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Synthesis of Cobalt–Glycerate hierarchical structure and their conversion into hierarchical CoP nanospheres for the hydrogen evolution reaction

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ABSTRACT

One of the effective strategies to enhance hydrogen evolution reaction (HER) performance is to increase the catalytic sites of catalyst by designing and tailoring the nanoscale morphology of the catalyst. In this work, by using solid Co-glycerate (CoG) nanospheres as sacrificial template, various CoG hierarchical structures were successfully fabricated in water/ethanol mixed solution via a solvothermal reaction. The microstructure and morphology of obtained CoG nanospheres could be simply tuned by varying the water content. After a subsequent phosphorization reaction, multi-structural CoG was converted into hierarchical CoP nanospheres with well-preserved morphology. The essential influence of water on the microstructure of CoG was discussed in detail. Owing to the ultrathin nanosheet subunits, the as-prepared CoP nanospheres exhibited high performance with overpotential of 121 mV to achieve the current densities of 10 mA cm^{-2} , small Tafel slope of 56 mV dec^{-1} , and good stability under acidic condition. This work could provide an effective strategy to fabricate metal phosphide electrocatalysts with delicate hierarchical nanostructure for the application of HER.

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Introduction

The increasing concern on environmental pollution has urged researchers to find clean and sustainable energy alternatives to fossil fuels [1–4]. Hydrogen is considered as an ideal candidate for the replacement of fossil fuels due to its ease of storage and distribution, high conversion efficiency and zero carbon emission [5–9]. Water electrolysis is one of the most promising methods for hydrogen production [10]. In this

electrochemical process, an efficient electrocatalyst for HER is the prerequisite for affording high cathodic current at low overpotential [11–17]. To date, Pt is the best electrocatalytic material in acid but suffers from scarcity and high cost in nature, which limits its large-scale use in water electrolysis [18–20]. Therefore, it is of great importance to develop excellent efficient, robust stable, and cost effective electrocatalysts based on earth abundant materials. Recently, cobalt phosphide (CoP) has been identified as a promising catalyst for highly active HER in acid solutions [21–24]. In the past few

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years, a few of CoP electrocatalysts with different morphologies, including nanospheres, nanoboxes, nanowires and nanotubes, have been synthesized [25–32].

Tailoring the nanoscale morphology of the catalyst can further increase specific surface area, surface/body ratios, and electrochemically active sites, which is one of the effective strategies to improve HER activity [33,34]. Therefore, much efforts have been devoted to produce multi-shelled nanostructures, hierarchical nanostructures and high complexity structures [35–42]. Moreover, these intriguing structures exhibit more excellent electrochemistry performance. For instance, Ho et al. synthesized hollow NiCo-LDH/Co₃S₈ hybrid using a pseudomorphic transformation strategy and achieved excellent electrochemical performances and outstanding stability [35]. Lou et al. developed complex Co-based double shelled nanocages from different MOFs, which showed exceptional performance as a battery-type electrode [36]. Dai et al. synthesized 2D Co-based ultrathin metal-organic framework nanosheets using Zif-67 as the precursors via ion-assisted solvothermal treatment, which showed remarkable oxygen evolution activity in alkaline electrolytes [37]. Zhu et al. fabricated the hierarchical yolk-shelled Ni-Co phosphides nanospheres using the Ni-Co alkoxide as template, which yielded synergistically active site, mass transport and dynamic modulations for the oxygen evolution reaction (OER) [38].

Herein, the various CoG hierarchical structures with nanosheet-constructed shells have been successfully synthesized by treating solid CoG nanospheres in water/ethanol via a two-step hydrothermal method. By varying the content of water, the morphology of obtained CoG nanospheres can be accurately adjusted. After phosphating obtained CoG with NaH₂PO₂ in N₂ atmosphere, hierarchical CoP nanospheres with different morphologies have been obtained. Notably, the hierarchical structures can reduce the mass transfer resistances, improve electrolyte penetration and benefit ion diffusion. As expected, benefiting from their unique structural merits, the hierarchical CoP nanospheres with ultrathin nanosheets subunits show the highest catalytic activity for HER in comparison with other samples.

Experimental section

Reagents

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%), isopropanol (≥99.5%), glycerol (99%), sodium hypophosphite (NaH₂PO₂, 99%) were purchased from Macklin. Ethanol (99.7%) were purchased from the Tianjin BASF Chemical Co. Ltd..

Synthesis of solid CoG nanospheres

Typically, 162 mg Co(NO₃)₂·6H₂O was dissolved into 60 mL isopropanol and 12 mL glycerol to form a transparent pink solution by stirring. Then, the solution was transferred into a Teflon-lined stainless steel autoclave and kept at 180 °C for 6 h. After cooling to room temperature naturally, the precipitate was separated by centrifugation, washed with ethanol for several times and dried in an oven at 70 °C for 12 h.

Hydrothermal transformation of solid CoG into CoG hierarchical structure

30 mg solid CoG was dispersed in 60 mL mixed solution containing ethanol and water. Then, the dispersion was transferred into 100 mL Teflon-lined stainless steel autoclaves kept at 100 °C for 2 h. The product was harvested by centrifugation and washed with ethanol several times and dried at 60 °C overnight. For the sake of clarity, the product prepared in 60 mL mixed solution containing X mL water (X = 0, 15, 30, 60) was denoted as CoG–X.

Synthesis of hierarchical structure CoP nanospheres

The as-prepared CoG–X and NaH₂PO₂ were weighed by mass ratio of 1:10 and putted at two separate positions in a porcelain boat with NaH₂PO₂ at the upstream side of the furnace calcined at 160 °C for 20 min in nitrogen atmosphere with the heating rate of 5 °C·min⁻¹, and then heated at 300 °C for 1 h. Herein, CoP obtained from conversion of CoG–X was denoted as CoP–X.

Structural characterization

Scanning electron microscope (SEM) images and Energy dispersive X-ray spectrometry (EDS) was employed on the same FESEM equipment to analyze the composition and element distribution of CoP hollow microspheres (JSM–6700F, JEOL Japan). Transmission electron microscopy (TEM) images were taken on a transmission Electron Microscope (JEOL JEM–2100F). The phase composition of the samples were determined by X-ray diffraction (XRD, Rigaku D-max-γA XRD with Cu K_α radiation, λ = 1.54178 Å) from 5° to 80°. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin–Elmer PHI 550 spectrometer with Al K (1486.6 eV) as the X-ray source. Fourier-transformed infrared spectroscopy (FTIR) was conducted with a Nicolet iS 10 (Thermo Scientific, KI wafer technique, USA).

Electrochemical measurement

All the electrochemical measurements were conducted by using the AUTOLAB electrochemical workstation (Autolab PGSTAT302N, Metrohm, Switzerland) in a typical three-electrode, a graphite rod as the counter electrode, a glassy carbon electrode coated with catalysts as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. Firstly, the electrode was polished with polishing powder, washed with deionized water, and then dried with cold air. Subsequently, 4 mg CoP powder, 4 mg carbon black were admixed in 750 μL deionized water, 250 μL ethanol, 30 μL 5 wt% Nafion solution, forming a mixed solution, which was ultrasound for at least 30 min 5 μL the prepared solution was dropped onto the polished electrode eventually. Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s⁻¹, which yielded the relation E_{RHE} = E_{SCE} + 0.241 V in 0.5 M H₂SO₄ [39–42]. The HER electrocatalytic activities of these CoP with different morphologies were investigated in 0.5 M sulfuric acid solution with the same loading of 0.5 mg cm⁻² on a glassy carbon (GC) electrode. The electrochemical surface area (ECSA)

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