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Full Length Article

Seed-mediated synthesis of cross-linked Pt-NiO nanochains for methanol oxidation

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ABSTRACT

A simple method was reported for employing NiO nanoparticles act as seeds and then different amounts of Pt^{2+} were reduced on the NiO nanoparticles, forming a cross-linked Pt-NiO nanocatalysts. These as-prepared catalysts were characterized using different physical-chemical techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The results indicate that the morphology of the cross-linked Pt-NiO nanochain was successfully produced regardless of the molar ratio of Pt^{2+} to NiO precursors. The electrochemical characteristics of Pt-NiO nanochain catalysts were evaluated for the oxidation of methanol as a model reaction, which verify that the Pt-NiO catalysts show enhanced activity and high stability in comparison with the commercial Pt/C catalyst. The optimized ratio of Pt to NiO is 1:1, then tuned by simple adjusting the feed ratio of the precursors as well. The synthesized nanocatalysts will be found the great potential applications as electrocatalysts for fuel cells owe to their enhanced catalytic performance and long-term stability.

1. Introduction

With the increasing consumption of conventional energy sources coupled with concerns over environmental pollution, fuel cells have been widely considered to possess great potential to convert the chemical energy of combustion of small-molecule fuels directly into electricity. Among the various fuel cells, the direct methanol fuel cells (DMFCs) are a promising energy source due to their high operating power density, low emissions and low fuel crossover [1–4]. In the anode, Pt is an important class of metallic electrocatalysts according to their unique catalytic activity towards methanol oxidation reaction (MOR). However, it is pointed out that the pure Pt is highly susceptible to be poisoned by surface-absorbed intermediates along with the MOR, leading to quick decrease in electrocatalytic activity, sometimes within hundreds of seconds.

Currently, Pt is the main part of the catalysts, owing to its intrinsic activity for methanol oxidation. Pt has a wide range of applications such as catalysis, electrochemical, energy processing, and pollution control [5]. Up to date, great efforts have been focused on both reducing the use of noble-metal Pt and increasing electrocatalytic performance towards methanol oxidation [6–10]. One broadly adopted method that can increase the utilization of Pt and enhance its electrocatalytic activity is to disperse Pt nanoparticles on the catalyst supports which have large surface area and good conductivity. Another conventional wisdom to address this problem is via alloying Pt with a second metal such as Ru, Pd, Cu and Ni, by modifying the electronic properties among them to improve the catalytic performance [11–14]. Pt-based catalysts are still more efficient electrocatalysts for oxidation and reduction of small molecules because of their superior chemical and electrocatalytic performances. And Pt-based catalysts have been used to lower the electrochemical over-potential for a high-voltage output [15]. On the other hand, metal oxides, such as SnO_2, CeO_2, TiO_2, SiO_2, have aroused great attention for designing Pt-based electrocatalysts towards MOR [16–19]. These improvements could be attributed to the fact that transition metal oxides intrinsically possess thermodynamic characteristics which can activate the water discharge at low over-potentials to produce hydroxyl species (OHads) on the oxide surface, these OH adspecies then promote the oxidation of poisoning CO on neighboring Pt sites and thereby facilitate their regeneration for further methanol oxidation [20]. For example, Ran et al. have prepared porous TiO_2 thin film as a catalyst support for depositing Pt nanoparticles, which can greatly improve the CO tolerance of the Pt catalyst, thus leading to a better electrocatalytic activity towards MOR [21].

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In this study, we firstly prepared compacted sphere nanoparticles by calcining $Ni(NO_3)_2{\cdot}6H_2O$ in air at 500 °C, in which the NiO as a template material for growing Pt nanoparticles using $NaBH_4$ as reducing agent. Interestingly, the as-prepared Pt-NiO presented the cross-linked nanochains structure through this seed-mediated method. Moreover, we investigated the amount of NiO addition on the enhancement of Pt catalyst activity for methanol oxidation. Electrochemical results indicated that the as-prepared Pt-NiO(1:1 by molar) composites reveal an enhanced electrocatalytic activity and superior durability towards methanol oxidation in alkaline media as compared to Pt and the commercial Pt/C catalysts.

2. Experimental section

2.1. Materials and reagents

The commercial Pt/C catalyst, $Ni(NO_3)_2{\cdot}6H_2O$ and $H_2PtCl_6{\cdot}6H_2O$ (Shanghai Shiyi Chemicals Reagent Co., Ltd., China), acetone (CH_3COCH_3), methanol (CH_3OH), ethanol (C_2H_5OH), NaOH, $NaBH_4$ and other reagents were all of analytical grade and were used as received without any further purification. Doubly distilled water was used throughout the experiments.

2.2. Preparation of Pt-NiO

The Pt-NiO composites were prepared through the two-step procedure. In the first step, 80 mg of $Ni(NO_3)_2{\cdot}6H_2O$ was dissolved in 10 mL of acetone, and then NaOH solution were gradually added until the pH rose to 9 to ensure complete precipitation of $Ni(OH)_2$. The solution was put in the oven at 80 °C for 6 h and the solution's color was light green. After centrifuging and then washed with distilled water and ethanol thoroughly, the precipitate was calcined in air at 500 °C for 4 h to obtain NiO. Then, the as–obtained NiO was dispersed in 11 mL of deionized water in order to form a suspension liquid. In the second step, 3.24 mL of $H_2PtCl_6{\cdot}6H_2O$ (7.723 mM) and 1 mL NiO suspension liquid were added into 9 mL distilled water, keeping stirring for 15 min. Then, freshly prepared $NaBH_4$ solution (10 mL, 5 mM) was dripped to the mixture under vigorous stirring, and the brown solution immediately changed into black suspension. After reacting for 1 h, the precipitates were collected by centrifugation and washed repeatedly with deionized water and ethanol. Finally, the product was dispersed in 10 mL deionized water and treated ultrasonically to obtain a catalyst ink. The obtained sample was denoted as Pt-NiO(1:1 by molar). In addition, Pt-NiO(2:1 by molar), Pt-NiO(1:2 by molar) and the pure Pt catalyst were prepared in the similar method, together with the commercial Pt/C catalyst were all used for comparison.

