



Ultra-uniform PdBi nanodots with high activity towards formic acid oxidation



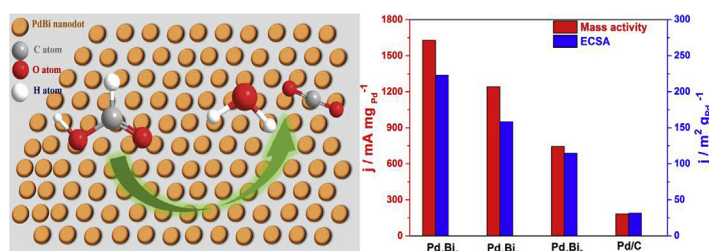
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HIGHLIGHTS

- The ultrasmall PdBi nanodots have been designed by a facile wet-chemical method.
- The composition of PdBi nanodots can be easily controlled.
- Mechanisms of formation have been explored.
- The morphologies of PdBi nanocomposites is time-depended.
- The obtained PdBi nanodots show superior electrocatalytic performances.

GRAPHICAL ABSTRACT



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ABSTRACT

Tuning the morphology and compositions of catalyst is an effective method for promoting electrocatalytic intrinsic activity. However, many newly-generated nanocrystals with better nanostructures often have a large size, which enforces them to display extremely limited surface area and ultimately lead to the limited electrocatalytic activity. To break this bottleneck, we herein report a facile and reproducible wet-chemical method to control the synthesis of a class of ultra-uniform and small PdBi nanodots endowed with both high surface areas and tunable compositions. The presented PdBi nanodots show the ultrasmall size (*ca.* 2.5 nm) and great uniform dispersion property. These significant characteristics enable them to exhibit unprecedented electrocatalytic activities and durability toward formic acid oxidation. The mass activity and electrochemical surface active (ECSA) of prepared PdBi nanodots for the formic acid oxidation is 8.9/3.75 times higher than that of commercial Pd/C, respectively. We speculate that both of this facile synthetic approach and remarkable electrocatalytic performance of the obtained catalysts in this work illustrate that they can be applied as a promising catalyst for direct formic acid cells.

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1. Introduction

Our society is now experiencing a burdensome challenge in the replacement of traditional fossil fuels with renewable resources [1].

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From the point of view of renewable energy, direct liquid fuel cells have aroused broad interests in the fields of both research and industry for considering to be a highly promising technology for solving the global environmental and energy crisis [2]. Among all the fuel cells studied, the direct formic acid fuel cell (DFAFC) exhibits a great deal of notable advantages when compared with typical direct methanol fuel cells [3,4], such as its excellent fuel

flexibility, low temperature dependence [5], low fuel crossover and environmental benignity [6–8]. Regardless of its recyclable and high-energy features, the lack of cost-efficient anodic catalysts for fuel cell reaction is still the biggest bottleneck restricting the development of DFAFC [9,10]. Therefore, tremendous efforts have been made in order to obtain advanced anodic catalysts with optimal catalytic performances towards formic acid electro-oxidation [11].

Among all the electrocatalysts investigated, nanoporous Pt-based catalysts have drawn more extensive research notices in DFAFCs [12–14]. However, the large-scale commercialization of fuel cells is still limited by two key factors referred to extremely low natural reserve of Pt and poor long-term stability [8,15]. In comparison with Pt-based catalysts, Pd is less expensive but more available, which has been exploited to serve as a substitute of Pt in DFAFCs [16] due to its great potential in the electrocatalytic oxidation of small organic molecules. However, there are still lots of problems for Pd-based catalysts when operated in acid medium such as particle dissolution, surface poisoning and so on [17], all of which result in the decrease of surface active sites available for formic acid and ultimately lead to the sluggish kinetics and poor long-term stability [18,19]. Inspired by this, one effective strategy has been applied to address these issues is alloying Pd with other transition metals such as PdAu [20,21], PdAg [22–24], PdCu [25], PdPb [26,27] and PdNi [28]. And many previous researches have demonstrated that binary catalysts are comparatively more active than their original mono-counterparts [29], the greatly enhanced electrocatalytic performances is presumably attributed to the bifunctional, electronic or surface effects [30].

Apart from the effects of compositions, the morphology and particle size of electrocatalyst emerged as additional parameters to influencing the catalytic activities [31]. Finely modifying the shape and morphology of electrocatalysts is beneficial for obtaining large surface areas together with abundant active sites, thereby achieving outstanding electrocatalytic performance and higher utilization efficiency of Pd [32]. Ultrasmall and well-dispersed nanodots in particular have been proven to increase the surface active sites, efficient mass transfer for organic molecules as well as electron mobility when compared with other bulk counterparts or agglomerated particles [33–35]. However, up till now, less researches on fabrication of ultrasmall and uniform nanodots at milder condition have been reported. If we can engineer multi-component Pd-based catalysts with desired sizes and morphology, it will be exceedingly favorable for the design and modification of Pd-based catalysts with elevated electrocatalytic activity and long-term stability.

