INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–6

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Seed-mediated grown platinum nanocrystal: A correlation between seed volume and catalytic performance of formic acid and ethanol oxidation

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ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form
7 May 2016
Accepted 7 June 2016
Available online xxx

Keywords:
Catalyst
Formic acid electrooxidation
Ethanol electrooxidation
Platinum
Seed-mediated solvothermal

ABSTRACT

Platinum (Pt) nanocrystals of cubic and octopod structures were synthesized via seed-mediated solvothermal growth with monoethanolamine as the solvent. The combination of nanocube and octopod structures was formed using 0.025 ml seeds loading, while increasing the seeds volume to 0.050 ml and 0.100 ml produced nanocube as the primary product. The octopod structure evolves from the overgrown nanocube via kinetic growth mechanism. Pt nanocube formed with 0.050 ml seeded solution has the potential to serve as a catalyst in formic acid oxidation by virtue of its high electrochemical surface area of 10.93 m^2/g, over that of Pt black at 8.62 m^2/g and resistance to poisonous CO. Nonetheless, it is less catalytically active in ethanol oxidation as depicted by the small electrochemical surface area of 8.64 m^2/g and low current density in longer period.

Introduction

Proton - exchange membrane fuel cells (PEMFC) has been recognized as one of the promising power sources for portable electronic device due to its low working temperature, less corrosion problem and compactness. Nevertheless, this system uses hydrogen gas as the preferred fuel, thereby raising some issues in handling, storage, production and distribution. Alternatively, aqueous solution of formic acid and ethanol represent two prospects of energy sources due to ease of handling, transportation and storage compared to the hydrogen gas.

In a fuel cell device, Platinum (Pt) is used at anode to catalyze hydrogen oxidation and at cathode to catalyze oxygen reduction [1]. Therefore, it is important to synthesize Pt with high catalytic activity. Controlled synthesis of Pt structures in a variety of shapes started to be rigorously explored due to the fact that their catalytic activity and selectivity are shape and size dependent. Various methods, including colloidal [2], polyol [3] and hydro/solvothermal [4] have been developed to produce Pt nanocrystal such as nanodendrites [5], tetrapod [6] and wire-like [7] structures due to its ease of handling, economical and scalability for large production. Recently, seed-mediated solvothermal growth has received

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http://dx.doi.org/10.1016/j.ijhydene.2016.06.032
0360-3199/

considerable attention due to its high potential in producing uniform nanocrystal with narrow size/shape distribution. Up until now, there have been sporadic work using this technique for noble metal synthesis whilst, no research involving seed-mediated solvothermal growth particularly on Pt has been reported. For example, Zhang et al. [8] synthesized monodisperse Pd nanoparticles using step-wise seed-mediated solvothermal growth. Their seeds were prepared by reducing Pd salt with formaldehyde in organic amine solvents (i.e. oleylamine, octadecylamine and butylamine). Besides functioning as a solvent, most organic amine molecules exhibit surface controller and reducing agent properties. Huang et al. [4] used methylamine as a surfactant to synthesize Pt nanocrystal with {411} high index facets. Our group extended their work by varying the methylamine concentrations, however, spherical nanoparticles were produced instead of concave polyhedral due to different chemical purity used in the synthesis [9]. We further studied the influence of different types of amines (i.e. monoethanolamine (MEA) and diethanolamine (DEA)) on platinum synthesis and these organic amines were observed to exhibit reducing properties similar to those of methylamine [10]. Also, MEA serves as a solvent in ionic liquid synthesis [11] and a surfactant in metal oxide synthesis [12]. As such, this work aimed to synthesize Pt nanoparticles using seed – mediated solvothermal growth using MEA as the growth solvent and to determine the correlation between different seeded loadings on the formation, structural and catalytic properties of the synthesized Pt nanoparticles.

Experimental procedure

The Pt "seed" synthesis was prepared according to our previous procedure [9]. The "growth solution" was prepared by adding 0.50 ml H_2PtCl_6, 0.20 g PVP and 0.17 ml N, N dimethylformamide in 10 ml monoethanolamine. Next, the growth solution was mixed with the seeded solutions (0.025, 0.050 and 0.10 ml, respectively) and autoclave at 170 °C for 11 h. After the reaction, the product was washed by acetone/ethanol and precipitated by centrifugation. The product was re-dispersed in ethanol for characterization.

