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An efficient and cost-effective tri-functional electrocatalyst based on cobalt ferrite embedded nitrogen doped carbon

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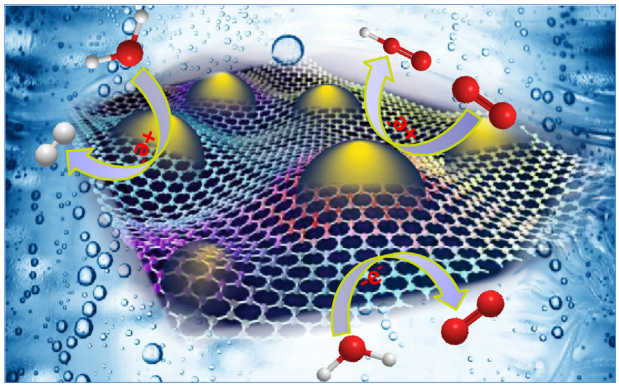
GRAPHICAL ABSTRACT



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ABSTRACT

The development of efficient, cost-effective and long-lived electro-catalyst is necessary for the realization of practically viable water-splitting systems. A trifunctional electrocatalyst for water splitting (hydrogen evolution, oxygen reduction and oxygen evolution reaction, HER/ORR/OER) was designed via eco-friendly and facial way. $CoFe_2O_4$ nanoparticles embedded in nitrogen doped mesoporous carbon were prepared using chicken egg white/albumin after pyrolysis at different temperatures, 700, 800, 900 and 1000 °C. The specific surface area, pore size and the interaction between $CoFe_2O_4$ nanoparticles and carbon matrix were tuned via pyrolysis temperature. The catalyst prepared at 900 °C, (N/CF-EC-900) exhibit superior catalytic activity as well as the superior stability than that other nanocomposites prepared and other commercial catalyst (Pt/C, RuO_2) for water splitting. Our findings emphasize the importance of $CoFe_2O_4$ nanoparticles embedded in the carbon and suggest the catalytic activities with low onset potential, high current densities, small Tafel slope in basic medium.

1. Introduction

The large consumption of energy, the crises of fossil fuels as well as environmental plight from the excessive rely on fossil fuels make it urgent to unfold eco-friendly and renewable energy sources. The use of hydrogen (H_2) as promising energy carrier generated by water splitting will reduce the environmental issues and provide sustainable power sources [1–3]. Water splitting involves hydrogen evolution (HER, $H^+ + e^- + \bullet \rightarrow 1/2H_2 + \bullet$), oxygen reduction (ORR, $O_2 + H_2O + 4e^- \rightarrow 4OH^-$) and evolution ($4OH^- +$ OER, $\rightarrow O_2 + H_2O + 4e^-$) reactions, which plays a paramount role in energy conversion and storage devices, particularly in the field of fuel cells

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and metal air-batteries. An efficient catalyst is mandatory for water splitting; several precious metal-based materials have been known to be very efficient catalysts for HER/ORR (Pt-based) and OER (Ru, Ir- based) [4–6]. However, the high cost and scarcity on earth of these precious metal-based electrocatalysts have precluded the renewable energy technologies from commercialization. Therefore, the development of alternative cost effective, stable and efficient tri-functional electro-catalysts with low over-potentials for HER, ORR and OER reactions remains great challenge with high efficiency and low cost [7–12]. Among the various electrocatalysts investigated for water splitting, earth-abundant metals based spinals strictures exhibit promising catalytic activities toward both OER and ORR [13–16]. However, the spinal such as $CoFe_2O_4$, $NiFe_2O_4$, and $FeCr_2O_4$ etc., prepared by the traditional synthetic routes and usually possess large particle sizes with low specific surface areas, and low electric conductivity, which have greatly reduced the electrocatalytic excitement of the spinal materials for the ORR and the OER [17,18]. Recently, we have reported Fe and Ni based alloy nanostructures as bifunctional catalysts in water electrolysis [19]. On the other hand, supported materials such as metal phosphate, carbon nanotubes, graphene and graphite are very interesting materials and already spread out in electrochemical devices due to their pre-eminent stability, conductivity, additionally carbon based materials have the prospect to control the size and morphology of the nanoparticles [20–23]. Moreover, doping of heteroatoms have been used improve the bulk properties and surface chemical properties in the carbon based nanomaterials. However, previously reported carbon-based electrocatalysts exhibit excellent catalytic activity, but efficient trifunctional electrocatalyst using carbon-based and spinals nanocomposites particular for water splitting have rarely been reported [24–26]. Therefore, the development of multifunctional nitrogen/cobalt-ferrite doped carbon electrocatalysts is highly desirable [27,28]. Up to date, only few kinds of precursors such as sucrose, polyacrylonitrile, phenol-formaldehyde (PF) resin, melamine-formaldehyde (MF) resin, gelatin and other polymers were used for the synthesis of porous carbons [25,29–31]. Different from other precursors, herein egg white protein was chosen as unique carbon precursor for the synthesis of nitrogen-doped porous carbon as well as the size-controlling agent in the production of $CoFe_2O_4$ nanoparticles inside the N-doped carbon by a simple one-pot thermal treatment. This method based on the principles of green chemistry for large scale and low cost synthesis of cobalt ferrite embedded nitrogen doped carbon (N/CF-EC). The prepared N/CF-EC nanocomposites possess synergistic relationships, large active surface area, unique composition and structure, and high performance tri-functional catalysts for HER, ORR and OER to realize the purposeful water splitting.

