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Two dimensional visible-light-active Pt-BiOI photoelectrocatalyst for efficient ethanol oxidation reaction in alkaline media

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ABSTRACT

Two dimensional (2D) BiOI nanoplates were synthesized and used as support for the deposition of Pt nanoparticles. Owing to broad visible light absorption (up to 660 nm), the as-obtained Pt–BiOI electrode was used as effective photoelectrocatalyst in the application of catalytic ethanol oxidation in alkaline media under visible light irradiation. Compared to dark condition, the Pt–BiOI modified electrode displayed 3 times improved catalytic activity towards ethanol oxidation under visible light irradiation. The synergistic effect of electrocatalytic and photocatalytic, and the unique of 2D structures contribute to the improvement of catalytic activity. The mechanism of enhanced photoelectrocatalytic process is proposed. The present results suggest that 2D visible-light-activated BiOI can be served as promising support for the decoration of Pt and applied in the fields of photoelectrochemical and photo–assisted fuel cell applications

1. Introduction

Direct ethanol fuel cells (DEFCs), as eco-friendly energy conversion devices, have drawn increasing attention because of their high energy conversion efficiency [1–3]. In the development of DEFCs technology, it's an importance to desire a highly active catalyst for the ethanol oxidation reaction (EOR) because of the complete oxidation of ethanol into CO_2 needs 12 electrons and the cleavage of the C—C bond. Currently, Pt-based nanostructures are selected to be the most effective electrocatalysts [1–4]. Unfortunately, the high-cost of pure noble metal of Pt as well as easily to be poisoned by the reaction intermediates (such as CO) are hampering traditional Pt electrocatalysts' further commercialization [1–4].

It's known that the catalytic activity of metal electrocatalyst depends on its environment, which can be enhanced by hybridization with support material, because the charger transfer between catalyst and support can enhance the electrochemical reactions [4]. On the other hand, the support materials also can improve the dispersion of metal electrocatalysts and decrease their loading amount. Accordingly, it's an importance to use a support material to address the above shortcoming of pure Pt for the improvement of catalyst performance. As the most optimal support material, two dimensional (2D) material, owing to its unique 2D structure and high surface area, have been attracting massive research interest [5–7]. Up to date, it has been reported various 2D material as promising supports for the decoration of Pt with high electrocatalytic activity towards EOR [8–11].

However, most of 2D materials such as graphene in the above examples only showed a single-function as catalyst support. Recently, some researchers have utilized semiconductors as supports for boosting the electrocatalytic performance towards methanol or ethanol oxidation [12–23]. In such system, the methanol or ethanol molecules are catalytic oxidized at the surface of noble metal/semiconductor through synergistic electrocatalytic and photocatalytic process under light illumination. Nevertheless, most of efforts in the study of photoassisted electrocatalytic oxidation of alcohol were based on UV-activated semiconductors such as TiO_2. There are limited indications on such photoassisted electrocatalytic oxidation of alcohol under visible light irradiation, whereas visible light accounts for *ca.* 45% in our solar energy spectrum [14].

As a series of 2D layered inorganic semiconductor materials, bismuth oxyhalides (BiOX, X = Cl, Br, and I) have received great research interest in various photocatalytic application owing to their suitable band gaps, chemically stabilized, nontoxic, and corrosion resistant [24–28]. Among three BiOX photocatalysts, BiOI is the most efficient visible-light harvesting photocatalyst because of its narrow band gap (1.7 eV) [29–32]. The absorption range of BiOI is up to 660 nm, which is highly important for the direct use of sun-

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light. Accordingly, the above researches inspired us to explore the potential application of 2D BiOI as a visible light activated support for the decoration of Pt to investigate the electrocatalytic activity towards ethanol oxidation under visible light irradiation.

In this paper, 2D BiOI nanoplates were facile synthesized by hydrothermal method and then used as a promising visible-light-active support for the decoration Pt nanoparticles. The as-obtained Pt–BiOI electrode was used as effective photoelectrocatalyst in the application of catalytic oxidation of ethanol in alkaline media under visible light irradiation. Compared to dark condition, the as–prepared Pt–BiOI composites display 3 times enhanced catalytic activity towards ethanol oxidation under visible light irradiation. Moreover, with assistance of light illuminated, such electrode also displayed long–term stability of electrocatalytic performance. The synergistic effect of electrocatalytic and photocatalytic, and the unique of 2D structures contribute to the enhancement of catalytic activity and stability. The high-efficient catalytic performance indicates that the 2D BiOI acts as an effective visible-light-active support for the synthesis of photoelectrocatalysts in photo-assisted fuel cells and other solar energy conversion applications.

2. Experimental

2.1. Materials and characterization

N,N-dimethylformamide (DMF), 1-butyl-3-methylimidazolium iodide ([bmim]I), $Bi(NO_3)_3{\cdot}5H_2O$, H_2PtCl_6, and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. without purification before use.

