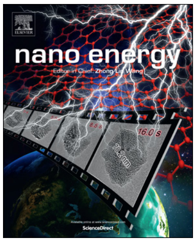
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy



RAPID COMMUNICATION

FePt nanodendrites with high-index facets as active electrocatalysts for oxygen reduction reaction

Di-Yan Wang[a,b,1], **Hung-Lung Chou**[c,1], **Ching-Che Cheng**[a],
Yu-Han Wu[a], **Chin-Ming Tsai**[a], **Heng-Yi Lin**[a], **Yuh-Lin Wang**[b],
Q1 **Bing-Joe Hwang**[d,e,*], **Chia-Chun Chen**[a,b,**]

[a] *Department of Chemistry, National Taiwan Normal University, Taipei 106, Taiwan*
[b] *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan*
[c] *Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10617, Taiwan*
[d] *Nanoelectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science & Technology, Taipei 106, Taiwan*
[e] *National Synchrotron Radiation Research Center (NSRRC), Hsinchu 300, Taiwan*

Received 11 August 2014; received in revised form 30 October 2014; accepted 8 November 2014

KEYWORDS
FePt;
Nanodendrites;
High-index facet;
Electrocatalyst;
Oxygen reduction reaction

Abstract

In this study, three different types of alloyed FePt nanostructures, nanodendrites, nanospheres and nanocubes, were prepared and their catalytic activities for oxygen reduction reaction (ORR) were studied. The ORR catalytic activity of the nanostructures was increased in the order of E-TEK Pt/C < FePt nanospheres < FePt nanocubes < FePt nanodendrites. In particular, a cation exchanging reaction was developed for the preparation of FePt nanodendrites, consisting of a dense array of branches on a core. The FePt nanostructures were analyzed by high-resolution transmission electron microscopy (HRTEM), high angle annular dark field (HAADF), scanning transmission electron microscopy (STEM) and electron energy loss spectrum (EELS) mapping. The HRTEM images revealed that the large surface area of FePt nanodendrites with a high density of atomic steps was enclosed by high-index {311} facet. The density functional theory simulation was performed to understand the origins of the enhanced electrochemical activity of FePt nanodendrites. The enhancement could be attributed to the exposure of high-index {311}

---

[*] Corresponding author at: Nanoelectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science & Q2 Technology, Taipei 106, Taiwan.

[**] Corresponding author at: Department of Chemistry, National Taiwan Normal University, Taipei 106, Taiwan.

E-mail addresses: bjh@mail.ntust.edu.tw (cjchen@ntnu.edu.tw) (C.-C. Chen).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.nanoen.2014.11.040

Please cite this article as: D.-Y. Wang, et al., FePt nanodendrites with high-index facets as active electrocatalysts for oxygen reduction reaction, Nano Energy (2014), http://dx.doi.org/10.1016/j.nanoen.2014.11.040

facet of the nanodendrite with high surface energy in comparison to that low-index {111} and {200} facets of FePt nanospheres and nanocubes, respectively. Our experimental and theoretical studies have opened a route toward the syntheses of new nonprecious alloyed nanostructures to replace Pt as active fuel cell catalysts.

Introduction

The development of synthetic methods for the fabrications of new bimetallic platinum-based nanocrystals (PtM) with high catalytic activity is one of the essential subjects in fuel cell research [1-3]. In comparison with pure Pt, PtM nanocrystals have shown great catalytic improvement on the decrease of overpotential and power losses in oxygen reduction reaction (ORR) [4-7]. Previous studies have indicated that the catalytic activity of the PtM nanocrystals could show strong dependency on the nanocrystals compositions, sizes and shapes [8-11]. Many wet chemical reactions have been developed to control the growths of bimetallic nanocrystals [12-14]. Recently, the cation exchanging reaction, using pure metal NC as a seed in the solution, was intensively tested for the growth of bimetallic nanocrystals with well-controlled composition and shape [15-17]. The driving force of the cation exchanging reaction was usually generated from the differences of the reduction potentials. For examples, AuAg bimetallic nanocrystals of various shapes such as nanobox and hollow nanostructure were formed by using pure Ag nanocrystals as a seed reacting with gold ions in the solution [18]. Previously, our group demonstrated a simple synthetic concept from binary FePt nanocrystals transformed to ternary FePtRu nanocrystals through the cation exchanging reaction to control the alloying extent of the ternary nanocrystals [19]. Our studies also demonstrated that the FePtRu nanocrystals exhibited superior catalytic ability to withstand CO poisoning in methanol oxidation reaction than do binary nanocrystals (FePt and J-M PtRu).

