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Platinum nanoparticles supported on core–shell nickel–carbon as catalyst for methanol oxidation reaction

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ABSTRACT

In this study, we report the fabrication of a trilaminar core–shell structured Ni–C–Pt nanocomposite and its application as catalyst for methanol oxidation reaction. The Ni nanosphere core with a mean diameter of about 130 nm has a good magnetic response, which facilitates the separation and collection of the nanocomposite. The Pt shell is made up of many tiny Pt nanoparticles with diameter of only several nanometers. The high specific surface area of Pt nanoparticles results in high catalytic activity and high Pt utilization. The carbon interlayer acts as a linker for the Ni core and Pt shell. The influence of Pt loading content in the Ni–C–Pt nanocomposite is studied, and the results indicate that the Ni–C–Pt nanocomposite with a 28% Pt loading exhibits the highest catalytic activity for methanol oxidation reaction.

1. Introduction

As an important electrochemical energy conversion device, direct methanol fuel cells (DMFCs) have attracted extensive attentions during the past several decades due to their low emission of pollutants, high power density, and high energy conversion efficiency [1–3]. The key factor that determines the performance of DMFCs is the catalyst [4]. For the methanol oxidation reactions, the single-component Pt catalysts suffer from low catalytic activity, high cost and low CO tolerance [5]. In the past few years, considerable efforts have been made in developing active and durable Pt-based catalysts for methanol oxidation reactions. A number of high activity and stability Pt-based nanocomposites has been reported [6,7].

Recently, Pt-based core–shell structured nanocomposites have been applied as catalysts for methanol oxidation reactions due to their excellent electrocatalytic activity and high efficiency [8–11]. For example, Han and co-workers have reported Pd@Pt core–shell nanocrystals with high electrocatalytic activity for the electrooxidation of methanol [12]. Li and Yamauchi have reported the synthesis of Ag@Pt core–shell nanoparticles in which dendritic Pt shells were grown on Ag nanoparticle cores, and the Ag@Pt nanoparticles also showed good electrocatalytic activity for methanol oxidation reaction [13].

Nickel is a kind of cheap and abundant metal with good magnetic response. It can be conveniently separated and collected either as single component or composite [14–16]. For this regard, we chose Ni as support for the loading of Pt nanoparticles. Ni–C–Pt nanocompostie with trilaminar core–shell nanostructure was obtained through a convenient method, as illustrated in Scheme 1. Firstly, Ni nanospheres were prepared through a hydrothermal method. Then, a layer of carbon was hydrothermally coated on Ni nanospheres in order to facilitate the loading of Pt on Ni. Finally, Pt nanoparticles were loaded on core–shell Ni–C nanospheres through a chemical reduction process. It is reported that the catalytic activity of a catalyst is highly dependent on its surface area, surface atomic structure, crystal size and shape [17,18]. In the Ni–C–Pt nanocomposite, Pt nanoparticles with a mean diameter of only several nanometers were well dispersed on the outer layer, the high specific surface area of Pt nanoparticles result in high catalytic activity and high Pt utilization. Ni–C–Pt nanocomposties with different Pt loading content were also prepared. Electrochemical measurements showed that the Ni–C–Pt nanocomposties with a 28% Pt loading exhibited the highest catalytic activity for methanol oxidation reaction. All of the Ni–C–Pt nanocomposties have a higher catalytic activity for methanol oxidation reaction than commercial Pt/C catalyst (with 20% Pt loading).

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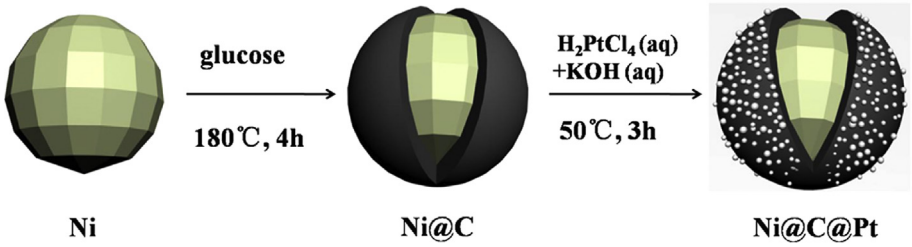

Scheme 1. The synthetic procedure of Ni–C–Pt nanocomposite.

