Materials Chemistry and Physics xxx (2016) 1–4

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Prominent electrocatalytic methanol oxidation from cauli-flower shape gold with high-index facets

Hui Wang [a], Lili Zhu [a], Lulu Yang [a], Fan Liao [a], Minqi Sheng [b, **], Binbin Jiang [a], Mingwang Shao [a, *]

[a] Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, 199 Ren'ai Road, Suzhou, 215123, Jiangsu, PR China
[b] School of Iron and Steel, Soochow University, Suzhou, 215123, Jiangsu, PR China

HIGHLIGHTS

- Cauli-flower shape gold (CSG) with exposed high-index facets was obtained.
- The CSG catalysts exhibit enhanced anode current for methanol oxidation.
- The CSG catalysts show excellent stability for methanol oxidation.
- High-index facets are confirmed in favor of methanol oxidation.

ARTICLE INFO

Article history:
Received 22 March 2016
Received in revised form
1 October 2016
Accepted 30 October 2016
Available online xxx

Keywords:
Electrocatalysis
Gold
Methanol oxidation
High-index facet

ABSTRACT

Nano-sized gold has been recognized as a potential catalyst in methanol fuel cells for both low cost and no formation of poisoning species compared with Pt. Previous techniques to prepare highly effective pure gold catalysts for methanol fuel cells are dealloying, which needs stern conditions. In this paper, cauli-flower shape gold nanoparticles with exposed high-index facets were obtained by a mild hydrothermal method. During the reaction process, sodium dodecyl sulfonate selectively protected high-index facets of gold, and H_2O_2 kept etching low-index ones and growing new ones at the same time. A possible growth mechanism for high-index facets was proposed. The as-prepared gold nanoparticles were employed as electrocatalysts in the methanol oxidation. The results show enhanced anode current of 1249.8 μA cm^{-2} at 0.18 V in solutions with 0.5 M KOH and 1.0 M CH_3OH, which is 10.68-fold larger than the previous reported value based on nanoporous gold catalysts. The preparation method of cauli-flower shape gold was easy to be operated and controlled, which is also universal in the synthesis of other materials with high-index facets.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Fuel cells have received a lot of attention owing to high efficiency, pollution free and noiselessness [1,2]. Especially, direct methanol fuel cells among others have extensive applications in automobile and portable electronics on account of simple operation and high energy density [3]. Platinum is mostly used for the high catalytic activity in the industries. However it is expensive and easily suffers from CO poisoning which dramatically reduces the catalytic ability. Besides, there are always intermediates during the methanol oxidation (MEO), resulting to low efficiency compared to the desired expectations [4].

Therefore, a good catalyst is in urgent need to achieve high efficiency and stability for methanol oxidation. Nano-sized gold is an attractive catalyst for satisfying both inexpensive and no catalyst poisoning in the MEO. Nanoporous gold (NPG) is a good choice to be used in methanol oxidation. The porous network of NPG gives large room for reactants to enter and leave, consequently enhancing the catalytic activity [5,6].

Erlebacher et al. [7] made the first attempt by dealloying Au32% Ag68% into NPG with interconnected morphology. After that, many

* Corresponding author.
** Corresponding author.
E-mail addresses: smqtg@hotmail.com (M. Sheng), mwshao@suda.edu.cn (M. Shao).

http://dx.doi.org/10.1016/j.matchemphys.2016.10.057
0254-0584/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: H. Wang, et al., Prominent electrocatalytic methanol oxidation from cauli-flower shape gold with high-index facets, Materials Chemistry and Physics (2016), http://dx.doi.org/10.1016/j.matchemphys.2016.10.057

people used de-alloying method to synthesize NPG [8–10]. However, the atomic percent of silver must beyond 55% for the formation of NPG, which greatly limits the practical catalysis application.

In a catalytic process, it has been reported that surface crystalline structure is closely related to the activity of catalysis [11–14]. High-index facets own a higher density of low-coordinated atoms on steps, edges, and kinks, which will produce prominent catalytic activity [15]. Methods to synthesize high-index facets of gold nanocrystals include using surface capping agents [16–20] or employing metal ions plus surfactants [21–26]. However these methods are mostly suffering from irreproducibility for nanocrystal shapes.

Here, we prepared gold nanoparticles with exposed high-index facets in a reproducible manner: excessive H_2O_2 was adopted to continually reacting with gold (gold went through thousands of times being etched and reborn during the process); and sodium dodecyl sulfonate (SDS) was chosen to selectively protect high-index facets at the same time and leading to the formation of cauli-flower shape gold (CSG). The cauli-flower shape gold nanoparticles exhibited high catalytic activity and excellent stability for methanol oxidation, which might offer potential applications in industrial applications.

2. Materials and methods

The reagents were analytically pure and were used without further treatments. CSG was prepared by a mild hydrothermal method. $HAuCl_4 \cdot 4H_2O$ (4.2 mL, 10 gL^{-1}) and 1.2 mL of 0.1 M SDS were added to 94.6 mL of deionized water and stirred. Subsequently, an adequate amount of H_2O_2 solution was added to the mixture. Afterwards, the mixture was transferred into a Teflon-lined reactor at 120 °C for 5 h. After cooling down, the product was filtered and washed several times using deionized water. Gold prepared without the addition of SDS was also synthesized to compare the catalytic activity with CSG.

The preparation of the working electrode was as follows: 100 μL of catalyst dispersion that was prepared by mixing 2 mg of gold catalysts, 1 mL mixed solution of 5: 1 v/v water-isopropanol and 100 μL of Nafion solution (5 wt %), was dripped on a polished glassy carbon electrode($\Phi = 3$ mm). A saturated calomel electrode served as the reference electrode and a Pt plate with surface area of 2 cm^2 as the counter electrode. The electrolyte solution was prepared by a mixed solution of KOH and CH_3OH. The solutions needed purging with high-purity N_2 for 10 min before each measurement.

Surface morphologies of CSG were observed by a scanning electron microscope (SEM, Zeiss Supra 55) operating at 10 kV. The high-resolution transmission electron microscopy (HRTEM) was conducted with (FEI Tecnai F20). Appling X-ray powder diffraction (XRD, Philips X'pert PRO MPD diffractometer) equipped with Cu Kα radiation ($\lambda = 0.15406$ nm) to characterize the crystallology of gold. All electrochemical experiments were measured using a Princeton VersaSTAT4 electrochemistry workstation with a conventional three electrodes system at room temperature (25 °C).

3. Results and discussion

The XRD patterns of the CSG with reaction time for 1 and 5 h and gold prepared without SDS are shown in Fig. 1a. All the peaks can be indexed as face-centered cubic structure of gold (JCPDS Card No. 89-3697). Note that the relative intensity of high-index peak of (311) for CSG increased along with the reaction, and reached to 0.76 after 5 h reaction compared with their standard value of 0.24. In the reaction process, the concentration of SDS is 1.2 mM, much lower than its critical micelle concentration of 8.1 mM, resulting in the ineffective coverage of the gold particle [27]. Some low index facets

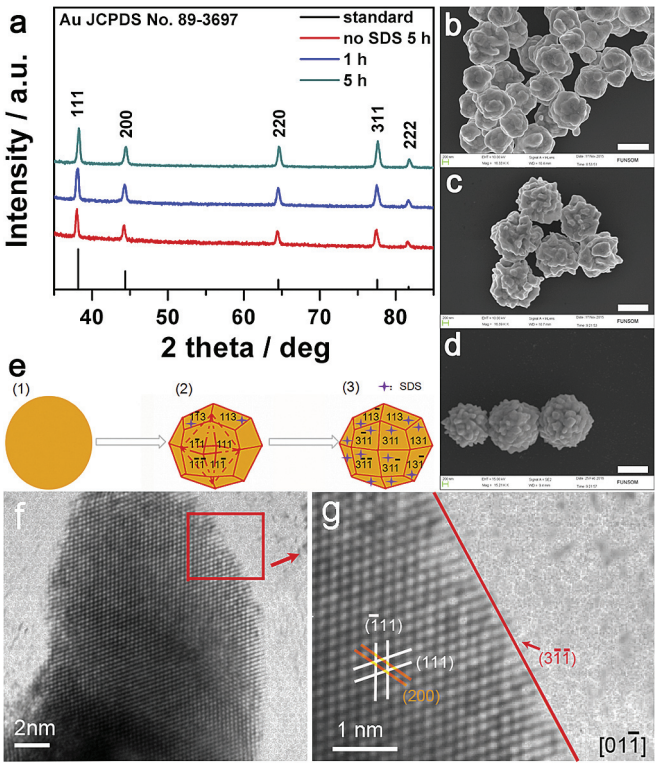

Fig. 1. (a) XRD patterns of CSG under different reaction time and gold prepared without SDS; (b,c) the evolution of CSG morphology with different reaction time: (b) 1 h and (c) 5 h. Scar bars, 200 nm; (d) the morphology of gold prepared without SDS. Scar bars, 1 μm; (e) the proposed mechanism for the formation of CSG; (f) HRTEM image of CSG; and (g) Enlarged HRTEM image of the red box of (f). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were etched by H_2O_2, resulting in the reservation of (311) facets. For the Au particles prepared without the addition of SDS, the intensity of (311) peak only reaches 0.47 after 5 h reaction, which indicates that SDS has an obvious contribution on the formation of high-index facets.

Fig. 1b and c shows SEM images of the as-prepared CSG for 1 and 5 h. The morphology of gold resembled to "cauli-flower" structure gradually as time went on, which finally formed a highly rough surface. The surface full of bumps and sags may offer more active reaction sites during methanol oxidation.

According to the above discussion, a possible formation mechanism of CSG was proposed as shown in Fig. 1e. Firstly, H_2O_2 react with $HAuCl_4$ and primary gold nanoparticles are produced.

$$3H_2O_2 + 2HAuCl_4 = 2Au + 8HCl + 3O_2 \quad (1)$$

Then the excess H_2O_2 continue to react and etch with gold nanoparticles. During the etching process, SDS prefers to adsorb onto high-index facets, such as (311), and protect them.

$$2Au + H_2O_2 = Au_2O + H_2O \quad (2)$$

At the same time, Au_2O is also reduced to Au. After thousands of etching and regeneration processes, high-index facets are reserved and CSG is formed.

$$Au_2O + H_2O_2 = 2Au + O_2 + H_2O \quad (3)$$

Please cite this article in press as: H. Wang, et al., Prominent electrocatalytic methanol oxidation from cauli-flower shape gold with high-index facets, Materials Chemistry and Physics (2016), http://dx.doi.org/10.1016/j.matchemphys.2016.10.057

Download English Version:

https://daneshyari.com/en/article/5448494

Download Persian Version:

https://daneshyari.com/article/5448494

Daneshyari.com