Journal of Power Sources 253 (2014) 1–8

Contents lists available at ScienceDirect

Journal of Power Sources

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

Fabrication of PtCu and PtNiCu multi-nanorods with enhanced catalytic oxygen reduction activities

Licheng Liu [a], Gabor Samjeské [a], Shinobu Takao [a], Kensaku Nagasawa [a], Yasuhiro Iwasawa [a,b,*]

[a] Innovation Research Center for Fuel Cells, The University of Electro-Communications, Choufugaoka, Chofu, Tokyo 182-8585, Japan
[b] Department of Engineering Science, Graduate School of Information Engineering Science, The University of Electro-Communications, Choufugaoka, Chofu, Tokyo 182-8585, Japan

HIGHLIGHTS

- Metallic PtCu and PtNiCu multi-nanorods with 5 nm diameter and 10 nm length were fabricated by a polyol reduction method.
- Copper precursor dependency on the fabrication of both PtCu and PtNiCu nanorods was observed.
- The multi-nanorods were successfully synthesized with $CuCl_2$, $Cu(CH_3COO)_2$ and $CuSO_4$ as Cu precursors but not with $Cu(NO_3)_2$.
- The multi-nanorods showed 2–5 times enhanced electrocatalytic activities with good stability for ORR than a Pt/C catalyst.

ARTICLE INFO

Article history:
Received 17 October 2013
Received in revised form
25 November 2013
Accepted 7 December 2013
Available online 14 December 2013

Keywords:
Metal multi-nanorods fabrication
Pt alloy nanorods
PtCu
PtNiCu
Electrocatalysts
Oxygen reduction reaction

ABSTRACT

1-D metallic nanomaterials have received much attention from the viewpoints of material functions of shape-controlled nanocrystals and applications to a variety of technologies. Metallic PtCu and PtNiCu multi-nanorods with diameter of about 5 nm and average length of around 10 nm were fabricated by polyol reduction method and characterized by TEM/EDS, XRD, XRF and electrochemical techniques. The multi-nanorods were successfully synthesized with $CuCl_2$, $Cu(CH_3COO)_2$ and $CuSO_4$ as Cu precursors but not with $Cu(NO_3)_2$, showing precursor dependency on the nanorod fabrication. The fcc alloy-crystal structures were observed with these multi-nanorods, which showed much more enhanced electrocatalytic activities with good stability for oxygen reduction reaction (ORR) than a conventional Pt/C catalyst. The results demonstrate that Pt-based multimetallic nanocrystals are promising candidates for cathode catalysts to develop next-generation polymer electrolyte fuel cells.

1. Introduction

Shape-controlled synthesis of metallic nanocrystals has received much interest in modern material chemistry as well as potential applications to a variety of technologies because the intrinsic property and functions of most nanomaterials strongly depends on the nano-shape and morphology [1–5]. Among various fabricated shapes, monometallic and multimetallic 1-D nano-materials, such as nanowires [6–9], nanobars [10], nanorods [11–14], and nanodendrites [15–18] have attracted much attention due to their unique photoelectric, magnetic and catalytic properties. Pt-based multimetallic nanocrystals have been applied to many technologies such as catalysis, electronics and photonics [19,20] and particularly polymer electrolyte fuel cells (PEFC), where they have been regarded as potential candidates for cathode catalysts for oxygen reduction reaction (ORR) [21–23]. Increasing ORR activity, improving durability, decreasing costs and high-volume production of cathode catalysts are still prerequisite for development of next-generation PEFCs [24].

The Pt mono- or bimetallic nano-composites with various shapes and morphologies, such as Pt nanocubes [25,26], Pd–Pt nanodentrites [15], octahedral Pt–Ni [27–29], have been synthesized and demonstrated to be highly active for ORR. Among them, 1-D Pt and Pt-alloy nanocrystals exhibited high ORR activities due

* Corresponding author. Innovation Research Center for Fuel Cells, The University of Electro-Communications, Choufugaoka, Chofu, Tokyo 182-8585, Japan. Fax: +81 42 443 5483.
E-mail addresses: iwasawa@pc.uec.ac.jp, iwasawa@chem.s.u-tokyo.ac.jp (Y. Iwasawa).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.12.028