Scanning electron microscope (SEM, S–4700) with energy-dispersive X-ray analyzer (EDX) and transmission electron microscope (TEM, TecnaiG220) were employed to study the morphology and the composition of as-synthesized samples. X-ray diffraction (XRD, PANalytical X' Pert Pro MRD) was measured to analyze the crystal structure of samples. UV–vis diffuse reflectance spectra (DRS, UV–VIS-NIR Shimadzu UV3150, Japan) were recorded to study the optical properties of samples. X-ray photoelectron spectroscopy (XPS) was measured on an ESCALab220i-XL electron spectrometer. The C 1s line at 284.8 eV from adventitious carbon was used as reference. The electrochemical measurements were carried out on electrochemical workstation (CHI 660E) in a standard three–electrode configuration by using Pt wire, saturated calomel electrode (SCE), L-type glassy carbon electrode (GCE) as counter, reference, and working electrodes, respectively. A 500 W Xe arc lamp equipped with a UV cut-off filter (420 nm) was utilized as the visible-light source.

2.2. Synthesis of BiOI nanoplates

The BiOI nanoplates were synthesized by a hydrothermal approach. Typically, 0.5 g $Bi(NO_3)_3{\cdot}5H_2O$ was ultrasonically dispersed into 10 mL ethanol-water ($V_{ethanol}$:V_{H2O} = 1:1) for 30 min to obtain a homogeneous solution A. On the other hand, 0.4 g [bmim]I was dissolve into 10 mL ethanol-water ($V_{ethanol}$:V_{H2O} = 1:1) to obtain solution B by same method. After that, the solution of B was added into solution A under strong magnetic stirring. Subsequently, the suspension was continuing with ultrasonication for 30 min. Finally, the suspension was transferred to a 25 mL Teflon autoclave and then held at 160 °C for 2 h. After reaction, the Teflon autoclave was cooled to air temperature naturally. The powder samples were collected by high-speed centrifugation and washed with water and ethanol thoroughly, and then dried in vacuum oven at 60 °C overnight, resulting in 2D BiOI nanostructures.

2.3. Preparation of Pt-BiOI nanocomposites and Pt-BiOI modified electrode

Firstly, the Pt-BiOI nanostructures were synthesized by a solvothermal method. Typically, 50 mg as-synthesized BiOI nanostructures and 1.3 mL H_2PtCl_6 (3.8×10^{-2} M) aqueous solution were added into 13.7 mL DMF with ultrasonication for 30 min. After that, the homogeneous solution was transferred to Teflon autoclave (25 mL) and held at 160 °C for 6 h. The obtained powders were collected by high-speed centrifugation and washed with water and ethanol three times, and then dried in oven at 60 °C overnight,

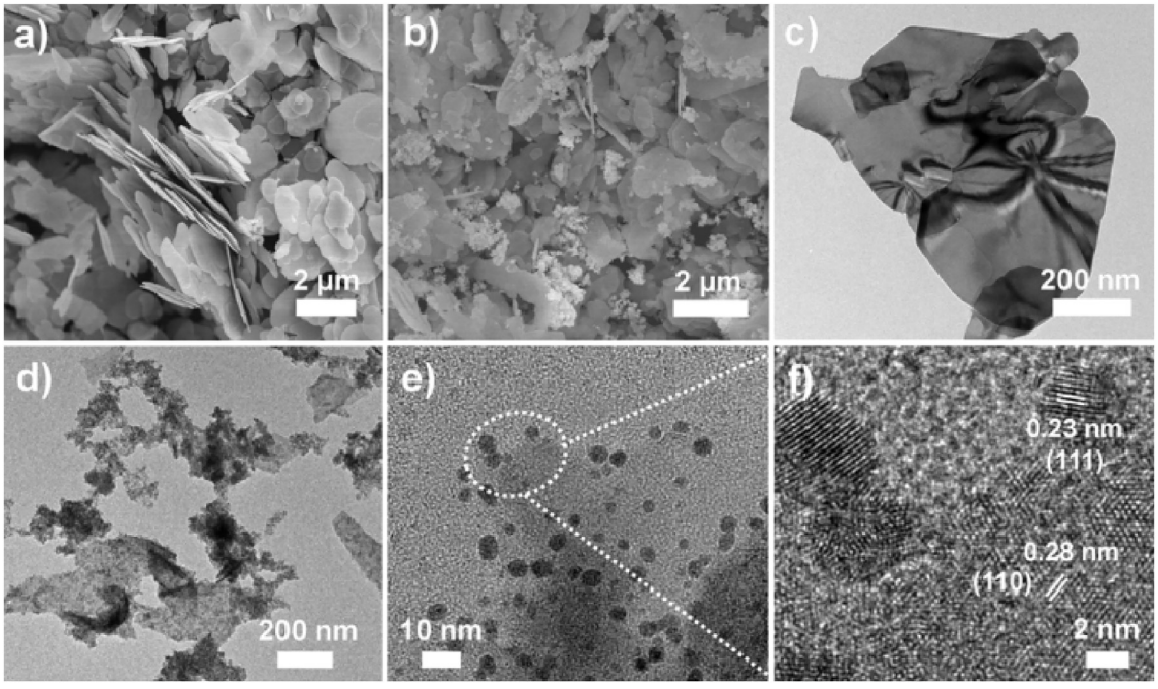

Fig. 1. SEM (a and b), TEM (c, d, and e), and HRTEM (f) images of BiOI (a and c) and Pt-BiOI (b, d, e, and f) samples.

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