



Gold–platinum bimetallic nanotubes templated from tellurium nanowires as efficient electrocatalysts for methanol oxidation reaction



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HIGHLIGHTS

- Au–Pt bimetallic nanotubes were synthesized via a sacrificial template method.
- Au–Pt bimetallic catalysts exhibit excellent electrocatalytic activities.
- The catalytic activities of samples with different Au/Pt ratio were studied.

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ABSTRACT

In this paper, gold–platinum (Au–Pt) bimetallic nanotubes with different Au/Pt ratio are successfully synthesized through a simple wet-chemical reduction route in which tellurium (Te) nanowires serve as both sacrificial template and reducing agent. The hollow nanostructure of Au–Pt nanotubes is formed due to Kirkendall effect. The as-prepared Au–Pt nanotubes can be applied as catalyst for methanol oxidation reaction, and the results indicate that the Au–Pt nanotubes with an Au/Pt ratio of 1:1 show the best electrochemical catalytic performances. Furthermore, the catalytic activity of the Au–Pt nanotubes is also better than Pt nanotubes and commercial Pt/C catalyst.

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1. Introduction

Platinum (Pt) has attracted a great deal of attentions because of its extensive applications in various fields, especially as a highly efficient methanol oxidation reaction (MOR) catalyst for fuel cells [1–5]. However, as Pt is a kind of noble metal with low reserves and high costs, the commercialization of fuel cells on a large scale is still limited. Tremendous efforts have been devoted to increase the catalytic efficiency and Pt utilization efficiency of Pt catalysts including the development of advanced synthesis strategies to control the size, shape and composition of Pt catalysts [6–10]. Among these methods, the introduction of other metals (e.g., Pd, Au, Ag, Fe, Ni, Cu) into Pt to form Pt based alloys or composites not only reduces the overall Pt consumption, but also enhances the electrocatalytic activity of Pt catalysts [11,12]. For example, Yu et al. synthesized ultrathin PtPdTe nanowires with enhanced activity

toward MOR [13]. Zhang et al. reported that Pt–Cu alloy concave nanocubes with high-index facets exhibited substantially enhanced activity for MOR [14]. Wong et al. prepared PtRuFe nanowires with higher MOR activity than Pt, Pt₇Ru₃, Pt₇Fe₃ nanowires, and commercial Pt/C catalyst [15]. Adzic and co-workers synthesized monolayer-level Ru- and NbO₂-supported Pt electrocatalysts with high Pt mass activity and improved durability for MOR through a galvanic replacement method [16]. Papadimitriou et al. prepared Pt–Cu, Pt–Ni, and Pt–Co binary catalysts by a galvanic replacement process for MOR [17]. The improved catalytic activities of these Pt based catalysts for MOR can be attributed to a combination of the electronic effect and bifunctional mechanism [18,19].

One-dimensional (1D) nanostructures, especially nanotubes have attracted particular interest because of their unique properties such as high specific surface areas, low densities, and well permeation, as well as their prospective applications in many fields [20]. Among the methods for preparing nanotubes, the sacrificial template method has been widely used due to its merit of simplicity, conveniency and controllability [21–24]. The morphology and size of the final product is confined to the

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template, and the template does not need to be removed as it has been consumed during the synthetic process. For example, Yu et al. prepared PtPdCu nanotubes by using Cu nanowires as partially sacrificial template [25]. Han and co-workers synthesized multi-metallic alloy nanotubes using ZnO nanowires as sacrificial template [26].

In this work, we report a new and facile approach for the fabrication of Au–Pt bimetallic nanotubes by using Te nanowires as sacrificial template. The Te nanowires not only function as templates, but also serve as the reducer for the reduction of PtCl_6^{2-} and AuCl_4^- . Since the Te nanowires templates are dissolved during the reaction process, there is no need to eliminate the templates. The as-obtained Au–Pt nanotubes can be applied as an efficient catalyst for MOR. The results indicate that the Au–Pt nanotubes with an Au/Pt ratio of 1:1 show higher specific activity and stability than other Au–Pt nanotubes, Pt nanotubes and commercial Pt/C catalyst. In comparison to Pt-based nanoparticle catalysts, the Au–Pt bimetallic nanotube catalyst has the following advantages. First, the Pt-based nanotubes are more stable than Pt-based nanoparticles because they can resist the dissolution and aggregation of the catalysts during fuel cell operation. Second, the Pt-based nanotubes do not need supports, and thus the support corrosion problem can be solved. Furthermore, the anisotropic Au–Pt nanotubes can improve mass transport and catalyst utilization.

2. Experimental

2.1. Synthesis of Te nanowires

Te nanowires were synthesized by using a method that has been developed by us previously [27]. Typically, 15 mg Te powder, 48 mL distilled water and 0.25 mL hydrazine hydrate (85%, w/w %) were successively added into a 60 mL stainless-steel autoclave with a Teflon liner. The autoclave was maintained at 160 °C for 6 h and then cooled to room temperature naturally. The product was collected by centrifuging and washed by distilled water and ethanol for several times each, and then dried under vacuum at 60 °C for 4 h.

