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Graphene supported atomic Co/nanocrystalline Co_3O_4 for oxygen evolution reaction

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ABSTRACT

Electrochemical water splitting by a robust electrocatalyst plays a key role in hydrogen production for clean and sustainable energy. In this work, a kind of nanohybrid of graphene supported atomic Co and nanocrystalline Co_3O_4 was synthesized through electrochemical synthesis of atomic cobalt onto graphene using 1-Butyl-3-methylimidzolium tetrachlorocobalt [$(BMIm)_2CoCl_4$] as an electrolyte. By virtue of the synergistic effect of single-cobalt atoms and Co_3O_4 nanoparticles, the nanohybrid presents enhanced electrocatalytic performance toward the oxygen evolution reaction. The low onset potential is 0.49 V (vs. Ag/AgCl) and the overpotential of the current density of 10 mA cm^{-2} is 0.30 V in aqueous solution, which is comparable to commercial RuO_2. Moreover, the nanohybrid exhibits remarkably long stability for over 45 h at a fixed potential of 0.6 V.

1. Introduction

As a sustainable fuel to meet the increased energy demands [1,2], hydrogen is currently produced in large scale by steam-methane reforming route [3,4], which results in huge amount carbon dioxide emission and has triggered considerable environmental attention. The energy conversion in water splitting reaction is a straightforward and clean process that does not generate any environmental pollution. However, the efficiency of water electrolysis still remains a grand challenge and needs to be improved [5]. The water splitting electrolysis process involves oxygen evolution reaction (OER) at the anode and hydrogen evolution reaction (HER) at the cathode. Compared to two electron transfer steps required for HER, the OER is kinetically sluggish and needs four electron transfer steps, resulting in a considerable efficiency loss. Therefore, OER is a key half reaction for determining the whole efficiency of water splitting electrolysis [6,7]. However, developing high active catalysts toward OER with economic cost remains great challenges since the most active OER catalysts consisting of noble metal oxides such as RuO_2 and IrO_2 [8–10]. However, their scarcity and high cost hinder their large-scale utilization, therefore, transition metal oxide based electrodes have thus been widely developed [11,12]. Recently, transition metal oxides including magnanimous oxide, iron oxide, cobalt oxide and nickel oxide as promising candidates have received considerable attention due to their low cost, rich sources, excellent chemical durability, intriguing ductility and excellent corrosion resistance [13,14]. Specifically, various cobalt-based catalysts such as metallic cobalt, precious metal-cobalt and cobalt-nonmetallic compound have been reported, of which cobalt oxides compound has been studied most. Xiang et al. reported a triadic photoanode consisting of Co-based layered double hydroxide (LDH) nanosheets which played an important role in water oxidation [15]. Apart from the elemental composition, the behaviour of OER electrocatalyst is usually dependent on the local microstructures and the size effect of active sites. Recently, Dai's group reported a hybrid material consisting of Co_3O_4 nanocrystals supported on graphene as a high-performance bi-functional catalyst for ORR and OER [16]. Zhao and co-workers also reported OER catalysts made of Co_3O_4 nanoparticle/graphene nanohybrids, fabricated by the layer-by-layer assembly [17]. Liang et al. have shown Co_3O_4/graphene hybrid can be used as an active OER catalyst as well as oxygen reduction reaction (ORR) catalyst.

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Co_3O_4/CNT materials were also prepared as high performance catalysts towards oxygen evolution [18,19]. A highly dispersed ultrafine Co_3O_4 nanoparticles within the N-doped carbon was reported to exhibit excellent activity outperforming RuO_2 [20]. Besides the elemental composition, the behaviour of OER electrocatalyst is usually dependent on the local microstructures and the size effect of active sites. Recently, cobalt based active components with well-aligned nanostructures have been successfully grown on conductive substrates, especially two-dimensional (2D) materials, are significantly beneficial for improving the catalytic activity [21,22]. Moreover, recent theoretical and experimental results have demonstrated that subnanometer clusters have better catalytic activity and/or selectivity than nanometer-sized particles [23–25]. For heterogeneous catalysis, only the surface atoms of the catalyst in unsaturated coordination environment are necessary and have higher reactivity [26]. Therefore, the innovative concept of single-atom catalysis (SAC) has attracted increasing attention in the field of heterogeneous catalysis [27–29]. A series of SACs have been reported, such as Ni_1/FeO_x [30], Pt_1/θ- Al_2O_3 [31], Pt_1 (Au_1)/ZnO [32], Pd (Pt)-C_3N_4 [33–35], Co-MoS_2 [36] and Co/nitrogen-doped graphene [37], which have shown excellent performances in different catalytic systems.

Herein, we synthesized an atomic Co-Co_3O_4/graphene nanohybrid by using tetrachlorocobalt $CoCl_4^-$-based ionic liquid as cobalt source via oxidative electrodeposition method. The electrochemical investigation demonstrates that the nanohybrid exhibits excellent activity for OER and much better durability than commercial RuO_2. We used high-angle annular dark field TEM combined EELS spectroscopy, fine XPS, and synchrotron x-ray absorption spectroscopy analyse single cobalt atoms dispersed on graphene and the catalytic active sites for oxygen evolution reaction.

2. Experimental

2.1. Chemicals

Graphite (99.95% purity) was obtained from Qingdao Huarun Graphite Co., Ltd., 1-Butyl-3-methylimidzolium tetrachlorocobalt [$(BMIm)_2CoCl_4$, 99%], KOH, commercial RuO_2 (99.9%), hydrochloric acid (HCl, 37%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification.

