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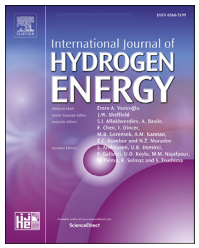

Facile preparing composite of $CoSe_2$ wrapping N-doped mesoporous carbon with highly electrocatalytic activity for hydrogen evolution reaction

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ABSTRACT

The composites of cobalt selenide ($CoSe_2$) wrapping nitrogen self-doped mesoporous graphitic carbon were facilely prepared by hydrothermally wrapping $CoSe_2$ on the carbon material derived from pyrolysis of N-containing zeolitic imidazolate framework. The composites exhibit excellent catalytic activities and durability for electrochemical hydrogen evolution reaction (HER) in 0.5 M H_2SO_4. The optimum composite catalyst needs only low overpotential of 159 mV to approach 10 mA/cm^2 and as low as 83 mV/dec of Tafel slope can be obtained. The results are among the most active for HER based on non-noble materials in acidic solution.

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Introduction

As a representative of new energies, hydrogen is a most promising renewable alternative to traditional fossil energy in respect of its high gravimetric energy density and zero-emission [1]. Among various methods for hydrogen production, the hydrogen evolution reaction (HER) by electrolysis of water has been widely considered as a most efficient and sustainable method to produce hydrogen [2]. So it is very important to develop high-performance electrocatalysts to improve the HER efficiency. To date, platinum-based catalysts are acknowledged as the most effective catalysts for HER. However, low reserves and high cost seriously limit the widespread application of platinum-based catalysts [3,4]. This fact has impelled much more attention being paid to exploit non-precious catalysts with high catalytic activity. Various earth-abundant materials have been fabricated as candidates for HER catalysts including transition-metal dichalcogenides (TMDs) [5–8], metal phosphide [2,9], carbide [10–12]and

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nitride [9]. However, the reported catalysts were still limited by insufficient activity and poor stability in acidic media comparing with Pt based ones. Thus, fabricating earth-abundant catalysts with both prominent activity and durability towards HER is still the main challenge [13].

Among the reported catalysts, the TMDs, such as MoS_2 [14,15], $CoSe_2$ [13,16] have received much more attention since their hydrogen binding energy is close to that of Pt-group metals as well as their low cost and high electrochemical stability in acid [16,17]. Within these catalysts, $CoSe_2$ displays the optimal activity, demonstrating it to be among the most active electrocatalysts based on non-noble metals [18]. Unfortunately, the HER activity of such TMDs composites is limited by intrinsic low conductivity, rare active edges as well as relatively small special surface area [19,20]. In order to further improve the electrocatalytic activity, many strategies have been adopted including improving the electronic contact between the active sites of TMDs and the underlying electrode. From this viewpoint, a most effective way is to composite the TMDs with carbon materials which have high specific surface areas and electricity conductivities. Various carbon materials were used as supports for TMDs to fabricate such composites, such as carbon black [21], ordered mesoporous carbon nanospheres [22,23]carbon nanotubes (CNTs) [24], graphene [25], ITO [26] and reduced graphene oxide (rGO) [25] etc. However, the star carbon materials of carbon nanotubes and graphene suffer from scarce production and high cost. Alternatively, heteroatom, especially nitrogen doped mesoporous carbon materials have been employed as good candidates benefiting from their high specific surface area, large pore volume, and adjustable mesopores. What's more, the above physical properties of carbon materials are strongly dependent on the pore structure and graphitization-degree of the catalysts which are closely related to preparation methods and the type of precursors used [10,22,27]. In addition, it has been extensively reported that addition of chemical agents so called activating agent, such as widely used $ZnCl_2$, can inhibit formation of tar, thus enhancing the yield of carbon [28–31]. $ZnCl_2$ is also usually used as a inorganic pore-fabricating agent and activation with $ZnCl_2$ can effectively fabricate a number of mesopores when followed by annealing treatment [32], and thus improving porous structure and surface area of the obtained carbon [28,33].

