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Surfactant-free synthesis of coral-like platinum nanochains for oxygen reduction reaction

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ABSTRACT

Three-dimensional coral-like Pt nanochains (Pt-3DCNCs) are synthesized in high yields by a simple hydrothermal reduction using HCHO as a reductant agent in the presence of NaI but without any other templates or surfactants. The size, composition, and structure of Pt-3DCNCs are inspected by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy. The controlled experiment show the introduction of NaI is the key influential factor for the formation of the specific structure of Pt-3DCNCs. The as-prepared Pt-3DCNCs show superior electrocatalytic activity and long-term stability towards oxygen reduction reaction, which can be ascribed to their unique structure and the low hydroxyl surface coverage.

1. Introduction

Low-temperature polymer electrolyte fuel cells (LPEFCs), such as direct methanol fuel cells and proton exchange membrane fuel cells, have been intensively attractive as promising power sources for portable electronic devices and automotive vehicles. Unfortunately, the development of LPEFCs has been severely hampered by sluggish kinetics of oxygen reduction reaction (ORR), catalyst degradation and carbon-support corrosion [1–9]. It is well known that the efficient of the ORR highly depends on the morphology and architecture of the employed catalysts [10–15]. For example, Xia and co-workers have synthesized highly faceted Pt nanocrystals with multioctahedral nanostructrues and Pt concove nanocubes with well-defined and controllable shapes, which have much more active sites and exhibit higher ORR activity [12]. Sun and co-workers have synthesized multiarmed starlike Pt based on the truncated octahedron seeds, which exhibit the improved electrocatalytic activity towards ORR [16]. Of particular interest are one-dimensional (1D) Pt nanostructures, such as nanochains or nanowires, owing to their large active surface areas, abundant active sites available for reactant species, and outstanding electron/mass transfer efficiency compared to zero-dimensional nanostructures [15,17–20]. Which generally endow the catalysts with the enhanced electrocatalytic performance towards ORR.

Recently, various 1D Pt nanochains or nanowires have been prepared by different methods, such as soft/hard template method, thermal decomposition methodology, surfactant-directed synthesis and galvanic replacement synthesis with the assist of high-molecular polymer [20–26]. For example, Wang and co-workers used a soft template method based phase-transfer route to prepare Pt nanowire networks [21]. Yuan and co-workers reported a Co nanoparticles template route to synthesize hollow Pt nanochains in the presence of polyvinylpyrrolidone [20]. Although there are lots of excellent works on the synthesis of high-quality 1D Pt nanostructures, most of them use polymer with high-molecular weight as surface capping agent, causing the excessive amounts of capping agent around the nanoparticles. As a result, the polymer on nanoparticles surface often undermine the overall electrocatalytic activity of electrocatalysts due to the lack of “clean” surface active sites. To remove these capping agent, plasma cleaning, calcination and UV-ozone treatments have to be utilized. As can be seen, the post-treatment step is slightly complicated and uneconomical [17,23,24]. Thus, the design of capping agent-free strategies for the fabrication of an effective ORR electrocatalyst is highly desirable.

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In this study, we developed a facile and capping agent-free method for the synthesis of “clean” 3D coral-like Pt nanochains (Pt-3DCNCs) with the assistance of I^- ions. Compared to commercial Pt black, the as-prepared Pt-3DCNCs possess definitely “clean” surface and larger surface area, resulting in improved electrocatalytic activity towards ORR compared to commercial Pt black.

2. Experimental

2.1. Reagents and chemicals

Potassium hexachloroplatinum (II) (K_2PtCl_4), formaldehyde solution (HCHO, 40%) and sodium iodide (NaI) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) Commercial Pt black was purchased from Johnson Matthey Corporation. Other reagents were of analytical reagent grade and used without further purification.

2.2. Synthesis of Pt-3DCNCs

In a typical synthesis, 0.5 mL of 50 mM K_2PtCl_4, 50 mg of NaI, and 0.5 mL of HCHO were added into 8.5 mL of water in order under constant stirring. Then, the mixture solution was transferred to a 25 mL Teflon-lined stainless-steel autoclave and then heated at 140 °C for 4 h. After reaction, the obtained 3D coral-like Pt nanochains (Pt-3DCNCs) were separated by centrifugation at 9500 rpm for 10 min, washed several times with water and then dried at 60 °C for 8 h in a vacuum dryer.

