



Platinum-based intermetallic nanotubes with a core–shell structure as highly active and durable catalysts for fuel cell applications



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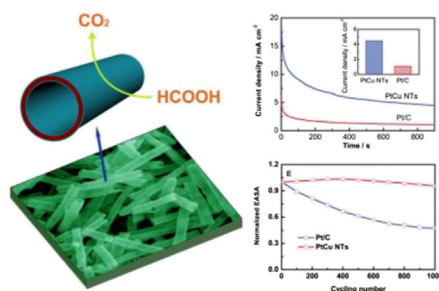
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HIGHLIGHTS

- PtCu intermetallic nanotubes with a Pt/PtCu core–shell nanostructure were synthesized by a galvanic replacement approach.
- The PtCu nanotubes exhibit superior catalytic activity toward the electrooxidation of formic acid.
- The PtCu nanotubes are >10 times durable than the conventional Pt/C catalyst.
- Tailored electronic structure and one-dimensional geometry synergistically contribute to the improved performance.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper describes the facile synthesis of the PtCu intermetallic nanotubes, which are obtained by a galvanic replacement reaction using Cu nanowires as templates followed by chemical etching and heat annealing. Scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy are used to characterize the PtCu intermetallic nanotubes. Both cyclic voltammetry and chronoamperometry results demonstrate that these PtCu nanotubes exhibit significantly high catalytic activity toward the formic acid oxidation reaction in comparison with the conventional Pt/C catalyst. Furthermore, the PtCu nanotubes show >10 times higher durability than the Pt/C catalyst in the accelerated ageing test. It is revealed that the PtCu intermetallic nanotubes have a Pt/PtCu core–shell nanostructure that combines the merits of tailorable electronic structures for core–shell nanoparticles and unique geometries for one-dimensional nanotubes, which synergistically contribute to the activity and durability. We believe that the design concept of hierarchy intermetallic nanotubes and the versatile synthetic strategy can not only be used for fuel cell catalysts but also be potentially extended to other catalysis fields.

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1. Introduction

Efficient anode catalysts with high activity and durability are critical to the development of direct type fuel cells, such as direct

methanol or formic acid fuel cells [1–4]. Unfortunately, the commonly used Pt or Pt alloy nanoparticles (NPs) suffer from the problems of significant CO poisoning (poor activity) and low stability [5,6]. Thus, numerous studies have been conducted to explore alternative high performance anode catalysts. In recent years, nanostructured catalysts have received substantial interests because their unique morphology, composition and structure often lead to greatly improved catalytic activity and

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stability [7,8]. The nanostructured electrocatalysts reported for fuel cell applications include heterogeneous Pt–Pd nanocomposites [9,10], Pt-based core–shell NPs [11,12], Pt nanocubes or nanopolyhedra [13–15], and Pt nanowires (NWs) or nanotubes (NTs) [16–18]. Among them, Pt-based core–shell NPs show superior catalytic properties, which can be largely attributed to the tailored electronic structure of surface atomic layers by the central cores [19–22]. For example, Pd@Pt and PtNi@Pt core–shell NPs showed over 1 order of magnitude and 5.4 times higher activity for oxygen reduction reaction (ORR) than conventional carbon supported Pt (Pt/C) catalyst, respectively [21,22]. In addition to core–shell NPs, one-dimensional Pt NWs or NTs also exhibit promising catalytic activity and stability, which is closely associated with their anisotropy and unique structures [18,23]. For instance, Sun et al. demonstrated that Pt NWs showed a 2.4-fold higher ORR activity than commercial Pt catalyst [23], while Yan et al. reported that Pt NTs exhibited superior stability as the ORR catalyst [18].

Apparently, the results for core–shell and one-dimensional Pt nanostructures as fuel cell catalysts are intriguing. However, to the best of our knowledge, there is still no effort devoted to the construction of hierarchy Pt nanostructures that combine the merits of core–shell and one-dimensional Pt nanostructures. Besides, present nanostructured electrocatalysts are mostly used for the ORR, and attempts to use them as the anode catalysts are rarely carried out. Herein, we report a novel concept of hierarchy PtCu intermetallic NTs with a Pt/PtCu core–shell nanostructure as an anode catalyst for direct type fuel cells. Our approach integrates the benefits of core–shell NPs and one-dimensional NTs, which would synergistically contribute to the catalyst activity and stability. First, the underlying PtCu alloy layer can tailor the electronic structure of surface Pt layers, which thereby, on the one hand, modifies the chemisorption energies and activation barriers for the anode processes, and on the other hand, reduces the Pt dissolution in fuel cell conditions. Second, the interconnected nature renders our hierarchy PtCu NTs less vulnerability to aggregation than Pt NPs. Third, Pt is stable so that the outer Pt surfaces can prevent the etching loss of underlying Cu atoms. Fourth, the PtCu NTs do not require a support, and the support corrosion problem in conventional Pt/C catalyst is thus eliminated. Catalytic properties of the hierarchy PtCu intermetallic NTs were evaluated towards the electrooxidation of small organic molecules for fuel cell applications, and they showed significantly higher activity and stability than the conventional Pt/C catalyst.

