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Synthesis of highly monodispersed PtCuNi nanocrystals with high electro-catalytic activities towards oxygen reduction reaction

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ABSTRACT

Pt-based ternary alloy PtCuNi nanocrystals were synthesized through a highly straightforward and adaptable hydrothermal approach. By using appropriate combination of capping agents, the size of the nanocrystals can be controlled between 7–9 nm with narrow size distribution, and their composition can be tuned in broad ranges. The composition and crystal structure of the nanocrystals were fully characterized by transmission electron microscope (TEM), X-ray diffraction (XRD), energy dispersive X-ray spectrum (EDX) and X-ray photoelectron spectroscopic (XPS). The nanocrystals show single-crystalline nature without twinning. The proposed growth mechanism involves forming Cu-rich interior at the early stage followed by Pt-rich surface. The electro-catalysis measurements towards oxygen reduction reaction indicate that PtCuNi nanocrystals, when loaded on high surface area carbon black, exhibit enhanced activity compared with binary PtCu nanocrystals. Among the four catalyst samples with different compositions, $Pt_{23}Cu_{51}Ni_{26}/C$ catalyst exhibit the highest specific activity at 2.1 mA/cm^2 and mass activity at 0.9 A/mg_{Pt}, which shows at least 2-time enhancement home-made PtCu/C catalyst. The enhancement possibly originates from the Pt-rich surface structure and the synergistic interaction between Cu and Ni atoms. This work demonstrates the unique advantage of using Pt-based ternary alloy for reduction of oxygen, and the potential of using them as cathode catalysts for proton exchange membrane fuel cell.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) has been vigorously pursued as a potential alternative environmentally friendly energy conversion device [1]. The factors that limit the widespread application of PEMFCs include the high cost and long-term reliability, both of which are partially related to the fundamental performance of the electro-catalysts used as electrodes, especially the oxygen reduction reaction (ORR) on cathode [2–6]. Currently, Pt-based nano-catalysts are the most active and accepted ORR catalysts [7–9].

A good ORR catalyst should exhibit intermediate adsorption of oxygen molecule on catalyst surface, lower the over-potential and hence expedite the electron transfer rate of the electrochemical process [10–12]. Although traditional Pt/C is the most stable catalyst for ORR, the low activity and high cost still limit its practical application in PEMFC. More recently, it was found that Pt-based alloys show more appropriate lattice constants and surface electronic structures for the oxygen adsorption and dissociation, and therefore attract enormous research interests in recent decades [13–16]. For example, studies on Pt_3Ni thin film indicate that the contraction of surface Pt atoms, combined with the downshift of d-band center of the density of states (DOS), inhibits the adsorption of nonreactive oxygenated species on surface and increases the number of active catalytic sites for oxygen adsorption [11,17,18]. Intensive efforts have been placed on PtM binary alloy electrocatalysts, where M is selected from other noble metal elements such as Au, Pd and Ir, as well as transition metal elements like Ni, Co, Fe, Co, Cu, etc. De-alloying, by heat treatment or electrochemical approach, was found to be an effective technique to enhance the activity of Pt-based alloys [19–28]. Binary alloys have been extensively studied, so roles of the non-Pt elements during catalytic process have been partially understood [29]. However, if two of the above elements are combined and alloyed with Pt, i.e., when forming ternary alloys, the case has not systematically entered the scope of the ORR catalyst community, which, however, is worth of investigation for fundamentally understanding the synergistic effect and approaching more rational and flexible catalyst design [30–35].

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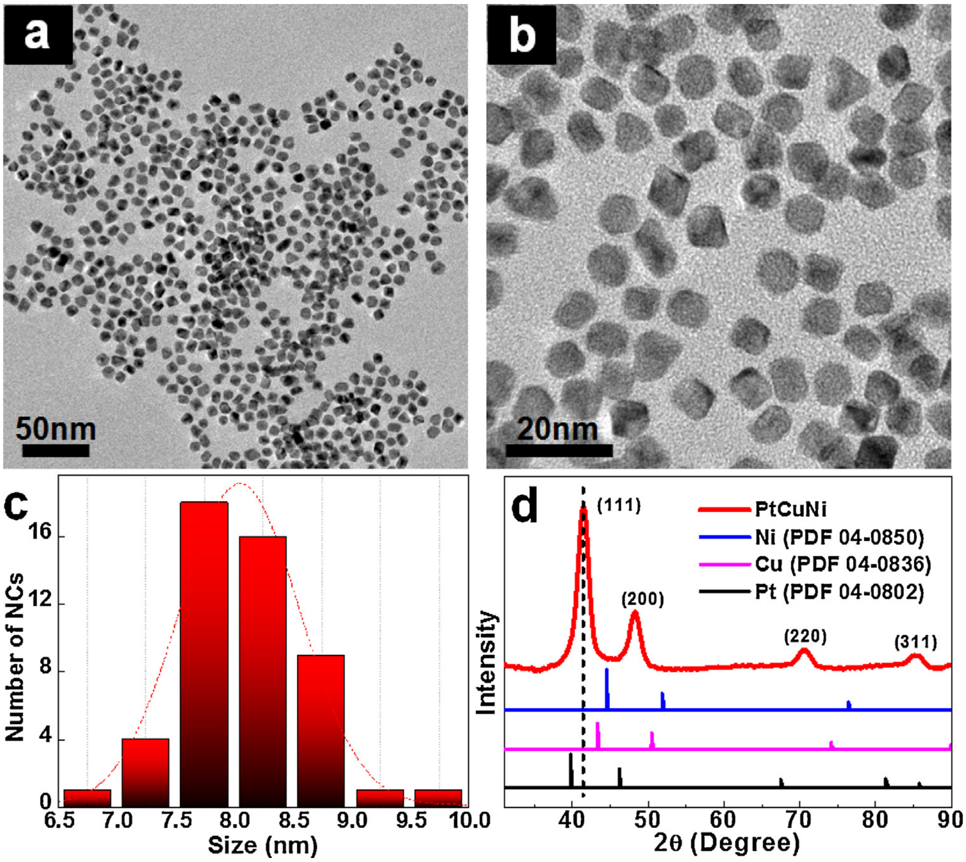