2.2. Material synthesis

Graphene was prepared based on a modified electrochemical exfoliation method [38,39]. Atomic Co-Co_3O_4/G electrocatalyst was synthesized by electrodeposition conducted in a conventional three-electrode setup. Graphite papers were used as current collector with a space of around 5 mm in the electrolytic cell. One graphite paper casted by graphene coating of around 1 mm thickness was used as positive electrode. The electrodeposition process was conducted under CV charge/discharge from −1 V to +4 V at scan rate of 2 mV s^{-1} in 1-Butyl-3-methylimidzolium tetrachlorocobalt ($(BMIm)_2CoCl_4$) at 60 °C. After that, the graphene coating charged was peeled off by hand and was further calcinated under Ar flow in a tubular furnace at 700 °C for 1 h with a heating rate of 5 °C min^{-1}, and then changed to air flow and annealed at 500 °C for 1 h. For comparative investigation, acid washed atomic Co-Co_3O_4/G, Co_3O_4+G, bare Co_3O_4 were along synthesized. Acid washed atomic Co-Co3O4/G and acid washed Co_3O_4+G were obtained by immersion atomic Co-Co_3O_4/G and Co_3O_4+G powders in concentrated 5 M HCl at 80 °C for 48 h to remove Co_3O_4 nanoparticles. And then it was washed to pH 7 with deionized water. For Co_3O_4+G control sample, the electrochemical process was excluded, graphene was simply mixed with $(BMIm)_2CoCl_4$ followed annealing at the same condition. Bare Co_3O_4 was synthesized through calcination step without adding any graphene content.

2.3. Characterizations

Surface morphology was determined by scanning electron microscopy (SEM) using a field-emission SEM JSM-7001 F (FESEM) operating at 10 kV. X-ray diffraction (XRD) analysis were performed using the Cu Kα (1.5406 Å) radiation recorded from 5° to 85° at a scan rate of 0.02° s^{-1}. Transmission electron microscopy (TEM) images were taken with FEI, TECNAI G2 F20 microscope at acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using Thermo ESCALAB 250 spectrometer, employing an Al-KR X-ray source with a 500 μm electron beam spot. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (Netzsch STA409PC) at a heating rate of 10 °C min^{-1} from 20 to 800 °C in Air. HAADF-STEM and EELS were performed on a JEM ARM200F equipped with double aberration correctors in Institute of physics, Chinese Academy of Sciences, and a cold field emission gun operated at 200 kV. STEM images were recorded using a HAADF detector with a collection angle between 70 and 250 mrad and a convergence angle of 25 mrad. Under these conditions, the spatial resolution is ca. 0.08 nm. Synchrotron x-ray absorption spectroscopy was conducted at beam line U19, National Synchrotron Radiation Laboratory, Hefei, China.

2.4. Electrochemical test

The electrochemical workstation (CHI660D, Shanghai, China) was used to conduct the electrochemical measurements for OER at room temperature using a typical three-electrode system with 0.1 M KOH electrolyte. A rotating disk electrode (RDE) with a glassy carbon disk (diameter: 5 mm, Pine Research Instrumentation, USA) coated with as-prepared materials was used as the working electrode. In a typical electrode preparation, 4.0 mg of as-synthesized samples were dispersed in a mixed solution with 10 μL Nafion (5 wt %), 500 μL ethanol and 500 μL deionized water to form a homogeneous slurry. Next, 10 μL of catalyst dispersion were loaded on the surface of rotating disk electrode by drop casting and dried in air. Catalyst loading were kept constant for all samples. Prior to use, the glassy carbon disk was polished with Al_2O_3 powder and then cleaned by sonication in water and ethanol for 5 min. A platinum wire was used as the counter electrode and Ag/AgCl (10 wt % KNO_3) as the reference electrode. All experiments were conducted at room temperature in an O_2-saturated 0.1 M KOH aqueous solutions. Linear sweep voltammetry (LSV) was conducted at a scan rate of 10 mV s^{-1} and corrected by 85% *iR* compensation [40], where *i* is the measured current and *R* is the compensated resistance between the working and reference electrodes. Cyclic voltammograms (CV) of atomic Co-Co_3O_4/G, Co_3O_4+G, bare Co_3O_4, acid washed atomic Co-Co_3O_4/G and acid washed Co_3O_4+G were measured in 0.1 M KOH solution in a potential window (−0.16 V to −0.08 V vs. Ag/AgCl) without faradaic processes with scan rates of 10, 30, 50, 70, 90 mV s^{-1}. The working electrode was rotated at 1600 rpm to remove oxygen gas bubbles formed at the catalyst surface. Potentials in the graphs vs Ag/AgCl and overpotentials were calculated by using equations $\eta(V) = E_{R.H.E}\text{-}.E_O$ and $E_{Ag/AgCl} + 0.208V + 0.0592$ pH, where $E_{R.H.E}$ corresponds to the potential at 10 mA cm^{-2} and E_o is equal to 1.23 V vs R.H.E. Stability test was carried out at 0.60 V (vs. Ag/AgCl) for 45 h on a nickel foam (1 cm × 1 cm), which was rinsed with acetone and dried in air. Catalytic performances of commercial RuO_2 (99.9%, Aladdin) toward OER was also measured for comparison.