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In-situ Selenization of Co-based Metal-Organic Frameworks as a Highly Efficient Electrocatalyst for Hydrogen Evolution Reaction

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ABSTRACT

Metal-organic frameworks (MOFs) derived cobalt diselenide (MOF-$CoSe_2$) constructed with $CoSe_2$ nanoparticles anchored into nitrogen-doped (N-doped) graphitic carbon has been synthesized through *in-situ* selenization of Co-based MOFs. The obtained MOF-$CoSe_2$ exhibits excellent hydrogen evolution reaction (HER) performance: it shows a small Tafel slope of 42 mV dec^{-1}, a low onset potential of 150 mV; it delivers a high current density and excellent long-term stability. Such enhancement can be attributed to the unique N-doped MOFs derived architecture with high conductivity, which can not only provide abundant active reaction sites, but also ensure robust contact between the $CoSe_2$ nanoparticles and N-doped carbon matrix, leading to outstanding electrocatalytic activity for HER. This study provides a route to prepared non-noble-metal catalyst with high efficiency and excellent electrocatalytic activity for HER.

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1. Introduction

Splitting of water into hydrogen and oxygen by electrochemical method to generate clean and renewable energy source is generally considered as one of the most promising strategies to address the issue of energy conversion [1,2]. As an efficient and facile route for hydrogen production, hydrogen evolution reaction (HER) has attracted increasing attention, because hydrogen is possible to replace fossil fuels and to meet the demands of energy supplies in the future [3–5]. More importantly, hydrogen can energize 286 kJ mol^{-1} by reacting with oxygen ($2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ ($\Delta H = -286$ kJ mol^{-1})), making hydrogen with the highest energy density [6]. Noble metals such as Pt, Ir, Ru have exhibited superior electrocatalytic properties with low Tafel slope and small overpotential for HER [7,8]. However, the high cost and the low earth abundance significantly hindered their practical application. Therefore, it is urgent to develop non-noble metal catalyst with highly efficient HER activity [4,9].

Transition-metal-based catalysts have captured intensive attention owing to their abundant earth resources, inexpensive cost and high electrocatalytic performance. Extensive efforts on transition-metal based catalysts have been made to design and optimize possible alternative to replace those expensive noble catalysts for HER and OER. In previous articles, Han et al. presented a mini review about transition-metal (Co, Ni and Fe)-based electrocatalysts for water oxidation reaction, with the purpose of summarizing and promoting the design and fabrication of novel catalysts with excellent electrocatalystic properties [10]; Cui group introduced a group of first-row transition-metal-dichalcogenides (ME_2, M = Fe, Co, Ni; E = S, Se) catalysts for HER, which exhibited superior catalytic activity [11]. In addition, the research of Cui about ME_2 suggested that the first-row transition-metal-dichalcogenides catalysts in nanoparticles form performed better than that in film form, in which $CoSe_2$ delivered the lowest Tafel slope [11]. It also revealed that nanostructured $CoSe_2$ delivered much better performance for HER than bulk $CoSe_2$, as nanostructured $CoSe_2$ can exposure much more active sites for HER [12]. Therefore, in the recent several years, various strategies on fabrication of nanostructured $CoSe_2$, including nanoparticles, nanowires, nanoarrays, nanobelt, nanocrystals and nanoneedles, have been reported to investigate the electrocatalytic properties [1,13–18].

Metal-organic frameworks (MOFs) have large surface, low density, controllable structure and good conductivity, which can provide abundant controllable nanoscaled cavities and offer congenital channels for small molecules and ions [19–22] to access, making them many potential applications in lithium-ion batteries [23–25], gas adsorption [26,27], catalysis [28–31], sensing [32,33], superconductors [20,34] and drug delivery [35,36]. In this regard, it is very promising to combine non-noble $CoSe_2$ with MOFs to obtain highly efficient electrocatalytic activity.

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Recently, some good progress has been made in MOFs-derived $CoSe_2$. Wu et al. prepared $CoSe_2$ nanoparticles from MOFs which exhibits excellent oxygen evolution reaction (OER) performance [37]. It suggests that MOF-derived $CoSe_2$ has good catalytic activity, and it maybe have potential application on HER. Zhou et al. reported that $CoSe_2$ obtained from selenization of pre-oxidized MOF-Co instead of MOF-Co through a carbonization-oxidation-selenization process delivered a HER Tafel slope as large as 82 mV dec^{-1} [38]. It suggests that it is still challengeable to synthesize MOFs-based $CoSe_2$ with high HER efficiency.

In this study, MOF-derived $CoSe_2$ (MOF-$CoSe_2$) nanoparticles anchored into N-doped graphic carbon matrix have been synthesized by *in-situ* sensitization of Co-based MOFs (ZIF-67). The MOF-$CoSe_2$ delivers excellent HER performance with low Tafel slope, small overpotential, and remarkable stability, which can be attributed to the unique MOFs structure with $CoSe_2$ nanoparticles anchored into nitrogen-doped (N-doped) graphitic carbon.

2. Experimental

2.1. Chemicals

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), 2-methylimidazole ($C_4H_6N_2$), methyl alcohol (CH_4O), selenium powder (Se), cobalt powder (Co) were all analytical grade purity and used as received.