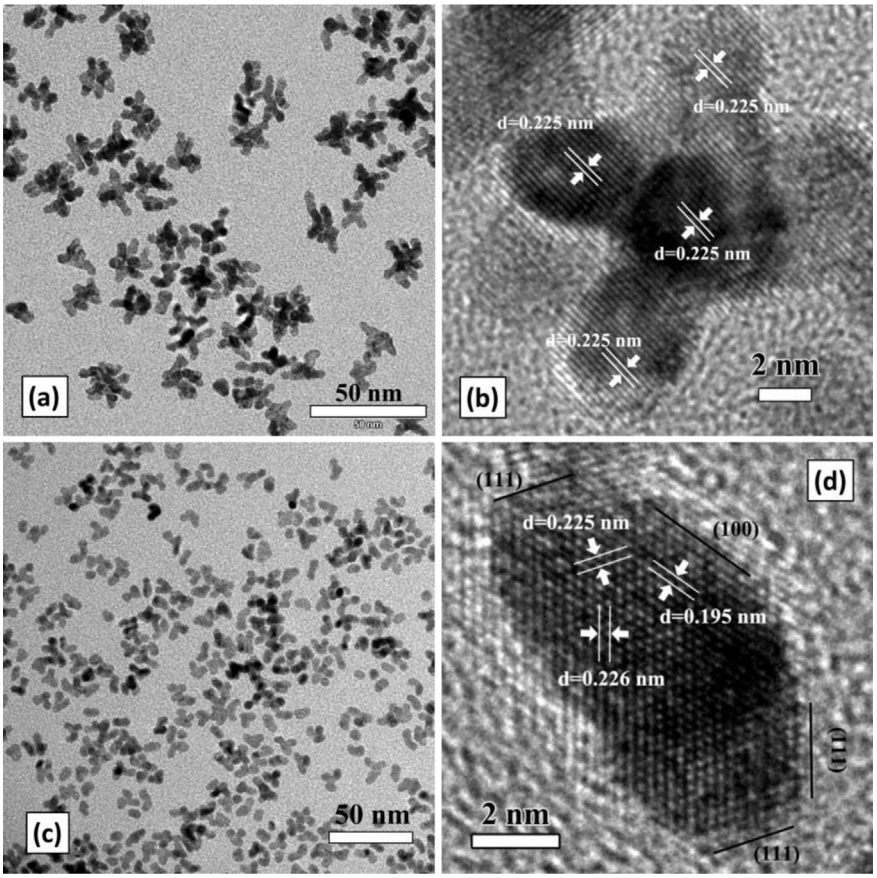

Fig. 1. TEM images of PtCu and PtNiCu multi-rods (a, c) and the corresponding high-resolution STEM images (b, d).

to their unique structures and electronic confinement effect. Sun et al. [30] synthesized star-like Pt nanowires with ≈4 nm diameter and ≈15 nm length by formic acid reduction method, which showed 1.5 times higher mass activity and 3 times higher specific activity compared to a commercial Pt/C catalyst. Koenigsmann et al. [31] reported the synthesis and electrocatalytic performance of ultrathin Pt nanowires with less than 2 nm diameter and up to 100 nm length, which displayed 7 times larger specific activity than spherical Pt nanoparticles. Zhang et al. [9] demonstrated that the mass activity of ultra-thin PtFe-nanowires with a diameter of 2–3 nm was 2 times larger than a standard Pt/C.

Herein, we report the synthesis of wormlike PtCu and PtNiCu multi-nanorods on carbon support by an ethylene glycol (EG) reduction method with PVP as a capping agent. The multi-nanorods with the dimensions of 4–5 nm diameter and 6–16 nm length exhibited 2–5 times larger ORR activities than a Pt/C (TKK, TEC10E60TPM).

2. Experimental

2.1. Syntheses of nanocrystals and carbon-supported nanocrystals

2.1.1. Chemicals

Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Sigma–Aldrich), copper chloride ($CuCl_2$, Wako), copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, Wako), copper acetate ($Cu(CH_3COO)_2$, Wako), copper nitrate ($Cu(NO_3)_2$, Wako), nickel chloride ($NiCl_2$, Wako), ethylene glycol (Wako), and polyvinyl pyrrolidone (PVP-k30, Wako) were commercially obtained. Solvents of analytical grade, such as ethanol, hexane and acetone were used without further purification.

2.1.2. Synthesis of PtCu multi-nanorods

A typical synthesis process was described as follows. 113 mg PVP was added to 11 ml EG. The mixture was heated at 373 K and kept for 30 min under stirring in a N_2 flow. Then 106 mg of $H_2PtCl_6 \cdot 6H_2O$ and 9.2 mg $CuCl_2$ were dissolved into above EG solution under stirring. The resultant solution was heated to 438 K in an oil bath under stirring, at which temperature it was kept for 1 h. After cooling down, the produced nanoparticles were precipitated by adding acetone and separated by centrifugation and washed by ethanol and *n*-hexane. The colloidal nanoparticles were suspended and stored in 10 ml of ethanol. For synthesis from other copper precursors, the amount of copper precursors was controlled to ensure the feeding Pt/Cu molar ratio is 3/1.

2.1.3. Synthesis of PtNiCu multi-nanorods

The synthesis procedures were similar to the above procedures except the use of 4.4 mg $NiCl_2$ and 4.6 mg $CuCl_2$ instead of 9.2 mg $CuCl_2$. For synthesis from other copper precursors, the amounts of nickel and copper salt were regulated to make the feeding Pt/Ni/Cu molar ratio to be 3/0.5/0.5.

2.1.4. Preparation of carbon-supported nanorod catalysts

The as-synthesized nanorods were dispersed in ethanol, to which 60 mg of carbon (Vulcan XC-72) was added. The resultant suspension was placed in an ultrasonic bath for 1 h and then stirred overnight. The obtained carbon-supported catalysts were collected by centrifugation and dried in air. For removing PVP residuals in the samples, the catalysts were calcined at 473 K for 2 h in 20% O_2/N_2 gas flow.