Based on above consideration, in this work, a nitrogen self-doped mesoporous carbon was prepared by pyrolysis of N-containing zeolitic imidazolate framework 8 (ZIF-8) in the presence of $ZnCl_2$ as activating agent. A series of composite catalysts were prepared by hydrothermally wrapping $CoSe_2$ on the as-prepared carbon. The resulted composite exhibits remarkable electrocatalytic activity and stability for HER in acidic media and much low overpotential and Tafel slope can be obtained.

Experimental

Preparation of the catalysts

ZIF-8 was prepared as reported previously [34]. The nitrogen doped carbon material was prepared by pyrolysis of ZIF-8 under activating of $ZnCl_2$. Typically, ZIF-8 was thoroughly mixed with six times weight of $ZnCl_2$. The mixture was then pyrolyzed in N_2 at 800 °C for 3 h with a heating rate of 5 °C/min. The off-gas was treated with KOH solution, H_2SO_4 solution and acetone successively. The obtained product was then treated with 1M HCl to remove the zinc residue, washed with ethanol and dried at 80 °C in an oven. The finally obtained carbon material was denoted as NC.

The catalyst of composite $CoSe_2$/NC was prepared as following: 170 mg NC was dispersed in 180 mL ethanol under vigorous stirring for 30 min. Then, 0.39 mmol $CoCl_2$, 0.79 mmol SeO_2 and 26 mmol sodium acetate were added to the NC suspension and the mixture was stirred overnight in N_2 atmosphere. After that, another solution of 4.92 mmol $NaBH_4$ dissolved in 20 mL ethanol was dropped to the above mixture and stirred overnight. The resulting mixture was separated by filtration and washed several times with ethanol. The black cake was dried at 60 °C for 48 h, and then annealed at 400 °C for 4 h in N_2 atmosphere to remove amorphous selenium. The finally obtained composite was assigned as $CoSe_2$/NC-170. To optimize the amount of NC, the other two composites were also prepared by the same method and denoted as $CoSe_2$/NC-85 and $CoSe_2$/NC-340, respectively. For comparison purpose, the sample of $CoSe_2$ was also prepared under the same conditions without adding the NC. The as-prepared composites were thoroughly grinded before further use.

Catalysts characterizations

The XRD patterns were characterized by a Shimadzu XD–3A (Japan) using filtered Cu-Kα radiation. X-ray photoelectron spectrum (XPS) analysis was performed on a PHI 5000 Versaprobe system using monochromatic Al Kα radiation (1486.6eV). All binding energies were referenced to the C1s peak at 284.6 eV. The morphologies of the samples were characterized by a scanning electron microscopy (SEM) using a Carl Zeiss Ultra Plus and a HITACHI H-8100 transmission electron microscopy (TEM) with an accelerating voltage of 200 kV. The specific surface area and the pore size distribution were determined by N_2 adsorption-desorption method using an ASAP 2020 Micromeritics instrument at 77 K.

Electrochemical measurement

Electrochemical measurements were performed with a CHI 760E electrochemical analyzer. All electrochemical tests were carried out by a three electrode cell system using 3 mm glass carbon (GC), graphite rod and Ag/AgCl (in 3M KCl) as working electrode, auxiliary electrode and reference electrode, respectively. The catalyst ink was prepared by dispersing 2.5 mg catalyst in 1.0 mL mixture solvent of 0.98 mL water and 0.02 mL ethanol under ultrasound for 30 min. Before test, 3 μL of the catalyst ink was loaded onto the well polished electrode and the electrode was dried at room temperature. The linear sweep voltammetry (LSV) and cycle voltammetry (CV) were performed in high-pure nitrogen saturated 0.5 M H_2SO_4 in the range of 0 to −1.0 V (vs. Ag/AgCl) at a sweep rate of 10 mV/s. CV measurements for long-term stability were performed in the range of −1.0 to 0 V (vs. Ag/AgCl) at a sweep rate of 50 mV/s. All the potentials were calibrated to a reversible hydrogen electrode (RHE) based on the equation of E (RHE) = E (Ag/AgCl) + 0.0591 pH + 0.197 V.

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