2. Experimental

2.1. Chemicals and reagents

Cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$] and iron nitrate [$Fe(NO_3)_3{\cdot}9H_2O$] were purchased from Sigma–Aldrich, Germany. Fresh albumen was extracted from fresh hen eggs. Commercial 20% Pt/C, and Ru_2O as reference electrocatalysts and other chemicals were purchased Sigma-Aldrich and directly used without further purification. Milli-Q water was used throughout all experiments.

2.2. Synthesis of N/CF-EC-nanocomposites

The fresh egg albumin (40 ml) was unyoked, homogenized and mixed with deionized water (60 ml), the pH of the solution was retain at 7.5 using acetic acid. The stoichiometric amounts, 1.45 gm of [$Co(NO_3)_2{\cdot}6H_2O$] and 4.04 gm of [$Fe(NO_3)_3{\cdot}9H_2O$] were added into the albumin solution. After stirring for 2 h at 40 °C, the solution was subsequently dried followed by stirring and heating at 250 °C until the precursor solution was turns in fluffy mass after the evaporation of water. Then the dried product was annealed in a tube furnace at 700, 800, 900 and 1000 °C with a heating rate of 5 °C/min and under the flow of helium (He, 300 ml/min). The resulting black products were dispersed in 1 M HCl solution and stirred for 2 h to partially remove metallic cobalt and iron.

2.3. Characterizations

The morphology and particles sizes details of N/CF-EC were determined using the field emission scanning electron microscopy (FESEM, JEOL JSM 7600F) and transmission electron microscopy (FE-TEM, JEM-2100F, JEOL). Thermogravimetric analysis was conducted in air atmosphere from room temperature to 800 °C with heating rate of 10 °C/min using SDT Q600 (TA instrument). X-ray diffraction (XRD) analysis was carried out on a PANalytical X′pert PRO X-ray diffractometer. Specific surface area was calculated using Brunauer–Emmett–Teller (BET) method and the pore size distribution plot was derived based on the Barrett–Joyner–Halenda (BJH) method. XPS analyses were performed using a Kratos Axis Ultra DLD electron spectrometer (PHI, PHI5300 system). Raman spectra were acquired on a RENISHAW in via instrument with an Ar laser source of 488 nm in a macroscopic configuration. The compositional analysis was carried on an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian VISTA-MPX). The FTIR and TG–FTIR-MS experiments were performed using simultaneous thermogravimetry (STD 600 TA Instrument) coupled with FTIR (Bruker Tensor 27) and mass spectrometry (Thermo).

2.4. Electrochemical measurements

The electrochemical measurements were carried out using a three-electrode system comprising a platinum wire counter electrode, a Ag/AgCl reference electrode and a catalyst-modified glass-carbon (3.0 mm) working electrode with a CHI 660D electrochemical workstation (Chenhua, Shanghai) [32]. To prepare the homogeneous ink, 10 mg catalyst and 0.05 ml Nafion was dispersed in 2 ml propanol, and then the mixture was sonicated for 1 h using probsonicator. The mass of as-prepared catalyst loading on the GCE was ~0.17 mg cm^{-2}. For comparison, the commercial available RuO_2 and Pt/C (20 wt%) modified GCE were carried out in the similar experimental condition. The details of catalytic procedure were provided as electronic supporting information (ESI).

3. Results and discussion

3.1. Microstructure and catalyst characterization

Egg albumin bimetallic complex (EABC) was adopted as templates to fabricate N/CF-EC nanocomposites. The precursor EABC was prepared via cobalt (II) nitrite, iron (III) nitrate in 1:2 M ratio and fresh unyoked albumin mixture, the main synthetic procedure to prepare N/CF-EC is illustrated by figure (SF-1, ESI) [33]. Thermal treatment of EABC at 700 °C, 800 °C, 900 °C and 1000 °C under inert atmosphere gave the $CoFe_2O_4$ nitrogen doped carbon nanocomposites, denoted as N/CF-EC-700, N/CF-EC-800, N/CF-EC-900 and N/CF-EC-1000 respectively. By tuning the temperature of the pyrolysis the $CoFe_2O_4$ nanoparticles size, surface area, pore size and the interaction of $CoFe_2O_4$ with nitrogen doped carbon matrix has been controlled. During the pyrolysis (TGA-FTIR-MS) of EABC the volatile products such as CO, CO_2, NH_3, NO and H_2N-NH_2 were evolved and measured using TG-FTIR-MS technique (SF-2 and SF-3 ESI)