The crystal structure was characterized using an X-ray diffractometer (Bruker D8 Advance, $\lambda = 1.54056$ Å by Cuka radiation). Morphological analyses were performed using a transmission electron microscope (EF-TEM Zeiss Libra). The Fourier transform IR (FT-IR) spectroscopy was characterized using FT-IR ATR Perkin Elmer. The electrochemical measurement was carried out using eDAQ (ER466) integrated potentiostat using a three electrodes system with glassy carbon, Pt rod and saturated calomel electrode (SCE) as the working, counter and reference electrodes, respectively. The working electrode was prepared by depositing colloidal Pt and Nafion® (0.05wt%, 3 μL) solution on the glassy carbon electrode (ø = 3.0 mm). The electrooxidation of formic acid (HCOOH) was recorded at a sweep rate of 50 mV/s in 0.5 M H_2SO_4 + 0.25 M formic acid. The electrooxidation of ethanol was examined at a sweep rate of 50 mV/s in 0.1 M $HClO_4$ + 0.1 M ethanol between −0.25 V and 1.2 V. The hydrogen adsorption/desorption analysis was performed using a cyclic voltammetry in 0.5 M H_2SO_4 and 0.1 M $HClO_4$ at −0.25 V and 1.3 V. These electrolytes were selected because their hysteresis in voltammograms of formic acid and ethanol oxidation is more pronounced due to its high specific conductivity at room temperature.

Results and discussion

The TEM monograph of the Pt nanocrystal prepared by the seeded method is shown in Fig. 1. It can be observed that quasi-spherical nanoparticles were produced and used as seeds for the seeding growth (Fig. 1a). The average size of the spherical nanoparticles was about 3 nm. Fig. 1b–d shows the images of Pt nanocrystal obtained by introducing different seeded solutions ranging from 0.025 to 0.100 ml. No spherical seed was observed in the samples implying completion of reaction. A combination of nanocube and octopod structures was observed for the sample synthesized via 0.025 ml seeds loading. The samples consisted of 52% nanocube at the size of 40 nm and 40% octopod of ~80 nm (measured from apex to apex). Nonetheless, increasing the seeds loading produced nanocube as the main product, at the size of about 30 nm (48% yield) for Pt synthesized via 0.050 ml and 25 nm (38% yield) upon seeds loading at 0.10 ml. The decrease in particles size with increasing seeds solution was expected. This is because increasing seeding loading produced higher amount of individual particles that serves as the crystallization sites which consume the same amount of supersaturation resulting in the generation of smaller particles.

The reaction mechanism in the growth solution can be explained according to the possible reaction mechanism of the growth solution [13]:

$$NH_2CH_2CH_2OH{-}2H - 2e^- \rightarrow NH_2CH_2CHO \quad (1)$$

$$[PtCl_6]^{2-} + 2e^- \rightarrow [PtCl_4]^{2-} \quad (2)$$

$$[PtCl_4]^{2-} + 2e^- \rightarrow Pt^{(0)} + 2Cl_2 \quad (3)$$

It was found that monoethanolamine can serve as a solvent and reduce the aqueous solution of metallic salt to metal. The reaction commences with the oxidation of the alcoholic group by removing its two hydrogen atoms to produce aminoacetaldehyde [13]. The electron produced from the ethanol oxidation subsequently reduces $PtCl_6^{2-}$ to $[PtCl_4]^{2-}$ and is absorbed on the seed surface for subsequent growth process. The aminoacetaldehyde will possibly chelate with a metal center owing to its high affinity to bind to nitrogen atom.

The formation of both nanocube and octopod via 0.025 ml seeds solution resulted from inhomogeneous nucleation as new nucleation centers were formed during the reduction reaction. The high temperature of the synthesis accelerated the rate of Pt^{2+} reduction and induced high supersaturation. As a result, metal generation was faster than adatoms diffusion at the Pt surface, which caused overgrowth [14]. Larger size of octopod compared to cubic suggests that the octopod was formed earlier than the cubic and evolved from overgrowth at the corner of the cubic structure as shown in Fig. 2. It is known that amine species strongly bond to (100) facets and inhibit growth along <100> direction. Therefore,

Please cite this article in press as: Johan Ooi MD, Abdul Aziz A, Seed-mediated grown platinum nanocrystal: A correlation between seed volume and catalytic performance of formic acid and ethanol oxidation, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.06.032