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Synthesis of worm-like PtCo nanotubes for methanol oxidation

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ABSTRACT

Worm-like PtCo nanotubes are synthesized by galvanic exchange reaction using Co nanowires as templates. As a novel electrocatalyst for methanol oxidation, the as-prepared PtCo nanotubes display better activity and stability compared with commercial Pt/C catalyst.

1. Introduction

Controlling the morphology of bimetallic Pt-based alloy can provide a great opportunity to improve their catalytic properties. Recently, tubular Pt-based bimetallic alloys have drawn more and more attention due to their potential application in proton exchange membrane fuel cell [1–12]. First, the Pt-based nanotubes are less vulnerable 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 could be eliminated. Additionally, the anisotropic Pt-based nanotubes could improve mass transport and catalyst utilization [5]. Controllable synthesis of Pt-based nanotubes is usually achieved using the galvanic replacement reaction between metal nanowires and precursors of desired elements. Up to now, Te, Ag, Co, Cu, Se and ZnO nanowires have been successfully employed as sacrificial templates to the synthesis of PtPd [4,5], PtRu [6], PtCu [13], Pt [14] and PtAu [15] nanotubes.

PtCo alloy has been proposed as anode catalyst for direct methanol fuel cell (DMFC) [16,17]. However, there is no report on employing PtCo nanotubes as anode catalyst for DMFC. Therefore, in the present communication, we propose a versatile synthesis method for the fabrication of PtCo nanotubes in which Co nanowires are employed as sacrificial templates. Compared with the former synthesis method for one-dimensional PtCo alloys [16], this method is cost-effective, time-efficient and eco-friendly because it does not need any hard template. Also, our results reveal that introduction of Co can increase the catalyst activity and resistance to CO poisoning. Most importantly, the prepared PtCo nanotube catalyst exhibits excellent stability than granular Pt/C catalyst (Johnson Matthey, 20%).

2. Experimental

Firstly, 20 ml of 12 mM $CoCl_2$ aqueous solution and 71 mg of trisodium citrate dehydrate were added to 200 g of DI water. After the solution was purged with N_2 for 15 min, $NaBH_4$ solution (18.2 mg in 10 g H_2O) was added dropwise under vigorous stirring, giving rise to a brown Co hydrosol. The hydrosol was aged for 0.5 h, then, 7 ml of 19.3 mM H_2PtCl_6 was added under vigorous stirring. The reaction system was kept on stirring for 0.5 h to complete the reaction. High-purity nitrogen was bubbled through the solution during the whole procedure. The product was collected by filtration, washed with DI water for several times, and dried in a vacuum freeze drier.

CO_{ad} stripping voltammetry was carried out by purging the electrolyte with high purity CO gas for 3 min at a holding potential of −0.2 V. The purging gas was then switched to nitrogen to remove dissolved CO. CO was then stripped by scanning the potential between −0.2 and 1.0 V at a scan rate of 50 mV s^{-1}. The structural and morphological investigations and other electrochemical measurements referred to the literatures [18].

3. Result and discussion

Fig. 1a shows the transmission electron microscopy (TEM) image of Co nanowires. It can be seen that the complete Co nanowires have been destroyed due to their instability in air. Although the nanowires have been broken, the wire-like morphologies remain visible. Fig. 1b reveals