In view of above-mentioned analysis, we herein demonstrate a very simple and effective wet-chemical method by reducing Pd(NO₃)₂, Bi(NO₃)₃·5H₂O in the N, N-dimethylformamide (DMF) solution with the assistance of ascorbic acid (AA) and polyvinylpyrrolidone (PVP) to construct a class of ultrasmall bimetallic PdBi nanodots with tunable compositions. Importantly, the obtained ultrasmall PdBi nanodots (particle size: 2–3 nm) deliver unprecedented electrocatalytic activity with the promising mass activities and ECSA of 1628.5 mA mg⁻¹ and 53.2 m² g⁻¹, which is 8.9 and 3.75 times higher than that of commercial Pd/C (20 wt %) catalyst, which may shed some light on constructing new bimetallic catalysts for future practical fuel cells and beyond.

2. Experimental

2.1. Materials and reagents

Bi(NO₃)₃·5H₂O, Pd(NO₃)₂, DMF, PVP, AA and other reagents used in this work were all analytical grade purity and purchased from

Sinopharm Chemicals Reagent Co., Ltd., China. Formic acid (HCOOH), sulphuric acid (H₂SO₄ (95%)), ethanol/cyclohexane are also used without any purification. The water (18 MΩ/cm) used in all experiments is prepared by passing through an ultrapure purification system.

2.2. Synthesis of ultrasmall PdBi nanodots

In a typical preparation of ultrasmall PdBi nanodots, 7.8 mg Bi(NO₃)₃·5H₂O, 70 mg PVP and 8 mL DMF were added into a glass vial (volume: 30 mL). After the vial had been capped, the mixture was stirred for 15 min to ensure complete dissolution of Bi(NO₃)₃·5H₂O. After that, 1 mL Pd(NO₃)₂ (15 mM) was added to above aqueous solution to form homogeneous mixture, and then the homogeneous mixture was heated from room temperature to 80 °C, the previously prepared AA solution (dissolved in 2 mL DMF) was added dropwise to the above mixture as soon as the temperature arise to 80 °C and maintained at that temperature for 1.0 h in an oil bath under magnetic stirring. The products were collected by centrifugation and washing three times with an ethanol/cyclohexane mixture. For comparison, the Pd₃Bi₁ and Pd₁Bi₃ nano-compositions were achieved by changing the amount of Bi(NO₃)₃·5H₂O to 2.6 and 23.4 mg, respectively, while keep the other parameters unchanged.

2.3. Apparatus

The morphologies of the as-obtained catalyst were examined by a TECNAI-G20 electron microscope (TEM) operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was employed to explore the valences and compositions of samples, which was performed on a VG Scientific ESCALab 220XL electron spectrometer using 300 W Al K α radiation. For accurately measuring the sample and get reliable data, the instrument must be calibrated every time before tests. The best way is to calibrate the energy scale of the spectrometer with the standard sample, such as high-purity Au, Ag and Cu. In this work, we have applied high-purity Au to calibrate the instrument, which is favorable for obtaining accurate XPS spectra. The alloy structure was measured by X-ray diffraction (XRD) which operated on a PANalytical X'Pert Pro MPD system with Cu K α radiation source ($\lambda = 1.54056 \text{ \AA}$).

2.4. Electrochemical measurements

In this work, all the electrochemical experiments were carried out on a CHI 760E electrochemical working station (CH Instrumental Co., Ltd, China) with typical three-electrode system, the working electrode was glassy carbon electrode (GCE, diameter of 3.0 mm), a saturated calomel electrode (SCE) was used as reference electrode and a platinum wire served as counter electrode. A series of electrochemical measurements were performed at room temperature. To prepare a catalyst-coated working electrode, we firstly need to polish it with alumina powders and ultrasonic with ethanol for 10 min. After that, 10 μ L of homogenous catalyst mixture was deposited on a glassy carbon electrode to obtain the working electrodes after the solvent was dried at ambient temperature. The loading mass of Pd for all catalysts is 1.6 μ g. Electrooxidation of formic acid was conducted in a solution containing 0.5 M H₂SO₄ and 0.5 M HCOOH at a scan rate of 50 mV s⁻¹.

3. Result and discussions

3.1. Physicochemical characterization

The prepared PdBi nanodots are characterized by various

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