2.3. Electrochemical measurements

All electrochemical experiments were performed at a CHI 760 electrochemical analyzer (CH Instruments, Shanghai, Chenghua Co.). A standard three-electrode system was used for all electrochemical experiments, which consisted of a Pt wire as the auxiliary electrode, a saturated calomel reference electrode protected by Luggin capillary with KCl solution as the reference electrode, and a catalyst modified glassy carbon electrode as the working electrode. All electrochemical measurements were carried out at 30 ± 1 °C.

The working electrode was prepared by using a previously reported procedure [11,22,27,28]. An evenly distributed suspension of catalyst was prepared by ultrasonication of the mixture of 2 mg of catalyst and 1 ml of ethanol for 30 min, and 12.0 μL of the resulting suspension was laid on the surface of the glassy carbon electrode (7 mm diameter, 0.3846 cm^2). After drying at room temperature, 5.0 μL of Nafion solution (5 wt%) was covered on the modified electrode surface and allowed drying again. Thus, the working electrode was obtained, and the specific loading of Pt metal on the electrode surface was about 62.40 $\mu g\,cm^{-2}$.

Cyclic voltammetry (CV) measurements were carried out in N_2-saturated 0.5 M H_2SO_4 solution at a sweep rate of 50 $mV\,s^{-1}$. The electrochemically active surface area (ECSA) of Pt catalysts was calculated from CVs in 0.5 M H_2SO_4 solution by measuring the charge collected in the hydrogen adsorption/desorption region after double-layer correction and assuming a value of 210 $\mu C\,cm^{-2}$ for the adsorption of a hydrogen monolayer [29].

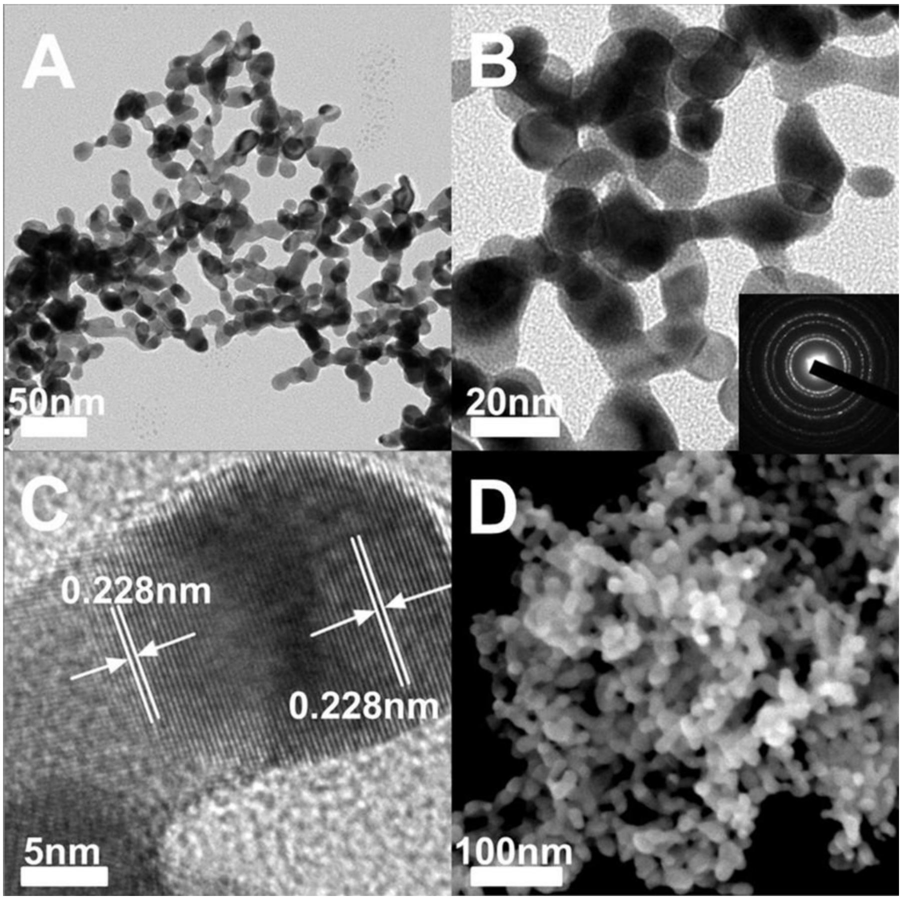

Fig. 1. (A and B) TEM, (C) HRTEM and (D) SEM images of Pt-3DCNCs. Inserted in Fig. 1B showed SAED image of Pt-3DCNCs.