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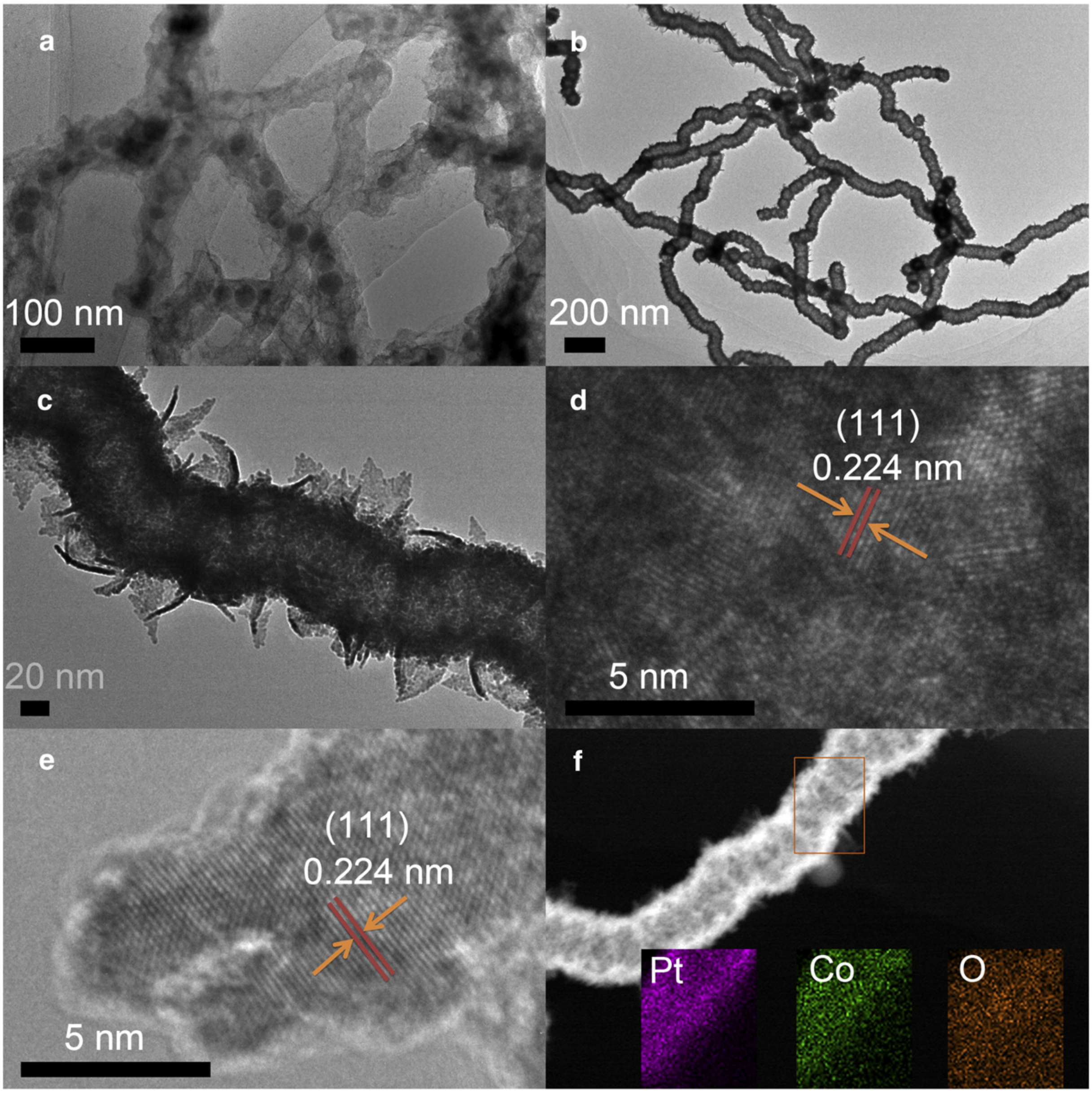

Fig. 1. TEM images of (a) Co nanowires, (b) PtCo nanotubes, and (c) one magnified PtCo nanotube; HRTEM images of (d) one nanotube and (e) one nanoflake; (f) STEM image of one PtCo nanotube and STEM-EDS mapping images (insets) of elements Pt, Co and O.

the presence of abundant worm-like one-dimensional nanotubes, which are ca. 60 nm in diameter and ca. 8 nm in wall thickness. It is interesting that these worm-like nanotubes have some nanoflakes on them (Fig. 1c). Both the high-resolution TEM images (HRTEM) of one nanotube (Fig. 1d) and one nanoflake (Fig. 1e) show well-defined lattice fringes, indicating that they have good crystalline structure. The

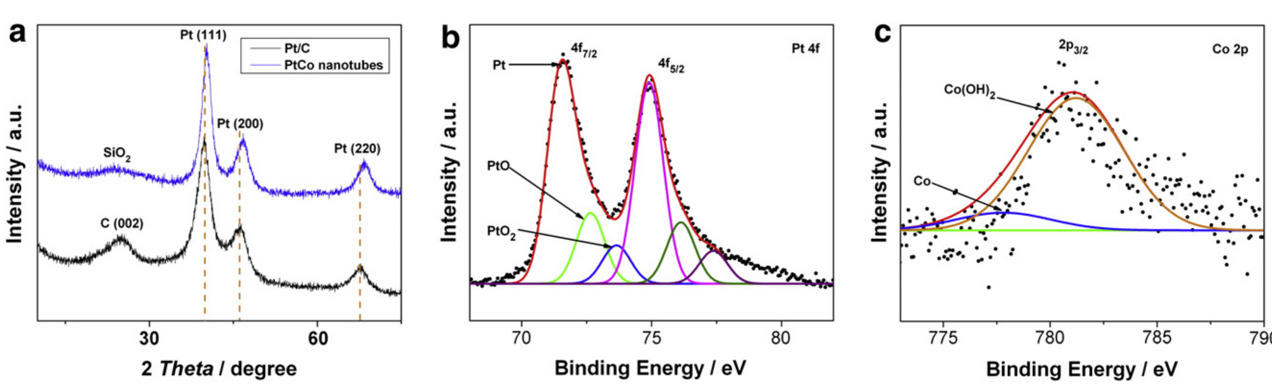

Fig. 2. (a) XRD patterns of Pt/C and PtCo nanotubes; XPS spectra of the (b) Pt 4f and (c) Co 2p of PtCo nanotubes.