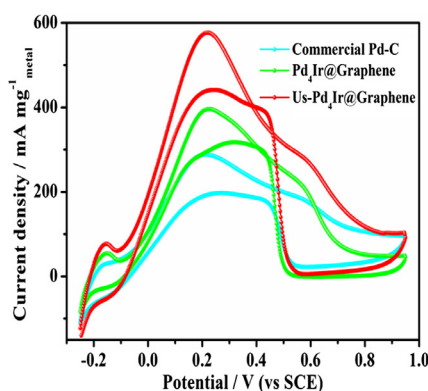
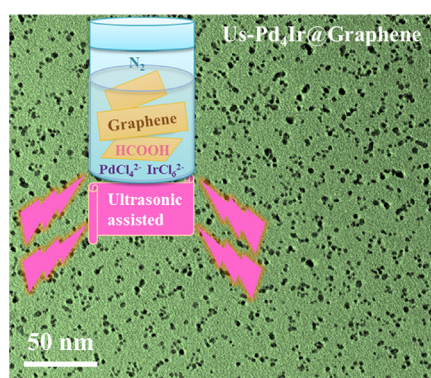




Short Communication

Graphene decorated with Pd₄Ir nanocrystals: Ultrasound-assisted synthesis, and application as a catalyst for oxidation of formic acidLian Ying Zhang^{a,b,c,*}, Ze Liu^{c,*}^a Institute of Materials for Energy and Environment, State Key Laboratory Breeding Base of New Fiber Materials and Modern Textile, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, PR China^b Chongqing Key Laboratory of Micro/Nano Materials Engineering and Technology, Chongqing University of Arts and Sciences, Chongqing 402160, PR China^c Institute for Clean Energy & Advanced Materials, Southwest University, Chongqing 400715, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 April 2017

Revised 20 June 2017

Accepted 24 June 2017

Available online 27 June 2017

Keywords:

Pd₄Ir nanocrystals

Ultrasound

Formic acid oxidation

Catalyst

Fuel cells

ABSTRACT

An effective strategy of ultrasmall and surface-clean Pd₄Ir nanocrystals uniformly decorated on graphene was developed using ultrasonic-assisted approach. The prepared Us-Pd₄Ir@Graphene reduces Pd loading while holds much higher catalytic activity and better stability toward formic acid oxidation than that of commercial Pd-C, offering great promise as a superior anode catalyst for direct formic acid fuel cells.

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1. Introduction

Graphene, a two-dimensional, single-layer sheet of sp² hybridized carbon atoms, has attracted tremendous attention owing to its exceptionally high electronic conductivity and excellent thermal stability [1,2], and becomes the subject of intense research for a promising catalyst support in energy conversion/storage sys-

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tems such as hydrogen storage, lithium ion battery and fuel cells [3–6]. Among various types of fuel cells, direct formic acid fuel cells (DFAFCs) catches tremendous attraction due to the high volume ratio energy and energy conversion efficiency, safety and reliability [7,8]. To develop efficient DFAFCs, it is essential to fabricate highly active and stable anode catalyst toward formic acid oxidation. Currently, Palladium (Pd) is believed to be promising one toward electrochemical oxidation of formic acid owing to its low oxidation overpotential and high resistance to CO poisoning [9]. However, several significant enhancements of Pd-based catalysts still wait to be achieved such as improving the catalytic properties with low Pd loading for the practical application of DFAFCs. Toward formic acid oxidation, Pd alloyed with transition metal could not only reduce expensive Pd usage and increase resistance for the intermediate poisoning, but also modify the electronic and geometric structures of Pd surfaces to improve the catalytic activity [10]. However, some non-noble metals such as Cu or Co alloyed Pd is thermodynamically unstable and could be leached from the alloy, thus it would be a significant problem in terms of catalyst durability [11]. Iridium (Ir) is one of the most stable element in acid medium among transition metals while relatively cheap in comparison with Pd. Recently, Lu et al. [12] synthesized PdIr nanoparticles using toxic sodium borohydride as reductant. Nevertheless, the electrochemical stability of PdIr catalyst toward formic acid oxidation has not been investigated while the synthesis approach has great difficulty to achieve small and uniform dispersion. Currently, stabilizers such as poly(vinylpyrrolidone) (PVP) is usually added to achieve small size and uniform dispersion of nanocrystals. However, since chemical reactions only occur on the catalytically “clean” surface of nanocrystals, the surface stabilizing agent molecule-enwrapped nanocrystals could badly suppress the reactant adsorptions to significantly reduce the catalytic activity [13,14].

