with the exposed area of  $1.5 \times 1.0 \text{ cm}^2$ , was prepared according to the literature procedure using a two-step dip coating process [18].

### 2.3. Electrochemical investigation of CEs

Cyclic voltammetry was used to investigate the catalytic behavior of catalyst electrodes toward iodide/triiodide reaction in the electrolyte composed of acetonitrile (AN) solvent, lithium perchlorate (0.50 M), lithium iodide (0.05 M), and iodine (0.01 M). FTO-supported catalyst ( $1.5 \times 1.0 \text{ cm}^2$ ), Pt sheet ( $2.0 \times 2.0 \text{ cm}^2$ ), and Pt wire were used as the working, auxiliary, and reference electrodes, respectively, in the three-compartment glass cell. The voltage of the catalyst electrode was scanned using a source meter (Keithley 2400) from  $-0.4$  to  $0.4 \text{ V}$  versus Pt at the rates of 5 and  $25 \text{ mV s}^{-1}$ . Electrochemical impedance spectroscopy (EIS) was used to evaluate the charge-transfer and/or diffusion processes in various interfaces of the symmetric cells. EIS of the cells was performed using a commercial potentiostat/galvanostat (Autolab PGSTAT-302 N) under open-circuit conditions. The ac amplitude and frequency range were 10 mV and  $0.1\text{--}1 \times 10^5 \text{ Hz}$ , respectively. The symmetric cell consisted of two identical FTO-supported catalyst electrodes, between which a sealing film with the thickness of  $30 \mu\text{m}$  (Surlyn) was placed as a spacer and the void space was filled with the AN-based electrolyte containing lithium iodide (0.10 M), 1-propyl-2,3-dimethylimidazolium iodide (0.60 M), iodine (0.05 M), and 4-*tert*-butylpyridine (0.50 M) [17]. The surface area exposed to electrolyte was  $0.785 \text{ cm}^2$  (circle diameter of 1 cm).

### 2.4. Photovoltaic performance of DSSCs

The  $\text{TiO}_2$  photoanode was fabricated by screen-printing a commercial  $\text{TiO}_2$  paste (25 nm in diameter) onto FTO glass several times. Finally, a light-scattering layer was screen-printed on the thick mesoporous  $\text{TiO}_2$  film using a commercial paste composed of submicrometer-sized  $\text{TiO}_2$  beads. The as-prepared electrode was heated to  $450^\circ\text{C}$  for 1 h in air atmosphere using an electric oven. The resultant  $\text{TiO}_2$  film had the thickness of approximately  $20 \mu\text{m}$  (4 and  $16 \mu\text{m}$  for the light-scattering layer and thick film, respectively). The  $\text{TiO}_2$  electrode was subjected to post-treatment by dipping the  $\text{TiO}_2$  electrode in a solution composed of titanium

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