Short communication

# A porous graphene/cobalt phosphate composite as an efficient oxygen evolving catalyst

Yang Li, Yang Zhao, Zhipan Zhang *

*Key Laboratory of Cluster Science, Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry, Beijing Institute of Technology, Beijing 100081, PR China*

## ARTICLE INFO

## ABSTRACT

An efficient oxygen evolving catalyst based on porous graphene film (PGF) and cobalt phosphate (Co-Pi) has been prepared by a convenient charge-controlled electrodeposition method. The Co-Pi@PGF is of high catalytic activity and stability towards water oxidation, superseding those of the Co-Pi planar film directly deposited on the electrode.

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## 1. Introduction

Harnessing the inexhaustible solar energy provides a practical solution to alleviate human beings' dependence on fossil fuels [1] and the direct storage of solar energy by splitting water to produce the chemical fuel of $H_2$ has attracted enormous interest in the past decade. However, electrochemical splitting of water into $H_2$ and $O_2$ is not an easy task. The formidable 4 proton, 4 electron proton-coupled electron-transfer (PCET) process demands a high energy input and usually leads to a large anodic overpotential ($\eta$) for oxygen evolution reaction (OER) at high current densities over long time periods, therefore limiting the overall operational efficiency [2]. Despite that various photo/electrochemical systems of oxygen evolving catalysts, both homogeneous and heterogeneous, have shown their promises in addressing this problem, the development of efficient, inexpensive and commercially viable OER catalyst remains a challenge [3,4]. Oxides of noble metals such as $RuO_2$ and $IrO_2$ are still the widely used catalysts in the industry, where the limited reserve and high cost hinder their further applications. Fortunately, recent results from electrolyzing aqueous solutions of $Co^{2+}$ salts in the presence of $KH_2PO_4$ to form the cobalt phosphate (Co-Pi) catalysts composed of amorphous $Co^{III/IV}$ mixed valence oxides provide new insights into developing low-cost alternatives to the expensive noble metal catalysts [5–7]. To further improve the catalytic current of OER, it is important to develop inexpensive OER catalysts with high active surface area through a three-dimensional electrode. Graphene, the two-dimensional single atomic carbon sheet of high electronic

conductivity, good chemical stability and high specific surface area, has shown great promise in acting as the support for various catalysts [8,9]. We have prepared porous graphene films (PGFs) with tunable macroscopic porous networks as a paradigm for electrode materials used in energy conversion and storage devices, and such an interconnected three-dimensional (3D) framework can bond all catalytic sites with fast electron transport and provide ample microporous/macroporous channels facilitating the diffusion of guest molecules and electrolytes [10]. Herein, we have electrodeposited Co-Pi on the PGF scaffold to form Co-Pi@PGF and demonstrated that the PGF can effectively optimize the Co-Pi/electrolyte interface with improved catalytic activity, qualifying Co-Pi@PGF as an efficient low-cost electrocatalyst for the OER.

## 2. Materials and methods

All chemicals were of puriss quality and used as received. Graphene oxide (GO) was prepared from natural graphite powder *via* acid-oxidation according to a modified Hummers method [11,12]. All samples were prepared in a three-electrode electrochemical system on a 660D potentiostat (CH660D working station), where the working, counter and reference electrodes were the F-doped tin-oxide (FTO) coated glass (TEC-15, Pilkington), a Pt plate and the Ag/AgCl reference electrode, respectively. The PGF sample was obtained by immersing the FTO glass (0.25 $cm^2$ in area) into a 4 mg $mL^{-1}$ GO aqueous solution with 0.1 M $LiClO_4$ as the supporting electrolyte and then applying a constant bias of $-1.2$ V to simultaneously reduce and deposit GO on the FTO electrode. The amount of the deposited GO was controlled by monitoring the charge (up to 10 mC). The working electrode was subsequently washed with deionized water to remove the unreacted GO