In this study, an effective strategy has been developed to synthesize ultrasmall and surface-clean distributed Pd₄Ir nanocrystals uniformly decorated on graphene (Us-Pd₄Ir@Graphene) under ultrasonic-assisted condition using formic acid as a reducing agent. The schematic illustration of the fabrication process and its application for formic acid oxidation is depicted as in Fig. 1. For comparison, Us-Pd₂Ir@Graphene, Us-PdIr@Graphene, Us-PdIr₂@Graphene and Us-Pd@Graphene were prepared with the same procedures except adjusting corresponding atomic ratio of Pd and Ir. In addition, Pd₄Ir@Graphene was also synthesized for comparison. Toward formic acid oxidation, as-prepared Us-Pd₄Ir@Graphene catalyst conveys outstanding improvement performances including much higher catalytic activity and better stability than that

of Pd₄Ir@Graphene and commercial Pd-C, respectively, offering great potential as a anode catalyst for DFAFCs.

2. Experimental

2.1. Synthesis of graphene

The general procedures for preparation of graphene was reported in our recent work [15]. In a typical procedure, the prepared graphene oxide was dried in oven under 60 °C, followed by transferring into a sealed glass bottle under high vacuum level at 80 °C overnight. Finally, the bottle was heated to 250 °C quickly, and the obtained highly loose black powder was denoted as graphene.

2.2. Synthesis of Graphene supported Pd₄Ir electrocatalyst under ultrasonic-assisted condition (Us-Pd₄Ir@Graphene)

In a typical synthesis of Us-Pd₄Ir@Graphene electrocatalyst, 15 mg graphene and 6 ml HCOOH solution were loaded into a 25 ml vial under stirring. The mixture was heated to 90 °C and treated in an ultrasonic bath to form a uniform aqueous dispersion under the protection of nitrogen. Then 0.286 ml H₂IrCl₆ (7 mg ml⁻¹) and 0.221 ml Na₂PdCl₄ (20 mg ml⁻¹) were injected into above solution at the same time, followed by the mixed solution was maintained at 90 °C for 4 h under ultrasonication and stirring. After cooling to room temperature, the obtained black power was isolated by centrifugation, cleaned by three cycles of centrifugation/washing, and oven-dried at 60 °C for more than 12 h. The obtained sample was denoted as Us-Pd₄Ir@Graphene. For comparison, Pd₄Ir nanocrystals were also synthesized with the same procedures of Us-Pd₄Ir@Graphene except using sodium borohydride as reducing agent to take the place of formic acid, and was noted as Us-Pd₄Ir@Graphene-1. In addition, Us-Pd₂Ir@Graphene, UsPdIr@Graphene, Us-PdIr₂@Graphene and Us-Pd@Graphene materials were prepared with the same procedure except adjusting corresponding atomic ratio of Pd and Ir.

2.3. Synthesis of graphene supported Pd₄Ir electrocatalyst (Pd₄Ir@Graphene)

In a typical synthesis of Pd₄Ir@Graphene electrocatalyst, 15 mg graphene and 6 ml HCOOH solution were loaded into a 25 ml vial under stirring. The mixture was heated to 90 °C and treated in an ultrasonic bath to form a uniform aqueous dispersion under the protection of nitrogen. Then 0.286 ml H₂IrCl₆ (7 mg ml⁻¹) and

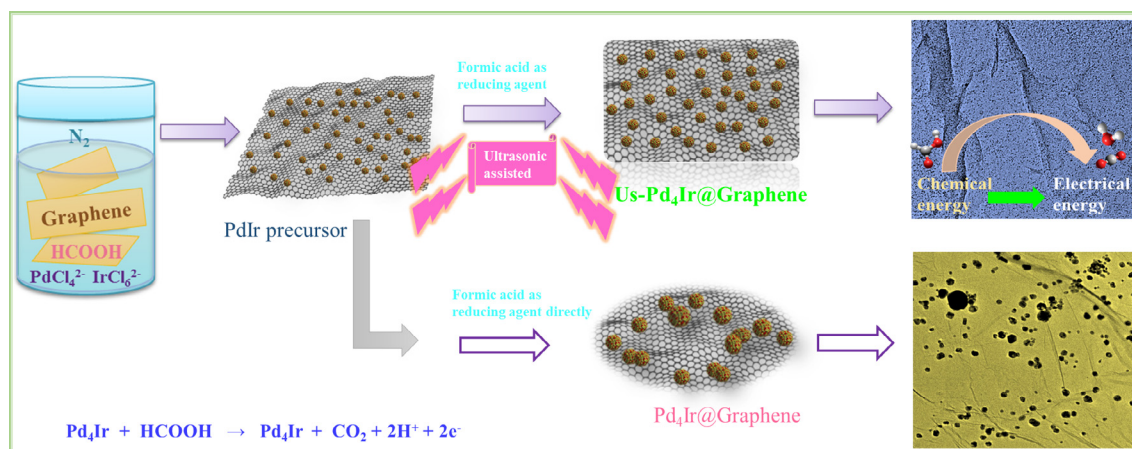


Fig. 1. Schematic illustration of preparation process of Us-Pd₄Ir@Graphene and its application for formic acid oxidation.

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