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Electrochemically synthesized nanostructured iron carbide/carbon composite as a low-cost counter electrode for dye-sensitized solar cells

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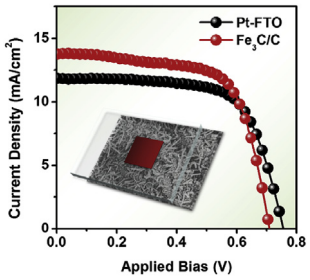
HIGHLIGHTS

- Nanostructured Fe_3C/C electrode was prepared by a facile electrochemical procedure.
- Fe_3C/C electrode exhibited superior catalytic activities to that of conventional Pt.
- Fe_3C/C electrode in place of Pt counterpart led to an enhanced performance in DSCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Owing to the rapid increase in global energy consumption, which is currently based on fossil fuel combustion, the importance of renewable energy has become increasingly apparent. Solar energy is one of the most promising candidates to replace conventional energy sources, and various types of photovoltaic devices, including dye-sensitized solar cells, are being intensively investigated as a means for the efficient utilization of sunlight. However, the use of Pt in the counter electrodes of dye-sensitized solar cells limits their economic feasibility for practical and industrial applications. In the present study, to develop an active and economical material to replace Pt in dye-sensitized solar cells, we prepare a nanostructured iron carbide/carbon composite by electrochemical anodization of Fe foil followed by heat treatment in carbon-bearing gas atmosphere, which lead to the formation of conformal carbon shell on the surface of crystalline Fe_3C. The superior catalytic properties of the iron carbide/carbon composite in the cobalt bipyridine redox electrolyte to those of Pt are confirmed by various electrochemical characterization methods. When used as the counter electrode in a dye-sensitized solar cell, the superior properties of the composite provide an 8.0% increase in power conversion efficiency compared to that achieved with a Pt counter electrode.

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1. Introduction

Dye-sensitized solar cells (DSCs) have garnered considerable research attention in both academic and industrial fields owing to their low manufacturing cost, application scope, high performance, and reliability [1–6]. Among the components of DSCs, the counter electrode (CE) plays a crucial role in the electrocatalytic reduction of the redox electrolyte, which is essential for the regeneration of sensitizers and continuous operation of the cell [3]. Pt is the best-performing catalyst material for the CE, but its limited reserves and high cost hinder the practical and commercial utilization of DSCs [7,8]. Therefore, increasingly intensive research activity is being dedicated to the development of economical CEs with activities comparable to those of conventional Pt CEs.

A variety of materials have been proposed as possible substitutes for Pt, including carbonaceous materials [9–12], conducting polymers [13–16], and their hybrid forms [17–20]. Various types of carbon with large surface areas have been shown to have high performances, some of which are even comparable to that of Pt. However, their poor attachment to conductive substrates causes significant problems in long-term operation [21,22]. Recently, earth-abundant transition metal compounds have been frequently applied in DSCs and have shown decent performances as CEs owing to their electronic structures, which are similar to that of Pt [23–27]. Among various metal compounds, carbide materials such as tungsten, molybdenum, and tantalum carbides have drawn attention as favorable substitutes for Pt [28–32], and there have been reports on the incorporation of iron carbide into the CE of DSCs. Iron carbide is a promising material with an abundance of constituent elements, excellent mechanical strength, chemical inertness, and favorable electrical properties [33]. Therefore, iron carbide has frequently been applied in various electrochemical energy systems for energy conversion and storage [34–38]. However, the incorporation of iron carbide in DSCs is only effective to a certain extent, and the trace amount of metallic Fe possibly present in the CEs can dissolve in conventional I_3^-/I^- redox electrolyte, leading to significant drops in performance [35,36].

In this study, in order to overcome the current limitations associated with carbonaceous materials and iron carbides, we prepared nanostructured iron carbide/carbon (Fe_3C/C) composite electrodes and applied them as CEs of DSCs employing a non-corrosive $[Co(bpy)_3]^{3+/2+}$ redox electrolyte. Unlike conventional bottom-up synthesis procedures, which entail a number of complicated steps [34–38], we prepared the Fe_3C/C composite via a facile two-step process involving electrochemical anodization of iron foil followed by post-heat treatment in a CO atmosphere. Anodic oxidation of iron resulted in the formation of nanostructured amorphous oxides on the surface, which had two following advantages; (i) large surface area originated from the nano-architecture area and (ii) high viability for transformation into compounds other than oxides, which is attributable to the amorphous nature. Owing to these favorable characteristics, highly conductive nanostructured Fe_3C films comprising thin (several nanometers thick) carbon films on the surface were synthesized on metallic Fe substrates. The composite electrodes show a superior electrocatalytic performance to that of conventional Pt CEs for the reduction of cobalt bipyridine redox species, as verified by various electrochemical techniques. Fe_3C/C composite electrodes were then directly incorporated in DSCs as CEs, and a significant increase in photovoltaic performance was observed.

2. Experimental

2.1. Syntheses of electrodes for counter electrode applications

Iron foils (Good Fellows, 99.5% purity and 0.25 mm thickness) were sequentially cleaned in acetone, ethanol and deionized water by ultrasonication for 10 min each. The iron foils were then electrochemically anodized at 50 V for 5 min using an ethylene glycol electrolyte containing 0.25 wt% NH_4F (Sigma Aldrich) and 2 vol% of H_2O. A Pt mesh was used as the CE for the anodization, and the electrode-to-electrode distance was 3 cm. The anodization was performed with the assistance of ultrasonication for effective transport of chemical species within the electrolyte. After the anodization, the iron foils were rinsed in ethanol, dried overnight, and thermally annealed at 450 °C in air or at 600 °C in CO atmosphere for 4 h in order to prepare iron oxide or iron carbide/carbon composite, respectively. Conventional platinum CEs were prepared by a thermal decomposition method [39] in which isopropanol containing 50 mM of H_2PtCl_6 was spin-cast on fluorine-doped tin oxide (FTO) glass (TEC-8, Pilkington) substrates followed by heat treatment in air at 400 °C for 30 min.

2.2. Preparation of dye-sensitized solar cells

For the preparation of mesoscopic TiO_2 photoelectrodes, TiO_2 paste containing 30 nm-sized colloidal nanoparticles (Dyenamo, DN-GPS-30TS) was cast onto the FTO glass substrates by the doctor-blading technique followed by thermal sintering at 500 °C for 30 min in air. The electrodes were then subjected to $TiCl_4$ post-treatment in order to maximize the surface area and enhance the dye-to-TiO_2 electron injection [40,41]. For dye-sensitization, the electrodes were immersed in a mixture of acetonitrile and *tert*-butanol (v/v = 1:1) containing 0.1 mM of Y123 dye (Dyenamo, DN-F05Y) for 48 h at 30 °C. The prepared photoanode and CE were assembled in a sandwich-type configuration using a 25 μm-thick thermoplastic sealant (Surlyn, DuPont). The cobalt bipyridine redox electrolyte prepared by mixing 0.22 M $Co(bpy)_3(PF_6)_2$ (Dyenamo, DN-C01), 0.033 M $Co(bpy)_3(PF_6)_3$ (Dyenamo, DN-C02), 0.1 M $LiClO_4$ (Sigma Aldrich) and 0.2 M 4-*tert*-butylpyridine (Sigma Aldrich) in acetonitrile was injected into the cells through pre-drilled holes.

2.3. Physical and electrochemical characterizations

X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX 2500 equipped with a Cu-Kα radiation source. Scanning electron microscopy (SEM) analysis was performed using a Carl Zeiss SUPRA 55VP, and transmission electron microscopy (TEM) analysis was carried out using a Jeol JEM-2100F. X-ray photoelectron spectroscopy (XPS) spectra were measured by using a Thermo SIGMA PROBE spectrometer with an Al-Kα source. Cyclic voltammetry (CV) analysis was conducted using an Autolab PGSTAT302 N potentiostat in a three electrode system based on a Pt mesh CE and a $Ag/AgNO_3$ (0.01 M $AgNO_3$, 0.1 M tetrabutylammonium perchlorate in acetonitrile) reference electrode. Solar cell performance was assessed under standard 1 sun condition (AM 1.5G illumination with a light intensity of 100 mW/cm^2) using a solar simulator (XIL model 05A50 KS source measure units) and a potentiostat (Solartron 1480), and incident photon-to-current efficiency (IPCE) was measured with a QEX7 instrument (PV Measurements). Electrochemical impedance spectroscopy (EIS) analysis was conducted using a Zahner Zennium electrochemical workstation under a sinusoidal perturbation amplitude of 10 mV.

3. Results and discussion

3.1. Characterization of nanostructured iron carbide/carbon composite electrodes

The Fe_3C/C composite electrodes were first characterized by XRD analysis, and the XRD patterns of an iron foil and electrochemically anodized iron foils before and after the heat treatment in air or CO are displayed in Fig. 1. An iron oxide electrode was also prepared for comparative investigations, because certain facets of α-Fe_2O_3 have been reported to be active in I_3^-/I^- redox electrolyte [42]. All samples show signals attributable to the Fe substrate, which presents peaks at 2-theta positions of 44.7°, 65.0°, and 82.3°, corresponding to diffractions by the