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Short communication

A facile room temperature chemical route to Pt nanocube/carbon nanotube heterostructures with enhanced electrocatalysis

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ABSTRACT

The fascinating heterostructure of carbon nanotube-supported metal nanoparticles continues to attract interest for developing electrocatalysts for energy sciences. Here, we report the fabrication of noble metal nanocubes carbon nanotube nanocomposites through an electroless deposition route. The assynthesized carbon nanotubes-supported Pt nanocubes with high active and selective {100} surfaces display excellent electrocatalytic activities towards the oxygen reduction reaction, which can/will replace current/state of the art cathode catalysts in fuel cells, and thereby improve the catalytic performance and utilization efficiency. The methodology presented here could be further extended to fabricate other one-dimensional materials/noble metal nanostructures.

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1. Introduction

In recent years, noble metallic nanostructures have been widely used as electrocatalysts in fuel cell [1]. Especially, Pt and its alloy nanostructures have been found as the key electrocatalyst in polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) [2]. Previous research has demonstrated that the catalytic activity of Pt nanostructures depends highly on their morphology and sizes, which is crucial for their applications in the field of electrocatalysis for fuel cells [3]. However, before achieving their commercial application in fuel cells, some major problems must be resolved, such as low electrochemical active surface area and low utilization efficiency of cathode catalysts [4].

In order to improve catalytic efficiency, and reduce cost, different kinds of carbon materials, such as black carbon (BC), carbon nanotubes (CNTs), and graphene have been used as supports to disperse noble metallic nanoparticles [5]. In particular, CNTs are an important support which have been extensively used as support materials for dispersing noble metal nanoparticles [6]. However, most of the previous studies mainly involved spherical noble metal nanoparticles or nanoparticles with an undetermined shape. Current investigations indicate that the reactivity and selectivity of noble metal nanoparticles can be tailored not only by controlling the size of the nanoparticles, but also by adjusting their morphology, which will determine the structure of crystallographic facets exposed on the surfaces of a nanocrystal and impact their potential applications [7].

Very recently, fabrication of noble metallic nanocrystals with specific shapes has attracted extensive interests because of their unique optical, magnetic, and catalytic properties and their potential applications in many fields, such as biodiagnostics, plasmonics, catalysis, and so on [8-12]. As a key catalyst for fuel cells, the morphologies of Pt nanostructures have received increasing attention [13]. Many researches have found that specific shapes of Pt nanostructures exhibit much superior catalytic action [14,7f]. Therefore, cubic Pt-based nanoparticles have drawn much attention owing to their unique structure and surface properties, as well as excellent electrocatalytic activities [15]. However, Pt nanocubes are general fabricated through a complicated process and the complex between Pt nanoparticles and supports often leads to the unwanted aggregation of the nanoparticles. Therefore, the fabrication of Pt nanocubes/CNTs composite catalysts with high dispersions is still a challenge.

In this paper, we report a facile room temperature wet chemical approach toward single-crystal platinum nanocubes/CNTs heterostructures with high dispersions. The as-synthesized CNTsupported Pt nanocubes with high active and selective {100} surfaces [16] display excellent electrocatalytic activities towards the oxygen reduction reaction (ORR) [17], which will replace current cathode materials in fuel cells, and thereby improve the catalytic performance and utilization efficiency. The obtained material is a promising fuel cell electrode material.

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Fig. 1. Structure characterization of the Pt nanocube/CNT heterostructures. (a and b) Typical SEM images of Pt/CNT hybrids at different magnifications. (c and d) TEM images of Pt /CNT heterostructures. (e) HRTEM image of the Pt nanocube. (f) EDX spectrum of the products.

2. Experimental

2.1. Chemicals

Multi-walled carbon nanotubes (MWNTs, CVD method, purity > 95%) were purchased from Nanotech Port. Co. Ltd. (Shenzhen, PR China) and were used as received. $H_2PtCl_6.6H_2O$ was purchased from the Shanghai Chemical Factory (Shanghai, PR China). Other chemicals were of analytical grade and were used without further purification. Water used throughout all experiments was purified with the Millipore system.

2.2. Nanotube processing

Polymer wrapping was performed by means of a variation of the method reported by O'Connell et al. [18]. A controlled amount of

MWNTs was dispersed in a 0.5 wt% aqueous solution of an anionic polyelectrolyte, polystyrene sulfonate (PSS, M_W = 70,000), to a concentration of 150 mg L⁻¹ by a combination of strong stirring and sonicating to ensure that well-dispersed individual MWNTs were present in the dispersion. Excess PSS was removed by three centrifugation/redispersion cycles.

2.3. Preparation of CNTs/metal heterostructures

The dispersion of polymer-wrappered MWNTs was then spuncoated onto a copper foil (25 mm^2) and subsequently immerged into an aqueous solution of $3 \text{ mM} \text{ H}_2\text{PtCl}_6$ in the presence of $1.25 \text{ mM} \text{ CoCl}_2$ at room temperature. The copper foil was taken out after reacting with solution for 1 min and thoroughly washed with distilled water. The size and loading control of metal nanoparticles were realized by changing the concentration of the metal salt ions and the reaction time. Download English Version:

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