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Concave cubic PtLa alloy nanocrystals with high-index facets: Controllable synthesis in deep eutectic solvents and their superior electrocatalytic properties for ethanol oxidation

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HIGHLIGHTS

- A concave cubic PtLa alloy NC catalyst with {410} high-index facets is reported.
- The PtLa alloy NCs of ca. 47.5 nm are evenly electro-deposited on the GC substrate.
- Strong charge transfer interaction from La to Pt atoms is present on the NC surface.
- The PtLa alloy NCs exhibit much higher electrocatalytic properties for the EOR.

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ABSTRACT

Due to their strong electronic interactions and excellent electrochemical properties, noble metal-based rare earth nanoalloys are considered to be promising electrocatalytic materials for fuel cell applications. However, due to the limitation of the very negative reduction potential for rare earth metals, the wet chemical or electrochemical preparation of noble metal/rare earth nanoalloys is still challenging. Herein, we report a novel and effective strategy for the electrochemical synthesis in deep eutectic solvents of concave cubic PtLa alloy nanocrystals with high-index facets and superior electrocatalytic properties for the ethanol oxidation reaction. Scanning electron microscopy and transmission electron microscopy characterizations confirm that the concave cubic PtLa alloy nanocrystals of approximately 47.5 nm in size are uniformly electro-deposited on the glassy carbon substrate in deep eutectic solvents and are bounded with the {410} and adjacent high-index facets. X-ray photoelectron spectroscopy analysis indicates the presence of strong charge transfer interactions from La to Pt atoms in the concave cubic PtLa alloy nanocrystals. Due to the synergetic effect of the high-index facets and the charge transfer interactions between Pt and La, the synthesized concave cubic PtLa alloy nanocrystals exhibit enhanced specific current activity and long-term durability for the ethanol oxidation reaction.

1. Introduction

Benefitting from high theoretical energy density (8.6 kWh kg^{-1} vs. 6.1 kWh kg^{-1} for methanol), low toxicity and easy large-scale preparation through the agricultural bio-fermentation of liquid ethanol fuel, direct ethanol fuel cells (DEFCs) have been considered the most promising power devices among direct alcohol fuel cells [1–3]. Nevertheless, serious problems such as sluggish electrode reaction kinetics, poor long-term stability and the high cost of noble metal electrocatalysts are still restricting the extensive development and practical applications of DEFCs [2,4,5]. Clearly, the design and synthesis of advanced electrocatalysts for the ethanol oxidation reaction (EOR) are closely linked to the development of commercially practical DEFCs. To date, Pt and Pt-based electrocatalysts have been widely employed as the EOR electrocatalytic materials in acidic media due to their excellent electrochemical properties [6]. However, the precious

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metal Pt resources are very limited in nature and the surface active sites on Pt catalysts are vulnerable to the poisoning species (e.g., CO_{ad}) produced from the EOR [7,8]. On the other hand, the complete oxidation of ethanol to CO_2 on Pt catalysts is relatively difficult due to the poor ability of pure Pt for cleaving the ethanol molecules' C–C bonds in acidic media, which evidently decreases the energy efficiency of DEFCs [3,9,10]. Therefore, pure Pt is almost never used directly as the electrocatalytic material for the EOR. It is highly important to further develop high-performance Pt-based electrocatalysts and new catalyst synthesis methods for the practical applications of DEFCs. In this context, many Pt-based electrocatalysts (e.g., PtRu [11,12], PtSn [8,9,13–15], PtPd [5,16], PtCo [17], PtRh [18], PtCu [19], PtMn [20], PtRuSn [21,22] and PtSnCe [23]) have been fabricated by the alloying of Pt with a second or even third transition metals. It is found that the addition of these metals can obviously improve the electrocatalytic performance of Pt catalysts toward the EOR, which can be attributed to the bi-functional mechanism or the electron transfer interaction between the Pt and other metals. Among these transition metals, the rare earth (RE) elements have received an especially extensive attention as the effective co-catalytic components because of their unique 4f shell electronic structure [24,25]. In recent years, numerous Pt-based materials with RE doping have been synthesized for the anodes in the electrocatalytic process of direct alcohol fuel cells [26–31]. It is noteworthy that the RE metals are very active and their reduction potential is approximately 3.5 V more negative than that of Pt. Consequently, the RE oxides are almost the main morphology present in the previously reported RE-doped Pt catalysts. Although RE oxides can enhance the electrochemical activity of Pt-based catalysts for alcohol oxidation to some extent, they exhibit two obvious disadvantages of poor conductivity and easy dissolution in acidic media, which will unavoidably result in the decay of their catalytic performance. To overcome these issues, the synthesis strategy of Pt-RE alloy catalysts has been explored. The alloying of Pt with RE metals can effectively promote the electronic synergetic interaction between the Pt and RE metals, and thus enhance their electrocatalytic activity and durability [32]. However, it is very difficult to realize the co-deposition of Pt and RE metals and form Pt-RE alloys in the aqueous solution. To date, much attention has been paid to the oxygen reduction reaction (ORR) on the bulk polycrystalline alloys of Pt and RE elements [32–34], and very few studies have focused on the wet chemical synthesis of Pt-RE nanoalloys and their applications as the anode and cathode electrocatalysts of fuel cells. Jeon et al. prepared a carbon supported PtY alloy catalyst with improved ORR activity through a $NaBH_4$ reduction process [35]. De Souza et al. synthesized an alloyed PtSnCe/C catalyst by using the polymeric precursor method, with the obtained catalyst showing higher electrocatalytic activity compared to the commercial PtSn/C catalyst for the EOR [36]. Therefore, the development of the Pt-RE alloy nanocatalysts with high performance and their synthesis methods remains a crucial challenge.

