



Full Length Article

Non-carbon titanium cobalt nitride nanotubes supported platinum catalyst with high activity and durability for methanol oxidation reaction



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ABSTRACT

Titanium cobalt nitride nanotubes (Ti_{0.95}Co_{0.05}N NTs) hybrid support, a novel robust non-carbon support material prepared by solvothermal and post-nitriding processes, is further decorated with Pt nanoparticles for the electrooxidation of methanol. The catalyst is characterized by X-ray diffraction (XRD), nitrogen adsorption/desorption, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and electrochemical measurements. The morphology, structure and composition of the synthesized Ti_{0.95}Co_{0.05}N NTs suggest that the nanotube wall is porous and consists of homogeneous cohesively attached nitrides nanocube particles. Notable, Ti_{0.95}Co_{0.05}N NTs supported Pt catalyst exhibits significantly improved catalytic activity and durability for methanol electrooxidation compared with the conventional JM Pt/C catalyst. The experimental data indicate that enhanced catalytic activity and stability of Pt/Ti_{0.95}Co_{0.05}N NTs towards methanol electrooxidation might be mainly attributed to the tubular nanostructures and synergistic effect introduced by the Co doping. Both of them are playing an important role in improving the activity and durability of the Ti_{0.95}Co_{0.05}N NTs catalyst.

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1. Introduction

Although direct methanol fuel cells (DMFCs) have received broad attention due to their virtually green emission, low operating temperatures, high energy conversion efficiency, and the simplicity of storing and transferring of liquid fuel, at the moment the restricted activity and stability of the catalysts used in DMFCs is a key constraint to the widespread commercialization and the power deployment [1–5]. In order to reduce the catalyst cost and enhance the catalytic activity, highly dispersed platinum (Pt) and its alloy nanoparticles with a evenly distribution on high surface area carbon supports have been made until now [3,6–11]. As a type of commonly used catalyst, Pt supported on carbon black (Pt/C) suffers from carbon-support corrosion, Pt nanoparticles (NPs) oxidation/dissolution, and Pt NPs aggregation under severe fuel cell operates conditions, which leads to activity and durability degradation of the catalysts [12–15]. The fuel cell typically operated at under almost steady-state conditions of less than 1.0 V, then during start-up and shut-down (start–stop) cycles, the local potential

can elevates to 1.5 V [16,17]. Under the above conditions, the degradation in electrocatalytic performance of the Pt/C catalyst is remarkably accelerated. Therefore, new strategies to design and fabricate efficient methanol oxidation reaction (MOR) catalysts with high activity and durability are still desirable.

The widely used strategies in those issues are substituting the carbon-support with novel non-carbon catalyst supports, transition metal nitrides (TMNs), exhibit high conductivity, corrosion resistant, electrochemical durability and strong metal–support interaction (SMSI), which have been explored as promising support for Pt NPs [1,18–28]. Various research groups have reported the application of TMNs with different nanostructures (nanoparticles, nanorods, films or nanotubes) as catalysts supports in fuel cell and energy storage applications [29–33]. Furthermore, Pt supported on bimetallic transition metal nitrides (BTMNs) as catalysts exhibit enhanced activity and stability towards MOR in comparison with the single transition metal nitride (TiN, Mo or NbN) supported Pt catalysts, which is probably due to the co-catalytic and electronic effects introduced by other metal doping [34,35]. Moreover, alloying Pt with a secondary transition metal, such as PtNi, PtCo, PtCu, PtFe and PtPd [36–43] have been explored extensively, and proven to be an effective way to improve the activity of the

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catalyst. The Pt based alloys not only minimizes the Pt use for catalysis, but also introduces the desirable Pt-M interactions to tune both electronic and strain effects, thus the performance can be greatly enhanced. However, the Pt alloy catalysts are suffered from poor durability in acidic and harsh oxidation conditions due to the transition metal leaching. In addition, it is necessary to explore alternative robust support to replace carbon support that is susceptible to corrosion. Among those studies, Pt supported on the single transition metal nitride nanotubes as catalyst in fuel cells has been reported, which exhibited better electrocatalytic activity and more excellent stability in comparison to the traditional Pt/C catalyst [22,30]. What is more, various researches depositing Pt nanoparticles on TMNs or BTMNs supports, but the available data on highly dispersed Pt NPs on BTMNs with hollow nanotube structures for catalytic applications is still lacking [16,26,44–47]. On the basis of above considerations, we are inspired to investigate the electrocatalytic activity of bimetallic titanium cobalt nitride nanotubes ($\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs) supported Pt catalyst toward methanol oxidation, since the introduction of cobalt element into titanium nitride might improve the electrocatalytic activity of supported Pt catalyst meanwhile the intrinsic electrochemical stability of the TiN nanostructures could be also preserved.

Herein, we use the non-carbon titanium cobalt nitride nanotubes hybrid material ($\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs) synthesized by an efficient method to support the Pt NPs. The $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs exhibit large surface area and hollow structure. For comparison, TiN NTs are also synthesized and tested. Compared with Pt/TiN NTs and commercial JM Pt/C (20 wt% Pt on Vulcan XC-72R) catalysts, Pt/ $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs exhibit not only higher electrocatalytic activity for MOR, but also better long-term durability and more excellent CO tolerance, verifying the $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs are indeed a promising

non-carbon support to enhance Pt electrocatalytic performance for applications in commercialization of DMFCs.

2. Experimental

2.1. Synthesis of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs and TiN NTs

$\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs was prepared by the classic solvothermal and post-nitriding method. First, TiCoO_2 NTs were synthesized by a solvothermal route without any structure-directing agent. Briefly, 2 g TiOSO_4 and 0.192 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursors, that the molar ratio of Ti:Co was 19:1, were dissolved in a mixture solution composed of absolute ethanol (26 mL), ethylene glycol (13 mL) and ethyl ether (13 mL) with vigorous stirring for 30 min. A mixed solution was formed, the mixture was transferred into an autoclave and kept in 110 °C for 24 h. Next the precipitate was filtered, washed with ethanol solution several times, dried at 80 °C in a drying oven for 12 h, and then calcined at 400 °C for 4 h. