



Incorporating transition metals (Ta/Co) into nitrogen-doped carbon as counter electrode catalysts for dye-sensitized solar cells



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ABSTRACT

Carbon materials are potential electrode materials in new energy devices such as solar cells, fuel cells, Li-ion batteries, and supercapacitors, because of their distinct advantages including low cost, high surface area, and high electric conductivity. Nitrogen doping can effectively improve the performance of carbon electrode materials, and introducing transition metals into nitrogen-doped carbon is a promising strategy to develop high-performance electrode materials. In the present work, we successfully prepared two kinds of metal-incorporated nitrogen-doped carbon materials (Co–N–C and Ta/Co–N–C) by pyrolyzing a cobalt (II) imidazolate polymer followed by ion exchange. The as-prepared Ta/Co–N–C materials present a better graphite crystal phase and higher Brunauer-Emmett-Teller (BET) specific surface area (421.5 m²/g) than that of Co–N–C (354.7 m²/g). As counter electrode (CE) materials in I⁻-mediated dye-sensitized solar cells (DSSCs), Ta/Co–N–C exhibits a superior catalytic activity and electrochemical stability than Co–N–C, resulting in a high power conversion efficiency (PCE) of 7.96%, which outperforms the level achieved using a Pt electrode (7.19%) in DSSCs. These Ta- and Co-incorporated nitrogen-doped carbon materials are expected to be used in extensive new energy applications, such as biomass, pollution control and hydrogen generation.

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1. Introduction

Dye-sensitized solar cells (DSSCs), which represent green solar energy conversion devices, have made considerable power conversion efficiency (PCE) improvements during the last two decades [1–4]. The counter electrodes (CEs) in DSSC systems played the roles of collecting electrons and reducing I₃⁻ ions [2]. This means that an ideal CE material must possess a good electrical conductivity and superior electrocatalytic activity for DSSCs. In general, Pt, a noble metal, has been the preferred CE material. However, the disadvantages of Pt, including its high cost and limited availability, limit its large-scale commercial application in DSSCs. In addition, Pt is easily corroded by the I₃⁻/I⁻ redox couple in the electrolyte [5], and is not effective for I-free redox electrolytes (e.g., Co²⁺/I³⁺ and T₂/T⁻) [6,7]. Meanwhile, Pt is readily poisoned in air and does not match the new anode materials and new dyes (e.g., Y123, D35, and

YD2-o-C8) [1]. Therefore, intensive efforts have been directed toward the search for low-cost alternatives to Pt CE materials.

Low-cost carbon materials with a high surface area and high electric conductivity were widely utilized as CEs in DSSCs, and several review papers have given detailed comments on carbon CE materials [1,3,4,8–12]. E. Ramasamy et al. reported a kind of nanocarbon CE for DSSCs that achieved a PCE of 6.73%, comparable to that for a Pt CE device (7.26%) [13]. T.N. Murakami et al. employed nanometer-sized carbon black as the catalyst for I₃⁻ reduction. The highest efficiency of 9.1% was reached by optimizing the film thickness [14]. This is the highest PCE record for DSSCs using conventional carbon materials for CEs. The mesoporous carbon was prepared and utilized as a CE in DSSCs that achieved a PCE of 6.18%, comparable to that of Pt-CE-based DSSCs [15]. An all-carbon CE in DSSCs without a fluorine-doped tin oxide (FTO) glass substrate exhibited a PCE of 8.63% [16]. Carbon nanotubes (CNTs) prepared using a screen printing method as CEs in DSSCs yielded a PCE of 8.03%, whereas CNTs grown using chemical vapor deposition (CVD) presented a PCE of 10.04% [17]. A PCE record of 13% was achieved by

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the Grätzel group using Co-mediated DSSCs that employed SM315 dye and graphene nanoplatelet (GNP) CEs [18]. Very recently, FTO/Au/GNP was used as a CE in Co-mediated DSSCs that were collaboratively photosensitized using ADEKA-1 and LEG4 dyes, superior PCEs of 14.3% and 14.7% were achieved at one sun and 0.5 sun illuminations, respectively [19]. These superior performances indicate that carbon catalyst materials are suitable as CEs in DSSCs for I_3^- reduction.

Transition metal compounds (TMCs) are regarded as hopeful alternatives to Pt because of their similar electronic structures to that of Pt [20]. In addition, research has confirmed that the metal atoms of TMCs show a prominent catalytic ability for I_3^- reduction on the surface of CE materials [21–23]. Of them, Co-based TMCs, such as CoS, Co₉S₈, Co_{0.85}Se, and CoTe, have attracted much attention because of their superior catalytic properties as CEs in DSSCs [24–27]. The best PCE for CEs composed of TMCs in I-mediated DSSC system is 9.4% in DSSCs with a Co_{0.85}Se CE grown on a conductive glass substrate using *in situ* technique. However, our group has reported NbO₂, HfO₂, Ta₂O₅, TaO, TaO_x, Nb_{3.49}N_{4.56}O_{0.44}, NbN, Ta₃N₅, Ta₄C₃, and corresponding hybrids as efficient CE materials in DSSCs [21,22,28–34]. Ta₄C₃ exhibited a significant electrocatalytic activity for I_3^- reduction as a CE material and reached 97% of the level achieved using Pt in DSSCs [30]. Ta and Co have been given a special consideration because they can form TMCs with non-metallic elements, such as O, N, and C.