Due to their excellent physicochemical properties (e.g., high conductivity, good thermostability, negligible vapor pressure, wide electrochemical potential windows and nontoxicity), deep eutectic solvents (DESs) have attracted considerable interest in the field of fabrication of nanoscale and functional materials [37,38]. Recently, several Pt-based or Pd-based nanomaterials have been synthesized in the DESs for the electrocatalytic applications of fuel cells [39–43]. For instance, using the choline chloride/urea DESs as the medium, we synthesized concave tetrahexahedral Pt nanocrystals (THH Pt NCs) with the {910} high-index facets and enhanced the ethanol electro-oxidation activity by a programmed square-wave electrodeposition method [39]. However, the size of the as-prepared concave THH Pt NCs is still too large, which is not conducive to further improvement of the catalytic performance and reduction of the cost of the noble metal catalysts. Herein, for the first time, a controllable synthesis route in DESs of concave cubic PtLa alloy NCs for highly efficient ethanol electro-oxidation is reported. The morphology, structure and composition of the as-obtained concave cubic PtLa alloy NCs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS). The electrocatalytic performance of the samples was evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The results indicate that the concave cubic PtLa alloy NCs with the average size of 47.5 nm and uniform distributions are enclosed by the {410}, as well as adjacent high-index facets, and this open structure can provide an abundance of surface active sites such as the high-density atomic steps and kinks. Moreover, the high alloying extent of the PtLa NCs significantly enhances the electron transfer interaction between the Pt and La atoms. As a consequence, the concave cubic PtLa alloy NCs with the Pt:La atomic ratio of 10:5 exhibit the best electrocatalytic performance for the EOR compared to the PtLa alloy NCs with other Pt:La atomic ratios and the pure Pt NCs.

2. Experimental

2.1. Materials

Choline chloride [$HOC_2H_4N(CH_3)_3Cl$], urea, $H_2PtCl_6\cdot 6H_2O$, La$(NO_3)_3$, absolute ethanol, and sulfuric acid were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Millipore water (18.0 MΩ cm) was supplied from a Milli-Q Lab apparatus (Nihon Millipore Ltd.). All chemical reagents were of the analytical grade level (99% purity).

2.2. Preparation of concave cubic PtLa alloy NCs

The choline chloride/urea DESs were first synthesized according to the method reported previously [39,40]. The electrochemical preparation of concave cubic PtLa alloy NCs in 10 mM H_2PtCl_6/DESs +5 mM La$(NO_3)_3$/DESs plating solution was carried out in a three-electrode glass cell linked to a CHI 631 electrochemical workstation (Shanghai Chenhua Instrumental Co. Ltd., China). A Pt wire and a Pt quasi-reference electrode were employed as the counter and reference electrodes, respectively. A pretreated glassy carbon disk (GC, $\Phi = 3$ mm) was used as the working electrode. The resulting PtLa alloy NCs with high-index facets could be directly deposited on the GC substrate in a glycerin bath (80 °C) by an electrochemical programmed square-wave potential method (denoted as $Pt_{10}La_5$). In a typical deposition process, the GC substrate was first stepped from the open circuit potential to the nucleation potential ($E_N = -1.9$ V) and maintained this potential for 90 s. Then, the growth of the as-generated crystal nuclei to PtLa alloy NCs was realized by the subsequent square-wave potential treatment ($f = 10$ Hz, $E_L = -1.65$ V, $E_U = -0.3$ V) for 30 min. For comparison, the $Pt_{10}La_1$ and $Pt_{10}La_{10}$ alloy NCs were also prepared by the same method except for the change of the La$(NO_3)_3$ concentration to 1 mM and 10 mM, respectively.

2.3. Physical characterization

The morphology and size of the prepared NC samples were characterized using a LEO-1530 scanning electron microscope. The surface structure and element distribution of the PtLa NCs were further analyzed using a JEM-2100 transmission electron microscope (JEOL, Japan) and a Tecnai-F30 transmission electron microscope (Philips-FEI, Netherlands). Energy dispersive X-ray spectroscopy (EDX) analysis was performed on the same TEM apparatus (JEM-2100). A Quantum 2000 system (Physical Electronics, USA) with Al Kα 1486.6 eV excitation source was used for the X-ray photoelectron spectroscopy (XPS) characterization. All binding energy values in the XPS spectra were calibrated with the C1s line (284.5 eV).

2.4. Electrochemical studies

To characterize the electrochemical properties of the prepared