2. Experimental

2.1. Synthesis of Ni–C nanocomposite

Firstly, Ni nanospheres were synthesized according to a previous report [19]. Then, 0.06 g Ni nanospheres, 0.18 g glucose and 30 mL distilled water were added into a 50 mL beaker, and the beaker was subject to ultrasonication for about 10 min. The solution was transferred into a 35 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 240 min. The product was collected with the help of an external magnetic force and washed with distilled water till the supernatant turned clear, and then was dried under vacuum overnight for further use.

2.2. Synthesis of Ni–C–Pt nanocomposite

The Ni–C nanocomposite was dispersed in ethanol with a concentration of about 3 mg mL^{-1}. Then, 1 mL of the colloidal solution was added into a mixture solution containing 15 mL ethanol and 15 mL deionized water. Under continuous mechanical stirring, 0.5 mL of 19 mM H_2PtCl_4 (aq) and 20 μL of 0.2 M KOH (aq) were added in turn. After further stirred for 10 min, the solution was incubated at 50 °C for 3 h. The final product was collected with the help of an external magnetic force and washed several times with deionized water, and finally dried under vacuum overnight. The as-obtained sample was simplified as S_1.

Control experiments were carried out by change the mass of Ni–C to 4 mg and 5 mg while kept other conditions constant. The obtained products were simplified as S_2 and S_3, respectively.

2.3. Characterizations

Scanning electron microscopy (SEM) images were captured on a Hitachi S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images, together with energy dispersive X-ray spectroscopy were recorded on a FEI Tecnai G^2 20 high-resolution transmission electron microscope. Elemental mappings were gained on a JEOL JEM-2100F transmission electron microscope. Inductive coupled plasma atomic emission spectra (ICP-AES) were analyzed with a Perkin-Elmer OPTIMA 5300DV spectrometer. X-ray photoelectron spectra (XPS) were measured on an ESCALab MKII X-ray photoelectron spectrometer with non-monochromatized Al Kα X-ray as the excitation source. Electrochemical characterizations were carried out on a CHI660D electrochemical working station (Chen-Hua Corp., Shanghai, China).

2.4. Electrochemical measurements

The working electrode was prepared according to the following procedure. Firstly, the catalyst was dispersed into 1 mL absolute ethanol by ultrasonication. Then, 8 μL of the ethanol suspension

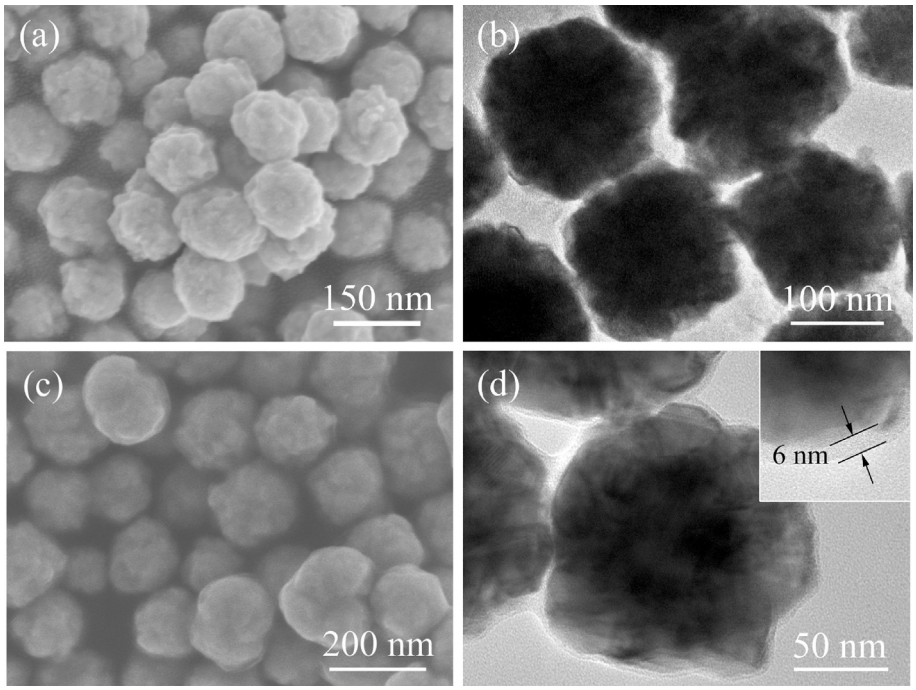

Fig. 1. (a,b) SEM and TEM images of Ni nanospheres; (c,d) SEM and TEM image of Ni–C nanoparticles, inset in (d) is a magnified TEM image of the carbon shell.