Recently, a wide variety of noble metal nanocrystals enclosed by high-index facets has been successfully synthesized and the catalytic activity of those nanocrystals has shown strong dependency on their surface structures [20-24]. For example, the tetrahexahedral Pt nanocrystals or Pd nanocrystals with high-index {730} facets have been synthesized by an electrochemical square-wave potential method [23,25]. Also, the hetero-structure bimetallic nanocrystals with many branches nanostructures, so called nanodendrites, have exhibited almost 10-fold enhancement of significant catalytic activities in comparison with commercial Pt catalysts in methanol oxidation and oxygen reduction reactions [26,27]. The excellent catalytic activity of the hetero-structure bimetallic nanodendrites was attributed to the large surface area and high-index facet of their dendritic structure [28,29]. Several reports have demonstrated a two-step strategy by using a seeded overgrowth method for the preparation of Pt-on-Pd nanodendrites that exhibited higher mass activity (4 times) than Pt black catalysts toward ORR [26,30]. The Pt-on-Pd nanodendrites during this growth process could lead to expose the high-index {311} facet surface on the nanodendrites. When the surface structure of metal nanocrystals exited some surface defects, such as step and kink atoms with low coordination numbers (CN $<$ 8), this surface usually exhibited very high chemical reactivity and catalytic activity for most structure sensitive reactions [31-33]. However, there were still some challenges for the syntheses of the alloyed PtM bimetallic nanocrystals to expose high-index facet surface, because the formation of alloyed bimetallic nanocrystals was usually enclosed by low-index facets, such as {111} and {100} under thermodynamic equilibrium conditions [34,35]. The design of new synthetic strategies to generate a new growth pathway for the high index facet termination under a kinetic control could be a quite interesting text for developing new high active electrocatalysts.

In this study, we have developed a new synthetic strategy to synthesize alloyed FePt dendritic shape FePt nanostructures (nanodendrites) by a cation exchanging reaction. The formation process of FePt nanodendrites consisting of a dense array of branches on a core was also investigated by high-resolution transmission electron microscopy (HRTEM). The mass catalytic activities of FePt nanodendrites, cubic shape FePt nanostructures (nanocubes), octahedra shape FePt nanostructure (nanospheres) and E-TEK Pt for ORR were compared by rotating disk electrode (RDE) voltammetry. The FePt nanodendrites exhibited the best ORR activity than the others. The alloyed FePt nanodendrites were further confirmed by X-ray diffraction (XRD), high angle annular dark field (HAADF), scanning transmission electron microscopy (STEM) and electron energy loss spectrum (EELS) mapping. Intriguingly, the branches of FePt nanodendrites exhibited high surface areas and terminated the particularly active {311} high facet terminated on the nanodendrites. A simulation based on density function theory (DFT) was used to obtain the coordination number and surface energy of FePt nanostructures with different facets terminated.

Experimental details

Synthesis of FePt nanospheres

$Pt(acac)_2$ (95 mg), 1,2-hexadecanediol (195 mg) and 10 mL dioctyl ether were added into a three-necked flask. The solution temperature was raised at 100 °C for about 15 min. While vigorously stirring the reaction mixture, oleylamine (0.08 mL), oleic acid (0.08 mL), and $Fe(CO)_5$ (0.06 mL) were injected by a syringe into the solution. The resulting solution was heated to the boiling point of dioctyl ether, 300 °C, refluxed for 30 min and finally cooled at the room temperature. Afterwards, ethanol (20 mL) was added to the reaction mixture. The resulting black precipitate was obtained by centrifugation.

Please cite this article as: D.-Y. Wang, et al., FePt nanodendrites with high-index facets as active electrocatalysts for oxygen reduction reaction, Nano Energy (2014), http://dx.doi.org/10.1016/j.nanoen.2014.11.040