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* Corresponding author at: School of Chemistry, Beijing Institute of Technology, Beijing 100081, PR China. Tel.: +86 10 68918608.
E-mail address: zhipan@bit.edu.cn (Z. Zhang).

solution, immersed in a fresh 0.1 M LiClO$_4$ aqueous solution and kept at −1.2 V for 1000 s to further improve the conductivity of the obtained PGF. To prepare the Co-Pi@PGF, the PGF electrode with the FTO glass was first soaked in the solution containing 1 mM Co(NO$_3$)$_2$·6H$_2$O and 0.1 M KH$_2$PO$_4$ (pH = 7.0) for 10 min before a bias of 1.05 V was applied to deposit Co-Pi without stirring [5]. Similarly, the amount of deposited Co-Pi was tuned by monitoring the charge ranging from 0.01 to 1 C. A control sample of Co-Pi planar film on the bare FTO was prepared by depositing 1 C Co-Pi directly on the FTO glass without the presence of the PGF. The control of an amorphous IrO$_2$ nanoparticle catalyst was prepared by dissolving IrO$_2$ powder in ethanol with sonication to form a 5 mg mL$^{-1}$ solution and directly coated on the FTO glass with a surface loading of ~160 μL cm$^{-2}$.

The morphology of the samples was observed by scanning electron microscope (JSM-7500F, JEOL) and transmission electron microscope (JEM-2100, JEOL). Electrochemical characterization was generally performed in the above-mentioned three-electrode system with an aqueous solution of 0.1 M NaOH (pH = 12.9) as the electrolyte except for kinetic studies where a series of aqueous NaOH solutions with pH values of 11.0 to 13.5 were used. Potentials are converted to a reversible hydrogen electrode (RHE) scale by

$$V(vs.\ RHE) = V(vs.\ NHE) + 0.059 \times pH$$

and the overpotential for oxygen evolution is calculated by the following equation,

$$\eta = \left(V_{appl} - iR\right) - 1.23$$

where $V_{appl}$ is the applied potential vs. RHE and $iR$ denotes the internal voltage drop in the solution. The internal resistance $R$ is determined by electrochemical impedance spectroscopy (EIS) and corrected in the analysis of the data. A frequency range of 1000 to 0.05 Hz was used for EIS measurements. The ratio of the electrochemical active surface area between the Co-Pi@PGF and the Co-Pi planar film was estimated by measuring the electrochemical double-layer capacitance ($C_{dl}$) using a simple cyclic voltammetry method. The potential range of 0.86 to 0.96 V vs. RHE was used due to the lack of any obvious Faradaic current involved in this region for each catalyst.