2.3. Characterization

X-ray diffraction (XRD) (Philips, X'Pert-Pro MRD, Amsterdam, Netherland) profiles of the as-synthesized catalysts were operated at 40 kV and 30 mA using Cu Kα radiation (λ = 1.54056 Å), using glass slide as substrate, which was used to analyze the crystalline structure of the as-prepared catalysts. The morphology and structure of products were carried out using a TECNAI-G20 electron microscope (TEM) (FEI Tecnai G2 F20 S-TWIN TMP, Hongkong, China), which were operated at 200 kV. An energy-dispersive X-ray analyzer (EDX) (Hitachi Corporation, Tokyo, Japan) was used to determine the morphology and composition of the as-prepared catalysts. The X-ray photoelectron spectroscopy (XPS) measurements were recorded on an ESCALab220i-XL electron spectrometer from VG Scientific with 300 W Al Ka X-ray radiation as the X-ray source for excitation.

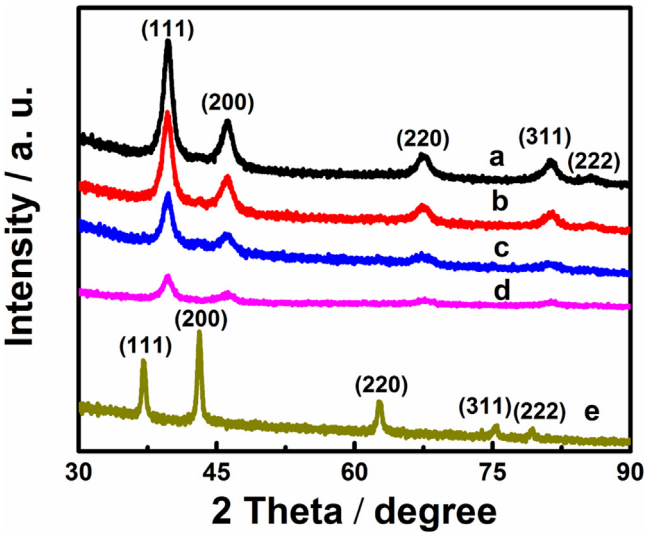

Fig. 1. XRD patterns of Pt-NiO(2:1 by molar) (a), Pt-NiO(1:1 by molar) (b), Pt-NiO(1:2 by molar) (c), Pt (d) and NiO(e).

2.4. Electrochemical measurements

All the electrocatalytic experiments were carried out with a CHI 760D electrochemical workstation (CH Instrument, Inc, Shanghai, China). The conventional three-electrode setup was made up of a saturated calomel electrode (SCE) as the reference electrode, a Pt wire as the counter electrode and a modified glassy carbon electrode (GCE, diameter of 3 mm) as the working electrode. Before each experiment, GCE was polished with alumina slurries (Tianjin AIDA hengsheng Science-Technology Development Co., Ltd., Tianjin, China, 0.05 m) on a polishing cloth, followed by washing with doubly pure water and ethanol, then dried in the oven at 60 °C. Subsequently, 10 μL of the as-prepared catalyst solutions and the commercial Pt/C dispersed in distilled water was dropped on the surface of the GCE and dried in the oven at 60 °C. Cyclic voltammetry (CV) measurements of the as-prepared catalysts were used to analyze the activity of methanol electrooxidation, while the amperometric i-t curves obtained under −0.26 V were conducted to detect the long-term stability of as-synthesized catalysts. The electrochemical experiments were performed at ambient temperature.

3. Results and discussion

The crystal structures of the as-synthesized composite samples were first analyzed by XRD. As it is showed in Fig. 1, the XRD of NiO (Fig. 1e) is characterized by peaks at 2θ = 37.1 (111), 43.1 (200), 62.7 (220), 75.3 (311) and 79.3° (222), while that of Pt (Fig. 1d) by peaks at 2θ = 39.9 (111), 46.2 (200), 67.9 (220), 81.0 (311) and 86.1° (222), which are in good agreement with the standard diffraction spectra data [22]. The XRD patterns of Pt-NiO(1:1 by molar)(b), Pt-NiO(2:1 by molar)(a), and Pt-NiO(1:2 by molar)(c) in Fig. 1 display primarily the characteristics of Pt with unobvious peak of NiO. This could be the result that a large proportion of NiO was well coated with Pt which was corresponding to the amorphous NiO phase.

As a result, transmission electron microscopy (TEM) measurements were used to characterize the morphology of the as-prepared samples. Fig. 2A and B shows the typical TEM images of the as-prepared Pt-NiO(1:1 by molar) composites with different magnifications, clearly observing that the product contains many interconnected nanochain nanostructures, while the TEM image of the pure Pt shows its aggregation of particles without nanochain in Fig. 2E. Specifically, this Pt-NiO cross-linked nanostructures were assembled by a considerably particles which were derived the