2.2. Synthesis of Au–Pt and Pt nanotubes

Au–Pt nanotubes were obtained through a galvanic displacement at the expense of Te nanowires, as illustrated in Scheme 1. Typical procedure for the synthesis of AuPt nanotubes is as following: Firstly, the above Te nanowires (~2 mg) was dispersed in 15 mL ethanol, and then was mixed with 15 mL distilled water. Under continuous stirring, 0.4 mL of 19 mM H_2PtCl_6 (aq), 0.4 mL of 19 mM HAuCl_4 (aq) and 20 μL of 0.2 M KOH (aq) were added dropwise in turn. After further stirred for 20 min, the mixed

solution was shaken at a rotation rate of 120 rpm using an incubator shaker at 50 °C for 4 h. The product was collected through centrifugation, and then was washed with absolute ethanol for several times.

For comparison, Au_4Pt_5 , Au_3Pt_5 and Pt nanotubes were prepared by simply adjusting the ratio between HAuCl_4 and H_2PtCl_6 while kept the total amount of HAuCl_4 and H_2PtCl_6 constant.

2.3. Characterizations

X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation. X-ray photoelectron spectroscopies (XPS) were performed on an ESCALab MKII X-ray photoelectron spectrometer with Al $K\alpha$ radiation. Scanning electron microscopy (SEM) images together with energy dispersive X-ray spectroscopy (EDS) were captured on a Hitachi S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a FEI Tecnai G² 20 high-resolution transmission electron microscope. Elemental mappings were obtained on a JEOL JEM-2100F transmission electron microscope equipped with an EDX spectrometer. Electrochemical characterizations were carried out on a CHI-660D electrochemical working station (ChenHua Corp., Shanghai, China).

2.4. Electrochemical measurements

The working electrode was prepared according to the following procedure. Firstly, the catalyst was dispersed into 1 mL ethanol by ultrasonication. Then, 6 μL of the ethanol suspension was dropped onto a glassy carbon electrode (GCE, 3 mm in diameter, 0.071 cm^2) and dried in air. The mass loading of Pt is about 9 μg and 2.5 μg for the prepared catalysts and commercial Pt/C, respectively. Finally, 5 μL Nafion (aq) was pipetted onto the catalyst film, and dried in air. A saturated calomel electrode (SCE) and a platinum plate were used as the reference electrode and the counter electrode, respectively. The acidic blank scans were carried out in 0.5 M sulphuric acid aqueous solution purged with nitrogen and cycled from –0.2 to 1.0 V.

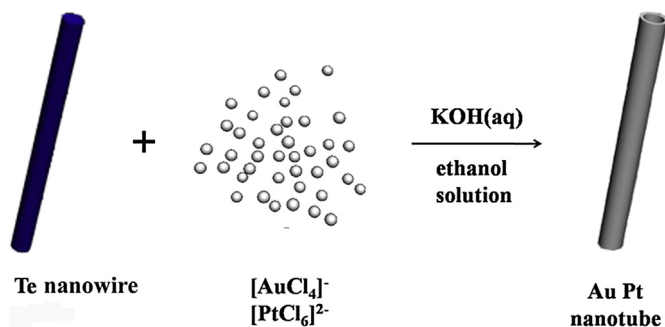
Methanol oxidation reactions (MOR) in acid were carried out in a N_2 -saturated aqueous solution containing 0.5 M methanol and 0.5 M sulphuric acid. CO stripping voltammetry measurements were performed according to the previously reported procedure [28,29]. All the measurements were performed at room temperature with a scan rate of 50 mV s^{-1} . Chronoamperometric curves for MOR were recorded at the potential of 0.60 V for 3600 s.

3. Results and discussion

3.1. Morphology and sample characterizations

The Te nanowires that acted as sacrificial template were synthesized by a hydrothermal recrystallization process [27]. Fig. 1a and b shows SEM images of the Te nanowires, from which many monodisperse Te nanowires with a mean diameter of about 40 nm can be seen. These Te nanowires are smooth and long. The inset in Fig. 1a shows a photograph of a blue ethanol suspension of Te nanowires. The suspension can be well maintained for a long time.

Au–Pt nanotubes with different Au/Pt ratio were obtained by galvanic exchange reactions that have been reported for the synthesis of highly active Pt catalysts [30–33]. According to the literature [34], the Te nanowires can be oxidized into soluble TeO_3^{2-} during the replacement reaction, and the reactions between Te nanowires and metal ions (PtCl_6^{2-} and AuCl_4^-) can be formulated as follows:



Scheme 1. The synthetic procedure of Au–Pt nanotubes.

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