## 3. Results and discussions

The morphology of the Co-Pi@PGF catalyst was characterized by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 1a, a typical SEM image reveals that the Co-Pi@PGF features a three-dimensional structure rich in macroporous channels and the elemental mapping (Fig. 1c) shows a uniform distribution of Co element over the material, suggesting the homogeneous presence of Co-Pi on the PGF. While the Co-Pi is not directly seen in the SEM image, it is more visible in the TEM images. Fig. 1d to i are TEM images of Co-Pi@PGF samples with different Co-Pi loadings of 0.01 (d, e), 0.1 (f, g) and 1 C (h, i), where the PGF loading was kept the same as 1 mC. As demonstrated in Fig. 1d, the graphene scaffold is a few layer in thickness and a homogenous distribution of the Co-Pi on the scaffold can be clearly resolved. At a higher magnification (Fig. 1e), the deposited Co-Pi is shown to exist in isolated domains of around 5 nm, while with increasing amount of charge (Fig. 1f to i), the deposited Co-Pi nanoparticles get closer and tend to form a continuous film (Fig. 1i). The energy-dispersive X-ray analysis (EDX) spectrum of the Co-Pi@PGF confirms the presence of Co, C and O as the main elements, suggesting the Co-Pi has been deposited onto the graphene scaffold (Fig. 1i inset). Such an architecture of high Co-Pi nanoparticle loadings on the PGF would enable the fast electron transport between the uniformly distributed Co-Pi catalytic sites
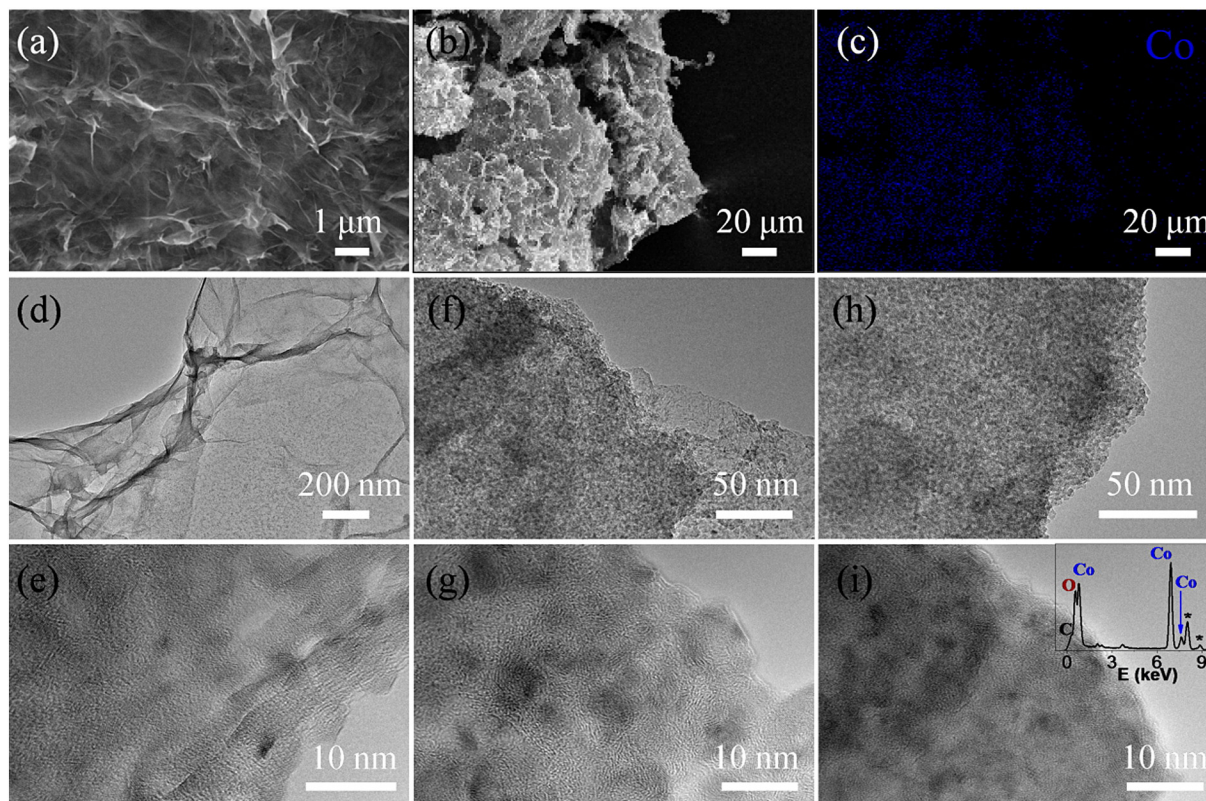


**Fig. 1.** (a, b) Typical SEM images and (c) elemental mapping image of the Co-Pi@PGF catalyst, where the charge for graphene and Co-Pi deposition is 1 mC and 1 C, respectively. Scale bars are 1, 20 and 20 μm in (a), (b) and (c), respectively. (d–i) TEM images of different Co-Pi@PGF samples. The charge for graphene deposition is kept as 1 mC while the charge for Co-Pi is 0.01 (d and e), 0.1 (f and g) and 1 C (h and i), respectively. Inset in (i) is the corresponding EDX spectrum and stars denote peaks of Cu element from the Cu grids. Scale bars are 200, 10, 50, 10, 50, 10 nm for (d), (e), (f), (g), (h) and (i), respectively.