2.2. Synthesis of MOF-$CoSe_2$ and bare $CoSe_2$

Co-based MOFs (ZIF-67) were synthesized according to previous report [25]. Typically, 5.238 g $Co(NO_3)_2{\cdot}6H_2O$ and 3.955 g $C_4H_6N_2$ were dissolved in 200 ml CH_4O, respectively; and then, the latter solution was slowly added into the former under continuous stirring. The mixed solution was aged for 24 h at room temperature, and ZIF-67 was obtained. Subsequently, the prepared purple ZIF-67 powder was transferred into an Ar_2 filled furnace tube and annealed at 900 °C for 5 h with a heat rate of 10 °C min^{-1} to obtain MOF-Co powder. Finally, the MOF-$CoSe_2$ was synthesized by *in-situ* sensitization for MOF-Co powder. A quartz boat loaded with MOF-Co powder was placed downstream to another quartz boat loaded with excessive Se powder in a furnace under Ar_2 flow which was heated up to 600 °C and kept for 3 h. When the furnace was cooled down to room temperature, the MOF-$CoSe_2$ sample was obtained. As comparison, bare $CoSe_2$ sample was prepared by direct selenization of commercial Co powder (about 300 nm) with same selenization condition as that for MOF-Co powder.

2.3. Materials characterization

X-ray diffraction ((XRD Rigaku D/MAX-rA diffractometer) was employed to characterized the phase of the obtained samples with Cu Ka radiation, and X-ray photoelectron spectroscopy (XPS, Kratos XSAM800, Al Ka radiation) were carried out to investigate the electronic binding energy. The mass ratio of the as prepared sample was confirmed by thermal gravimetric analysis (TGA, TG-DSC HT/1600). Raman spectra was performed at room temperature using excitation laser line of 532 nm (Horiba). Field emission scanning electron microscopy (FESEM, JSM-7000F, JEOL) and transmission electron microscopy (TEM, Tecnai F20 at 200 kV) were performed to examine the morphology and structure of the samples.

2.4. Electrochemical measurements

The electrochemical measurements, including linear sweep voltammetry (LSV), cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS), were performed on an electrochemical station (CHI660D) by a three-electrode method in 0.5 M sulfuric acid solution at room temperature. The working electrode was prepared by dropping 10 μL slurry which consisted of 4 mg catalyst, 750 μL deionized water, 250 μL alcohol and 50 μL Naflon (5%w/w in water and 1-propanol) onto a glassy carbon electrode (GCE, 3 mm in diameter) followed by drying.

3. Results and discussion

The XRD patterns of the MOF-$CoSe_2$, MOF-Co and bare $CoSe_2$ were shown in Fig. 1(a). The characteristic peaks of $CoSe_2$ in the patterns of MOF-$CoSe_2$ and bare $CoSe_2$ match well with pyrite phase $CoSe_2$ (PDF No.65-3327), and the sharpest three diffraction peaks centered at 34.4°, 37.8° and 51.9° corresponds to (210), (211) and (311) lattice plane, respectively. The special peak at 26.5° which existed in the patterns of MOF-Co and MOF-$CoSe_2$ represents the carbon framework formed after the carbonization during annealing process. The strong peaks in the pattern of MOF-Co matches well to (111), (200) and (220) plane to cubic Co metal (PDF No.89-7093). In the carbonization process at high temperature, the organic ligands fractured and the related cobalt ions were reduced, resulting in the formation of Co nanoparticles embedded into MOFs derived carbon [25]. The $CoSe_2$ was formed through the reaction of Co nanoparticles and vaporous Se which got inside through the MOFs structure.

The component of the MOF-$CoSe_2$ was confirmed by thermal gravimetric analysis (TGA) with a heating ratio of 10 °C min^{-1} from room temperature to 800 °C under air. The TGA curves of the bare

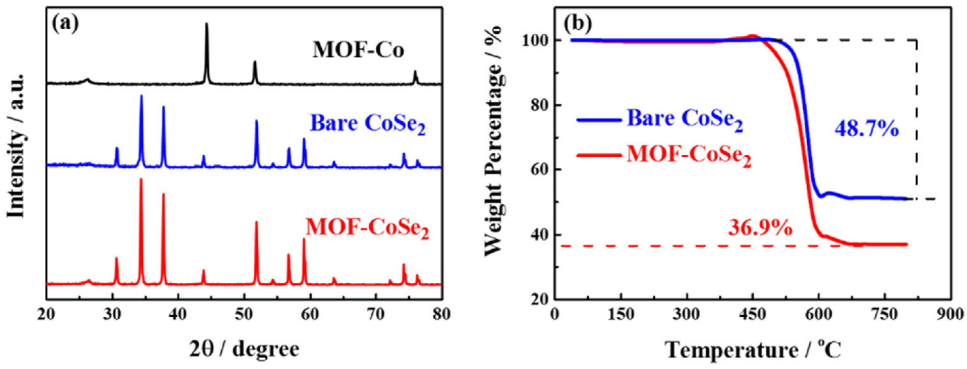

Fig. 1. (a) The XRD patterns of MOF-$CoSe_2$, bare $CoSe_2$ and MOF-Co. (b) The TGA curves of MOF-$CoSe_2$ and bare $CoSe_2$.

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