Fig. 1. (a, b) TEM images of PtCuNi NCs synthesized with feeding Pt/Cu/Ni ratio equals to 2/1/1. (c) Statistical size analysis based on 50 randomly picked NCs from TEM image. (d) XRD pattern of PtCuNi NCs as shown in (a), compared with XRD patterns of pure Ni (blue), Cu (magenta) and Pt (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

According to a first-principle study, binary $Cu_{76}Ni_{24}$ alloy shows strong attractive atomic interaction between Cu and Ni atoms and appropriate lattice constant to contract surface Pt atoms, hence could potentially be active and durable catalyst towards ORR when alloyed with Pt [36]. It is expected that the synergistic effect could possibly be generated between Ni and Cu atoms. In this manuscript, monodisperse ternary PtCuNi nanocrystals (NCs) with various compositions were synthesized through facile wet chemistry protocol. They were found to exhibit high ORR activities, 6–10 times the commercially available Pt/C catalyst and 3 times the PtCu catalyst. The catalysts demonstrate the synergistic effect between Cu and Ni and its role in activity enhancement.

2. Material and methods

2.1. Syntheses of PtCuNi nanocrystals

The synthetic protocol is modified from previously reported method by our group [37]. Briefly, platinum acetylacetonate ($Pt(acac)_2$, Sigma–Aldrich), copper acetylacetonate ($Cu(acac)_2$, Sinopharm) and nickel acetylacetonate ($Ni(acac)_2$, Sinopharm) were used as metal precursors. Polyvinylpyrrolidone (PVP) and sodium bromide (NaBr), employed as stabilizing and capping agents, were dissolved in 1,3-propanediol (PDO) with appropriate amount of metal precursors. The starting solution was mechanically stirred for 10 min and transferred into reaction vial. The solution was heated from room temperature to 180 °C at the rate of 6 °C/min and held at this temperature for 6 h, and then cooled down in ambient temperature. The products were collected from the reaction solution by centrifuge. The NCs were dispersed in 2 mL of ethanol, precipitated by 15 mL of acetone. The solution was ultrasonicated for 10 min, and then centrifuged at 8000 RPM for 10 min. The washing procedure was repeated three times. As-prepared NCs were re-dispersed in ethanol and sealed as stock solution.

2.2. Preparation of carbon-supported catalysts

Vulcan XC-72 carbon black (CB) is used as the supporting material. For a typical catalyst loading procedure, CB dissolved in iso-propyl alcohol (IPA) at the concentration of 1 mg/mL was ultrasonicated for 30 min. A certain amount of NC stock solution was mixed with the CB solution, to achieve NC loading at 20 wt%, and further sonicated for another 30 min, and then stirred overnight. The products were then collected by centrifuge at the rate of 6000 RPM, washed with ethanol, and then dried with N_2 stream. As-prepared PtCuNi/C catalysts were stored in ethanol or IPA.

2.3. Characterization

Transmission electron microscopic (TEM) images were captured on JEOL JEM 2100 at the accelerating voltage of 200 kV. High resolution TEM (HRTEM), energy dispersive X-Ray spectrum (EDX), and high angle annular dark-field scanning TEM (HAADF-STEM) were taken on FEI TECNAI F-20 field emission microscope at the accelerating voltage of 200 kV. X-ray diffraction (XRD) data of the NCs were obtained from Bruker D8 Advance. X-ray photoelectron spectroscopic (XPS) data were captured on Thermo ESCALAB 250XI. Composition of the bulk catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on Leeman PROFILE SPEC.

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