Nitrogen-doped carbon can generally enhance electronic conductivity and electrocatalytic performance [35–42]. In nitrogen-doped carbon, the lone-pair electrons of the N atoms act as a donor to the delocalized π system of the hexagonal framework to enhance electron conduction [35,39]. The electronic conductivity and rate of electron transfer of carbonaceous materials are related to the density of state at the Fermi level $D(E_F)$ [43]. Nitrogen doping increases $D(E_F)$, and thus increases the electron-transfer rate due to the electronic modification of the carbon rather than the addition of a surface chemical site [37,40,44,45].

Ma et al. synthesized Co-based nitrogen-doped carbon (Co–N–C) by pyrolyzing a cobalt (II) imidazolate polymer, which satisfactorily catalyzed the oxygen reduction reaction in fuel cells [46]. Clearly, introducing transition metals into carbon-based materials to produce abundant catalytic sites is a promising strategy for achieving high-performance DSSCs.

So far, almost all early TMCs (oxides, carbides, nitrides, sulfides, etc.) and carbon materials have been developed and tested as CEs in DSSCs, and several review papers have given completed summaries of them [1,3,4,8–10,47,48]. However, we are not aware of any research on the fabrication of transition metal-based nitrogen-doped carbon in DSSCs. Herein, we attempt to incorporate Co into nitrogen-doped carbon to obtain Co–N–C by pyrolyzing a cobalt (II) imidazolate polymer, and then incorporate Ta into Co–N–C by ion exchange to obtain Ta/Co–N–C materials for use as active CE catalysts in DSSCs. The Ta/Co–N–C CE showed a PCE of 7.96%, which outperforms that of the Pt CE (7.19%).

2. Experimental

2.1. Preparation of Ta/Co–N–C and Co–N–C

The preparation scheme for Ta/Co–N–C and Co–N–C is shown in Fig. 1. First, Co–N–C was synthesized by a modified pyrolysis of the cobalt (II) imidazolate polymer [46,49,50]. Briefly, Co(NO₃)₂·6H₂O (5.82 g), imidazole (3.40 g) and piperazine (2.15 g) were sequentially added to N,N-dimethylacetamide (130 mL) with magnetic stirring. The stirring continued for 12 h. Then, the suspension was transferred to a Teflon-lined autoclave, which was sealed and placed in an oven (preheated to 135 °C for 24 h). The

autoclave was naturally cooled to room temperature, and violet crystals (the precursor of Co–N–C) were centrifuged. The precursor was pyrolyzed in a tube furnace in flowing N₂ gas at 750 °C. A subsequent acid treatment was performed with a mixture of H₂SO₄ (0.5 M) and absolute ethanol (volume ratio 100:1) under mechanical agitation at 35 °C for 11 h, to obtain Co–N–C, which is a black powder. Then, Ta/Co–N–C was obtained from Co–N–C by ion exchange. Co–N–C (210 mg) was dispersed in a solution of TaCl₅ (0.21 g) in absolute ethanol (60 mL), and the mixture was held at 35 °C for 30 h under periodic agitation. The ion-exchanged product, Ta/Co–N–C, was centrifuged and collected.

2.2. Fabrication of CEs and photoanodes

The as-prepared Ta/Co–N–C or Co–N–C powder (120 mg) with ZrO₂ peals (3.5 g) was added to isopropanol (4 mL), and the hybrid system was ball-milled for 5 h. The resultant ink was slowly sprayed over Fluorine doped Tin Oxide (FTO) glass substrates using an air spray gun. The coated FTO glass with a Ta/Co–N–C (Co–N–C) film was annealed in flowing N₂ gas at 400 °C for 30 min in a tube furnace. The expected Ta/Co–N–C (Co–N–C) CE was obtained. A Pt CE was prepared by spraying a chloroplatinic acid solution onto an FTO plate, followed by annealing at 500 °C for 30 min. A commercial TiO₂ photoanode (Yingkou OPV, Tech New Energy Co., Ltd.) was annealed at 500 °C for 30 min, followed by soaking in N719 dye for 24 h in the dark.

2.3. Assembly of DSSCs

A sandwich DSSC was assembled with a photoanode, CE and electrolyte. The photoanode and the CE were sealed using double-faced insulated adhesive tape, and the electrolyte was injected into the space between the photoanode and CE. The active area of the DSSC was 0.16 cm². More details can be found in our previous papers [21,22,29,30,34].

2.4. Characterizations

The crystallographic phases were identified by X-ray powder diffraction (XRD, Empyrean, Holland) measurements, and the elements in the materials were detected using an X-ray photoelectron spectrometer (XPS, K-Alpha, USA). The sample morphologies were observed by field emission transmission electron microscopy (FE-TEM, Tecnai2000, FEI, Japan), and cross-sectional images of Ta/Co–N–C and Co–N–C CEs were observed by field emission scanning electron microscopy (FESEM, JSM-6700F, Japan). The BET specific surface areas and pore distributions were measured using a volumetric adsorption analyzer (Micromeritics, TriStar II 3020, USA). The coordination number of Ta was determined by X-ray absorption fine structure (XAFS) experiments, which were performed at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (SRF, Beijing Synchrotron Radiation Facility, China).

Voltammograms were recorded using a CHI 602E electrochemical analyzer (Chen-Hua, Shanghai, China) in a supporting electrolyte consisting of LiClO₄ (0.1 M), LiI (10 mM), and I₂ (1 mM) in acetonitrile. Electrochemical impedance spectroscopy (EIS) measurements were performed using a CHI 606E electrochemical workstation (Chen-Hua, Shanghai, China). The EIS spectra and parameters were fitted using the Z-view software. The Tafel polarization was also measured using the CHI 602E electrochemical analyzer. The characteristic *J*-*V* curves of the DSSCs were recorded using a Keithley 2400 digital source meter connected to a solar simulator (100 mW cm², Oriel 94023A, USA).

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