2. Experimental section

2.1. Synthesis of Cu NWs

Cu NWs were prepared by an electrodeposition method. An anodic alumina film (Whatman, Anodisc 25) with a nominal pore size of 200 nm was used as the template for the electrodeposition. A 500-nm-thick Cu film evaporated onto one side of the template served as the working electrode in a three-electrode cell with a Pt mesh as the counter electrode and an Hg/Hg₂SO₄ electrode as the reference electrode, respectively. Cu NWs approximately 20 μm long were deposited from a solution containing 0.1 M CuSO₄, 0.1 M H₃BO₃ and 25 mg L⁻¹ polyethylene glycol at -0.6 V (vs. Hg/Hg₂SO₄). After deposition, the Cu film was stripped by etching in a solution of 0.3 M CuCl₂ and 0.1 M HCl. The alumina template was then dissolved in 2.0 M NaOH for 2 h, and the remaining Cu NWs were centrifuged, washed thoroughly, and suspended in N₂-saturated deionized water containing 8.0 mM poly(vinyl pyrrolidone).

2.2. Synthesis of PtCu intermetallic NTs

The PtCu intermetallic NTs were synthesized by a galvanic replacement reaction followed by chemical dealloying and heat annealing processes. In a typical synthesis, the solution containing Cu NWs was heated to 80 °C. Subsequently, 0.5 mM H₂PtCl₆ aqueous solution was added. After the mixture was vigorously stirred for >30 min, the resulting PtCu alloy sheathed Cu NWs were separated and washed with deionized water. The chemical dealloying treatment was performed by immersing the sheathed Cu NWs into 10 wt% NH₃ solution for 2 h. The samples were then filtered and washed by deionized water and ethanol to obtain the hierarchy PtCu NTs. The heat annealing was carried out under an Ar–H₂ flow (5% H₂) in a tube-oven at 500 °C for 3 h.

2.3. Physical characterization of PtCu intermetallic NTs

Scanning electron microscopy (SEM) was carried out on an FEI Quanta 200FEG instrument equipped with an energy dispersion X-ray spectroscopy (EDX) device (10 kV). X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-3B diffractometer with Cu K α radiation. Transmission electron microscopy (TEM) was conducted on a Hitachi H800 system (200 kV). X-ray photoelectron spectroscopy (XPS) was performed on a PHI model 5700 spectrometer using Al K α X-ray source.

2.4. Electrochemical treatment and tests

Electrochemical treatment and tests of the PtCu intermetallic NTs were performed on a rotating disk electrode (RDE) apparatus (Princeton Applied Research) in a three-compartment electrochemical cell with a Pt foil and an Hg/Hg₂SO₄ electrode serving as the counter and reference electrodes, respectively. Prior to each experiment, a suspension of the PtCu NTs was prepared as follows: To 3.5 mg dried PtCu NTs, 2.7 mL deionized water, 0.725 mL isopropanol and 0.075 mL Nafion solution (5%) were added; The resulting mixture was sonicated for 30 min to form homogeneous suspension. 12.5 μl of the suspension was coated onto a glassy carbon RDE electrode (4 mm diameter), which was then dried at 50 °C under a N₂ atmosphere for 30 min to serve as the working electrode.

Before electrochemical tests, a pretreatment of the working electrodes was performed by potentially cycling them between 0.05 and 1.2 V for 50 cycles at a scan rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ solution. Cyclic voltammetry (CV) measurements for formic acid oxidation were carried out in a N₂-saturated 0.5 M H₂SO₄ solution containing 0.5 M HCOOH at a scan rate of 50 mV s⁻¹ in the range of 0.05–1.2 V. Chronoamperometry (CA) tests were conducted by holding the working electrode at 0.4 V in a solution of 0.5 M H₂SO₄ and 0.5 M HCOOH. Electrochemically active surface area (EASA) of the samples was evaluated by the H₂ desorption peak in the CV profiles obtained in a N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹. For CO-stripping measurements, the working electrode was firstly poisoned with CO at 0.1 V by bubbling CO gas through 0.5 M H₂SO₄ aqueous solution for 30 min. Linear sweeping voltammetry was then conducted at a scan rate of 10 mV s⁻¹ after the remaining CO in the electrolyte solution was removed by purging N₂ for 40 min. All electrochemical experiments were carried out at room temperature and all potentials in this study are given relative to the reversible hydrogen electrode (RHE). For the sake of comparison, the Pt/C catalyst was also synthesized (see [Supplementary material](#) for details) and tested.

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