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Pt–Ni alloy hyperbranched nanostructures with enhanced catalytic performance towards oxygen reduction reaction

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ABSTRACT

Comprehensive design of alloy structure through a rational surface atomic arrangement, component, and well-defined shape will maximize atomic utilization and prompt fantastic oxygen reduction reaction enhancements. In this work, the Pt–Ni alloy hyperbranched nanostructures are synthesized successfully via a facile one-pot synthesis route without through any seeds or templates growth. The success of this approach relies on the use of cetyltrimethylammonium bromide (CTAB) to control the growth of branches on certain facets. The as-prepared Pt–Ni alloy hyperbranched nanostructures exhibit an enhanced catalytic activity toward oxygen reduction reaction in comparison with commercial Pt/C, owing to the synergistic effects among Pt and Ni atoms and the unique morphology of high branching degree. These findings provide a simple strategic design and a realizable method to create highly active catalysts for practical electrocatalytic applications.

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Introduction

In the past few decades, proton exchange membrane fuel cell (PEMFC) has attracted increasingly comprehensive attraction because of its outstanding storage efficiency, low operational temperature and energy loss, totally non-pollution to the environment and the sustainable of hydrogen resources [1–9]. Nanostructures based on platinum (Pt) are still the most efficient electrocatalysts to facilitate both hydrogen oxidation and oxygen reduction in fuel cells. However, the commercialization of fuel cell technology has been hindered by the

high cost and extremely rare reserves of Pt. To address these issues, the main efforts have been devoted to the development of bimetallic structures that alloy Pt with other transition metal, which can decrease the usage of platinum [10]. Pt-based bimetallic catalysts such as Pt–Co [11], Pt–Cu [12], Pt–Rh [13], Pt–Pd [14] and so on are beneficial to increase the catalytic activity because of the lattice strain, downshift of the d-band center and possible synergistic effects in Pt-based alloys [15–17]. Among various reported Pt-based bimetallic nanostructures, Pt–Ni nanocrystals have been considered for their potential use in PEMFC because of their high catalytic stability and durability [18–20].

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In addition, shape-controlled synthesis of Pt-based bimetallic catalysts is an effective strategy to adjust the catalytic performance and durability of face-centered-cubic (fcc) metal nanocrystals, because the morphology governs the size, crystal facets exposed on the nanocrystals surface, and utilization efficiency of Pt atoms [21,22]. Among various well-defined Pt–Ni NCs [23], the porous [24], wires [25], tubes [26], hollow ones [27] and nanodendrites [28] are of great importance because they exhibit enhanced catalytic performance with maximizing atomic utilization by high surface-to-volume ratio [29–32]. In particular, the synthesis of nanodendrites with branched structure is of great interest to researchers from recent experimental results. The branched structure possesses high density of edge/corners atoms and larger surface area, which significantly improved atomic utilization and catalytic performance [33,34]. For example, Nageh and co-workers have reported the synthesis of Pt–Ni nanodendrites, which possessed a much better catalytic activity compared to commercial Pt/C catalysts [35]. Despite these successes, it should be mentioned the branch length of most of the previously invested nanodendrites is too short to provide sufficient active sites, which severely limited the catalytic activity. Therefore, it remains a huge challenge to synthesize Pt–Ni nanodendrites with longer branches via a simple one-pot method.

Herein, we demonstrate a facile one-pot synthesis route for the preparation of Pt–Ni alloy hyperbranched nanostructures. The Pt–Ni alloy hyperbranched nanostructures could be synthesized by controlling an appropriate amount of CTAB, which plays a leading role in generating the Pt–Ni alloy hyperbranched nanostructures. By adjusting different amount of CTAB, the length and number of the branches can be operated. In addition, the presence of hyperbranched nanostructures endows larger surface area and more active sites for the nanocrystals due to much higher branching degree, which takes the advantages of nanodendrites and further show properties similar to nanowires or nanorods. This distinctive surfaces structure could influence the coordination and strain of surface atoms performing catalysis and thus the enhanced catalytic activity [36].

Experimental

Materials

Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), nickel acetylacetonate ($\text{Ni}(\text{acac})_2$, 95%), cetyltrimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP), trioctylphosphine oxide (TOPO), octadecyltrimethylammonium chloride (SATC) and oleylamine (OAM, 80–90%) were purchased from Mackin. All chemical reagents were used as received without further purification. The water used in this experiment was ultrapure (18.2 M Ω). Solvents such as ethanol and hexane were analytical grade and used as received without further purification.

Synthesis of PtNi nanocrystals

In a typical synthesis, 0.3 mL $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was added into a solution containing 7.3 mg $\text{Ni}(\text{acac})_2$, 50 mg CTAB and 10 mL

OAM. The mixed solution was stirred for 20 min. After that, the mixture was transferred to in 25 mL Teflon-lined stainless steel autoclave. The mixture was then heated from room temperature to 160 °C and kept at 160 °C for 12 h with magnetic stirring in an oil bath. After cooling down to room temperature naturally, the resulting colloidal product was collected with hexane by centrifugation.

Preparation of carbon-supported catalysts

A suspension of PtNi nanocrystals was mixed with 10 mg Vulcan-72 carbon dispersed in 20 mL n-butylamine. The solution under ultrasonication was stirred at room temperature for two days. The solids were then precipitated using ethanol and via centrifugation and then washed with methanol to remove the excess n-butylamine. The catalysts were then dried in a vacuum drying box at 100 °C for 12 h. Before using as electrocatalyst, the product was annealed in air at 200 °C for 2 h.

Materials characterization

Transmission electron microscopy (TEM) images were acquired on a FEI Titan ETEM G²80-300 operated at 120 kV. High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) observations were conducted on Titan G²80-300 operated at 300 kV. The catalysts were prepared by dropping hexane suspension of catalysts onto carbon-coated copper and immediately drying the samples. In order to understand crystal structure information, powder X-ray diffraction (XRD) patterns were recorded using a Rigaku Corporation diffractometer with $\text{CuK}\alpha$ radiation. X-ray photoemission spectroscopy (XPS) tests were done with a Thermo Fisher Scientific ESCALAB 250 photoelectron spectrometer and analyzed using CasaXPS.

Electrochemical measurements

All electrochemical tests were recorded by a conventional three-electrode cell system. A glassy-carbon Rotating Disk Electrode (RDE) (area: 0.196 cm²) from Pine Instruments was used as working electrode. The reversible hydrogen electrode (RHE) was used as reference electrode. The Pt flag was used as counter electrode. The catalyst ink was conducted by ultrasonically mixing 2.0 mg PtNi/C with 1.7 mL of ethanol, 300 μL of 0.05 wt% Nafion solution for 20 min. 10 μL catalyst suspension was deposited on the smooth glassy carbon electrode surface by using a micropipette and dried to form a uniform thin film that was further characterized in electrochemical cell. The Pt% on the Vulcan support is 30.0% for the Pt–Ni alloy electrocatalyst. And the Pt loading was 15.29 $\mu\text{g cm}^{-2}$ for Pt–Ni hyperbranched nanostructure, 15.30 $\mu\text{g cm}^{-2}$ for Pt–Ni nanoparticles, 21.44 $\mu\text{g cm}^{-2}$ for commercial Pt/C on the geometric electrode area of 0.196 cm². The electrochemical active surface areas (ECSAs) of the catalysts were estimated by hydrogen adsorption method. The ORR measurements were conducted in oxygen-saturated 0.1 M HClO_4 solution. The ORR polarization curves were collected at 1600 rpm with scan rate of 10 mV s⁻¹. The potential was scanned from 0.05 to 1.1 V

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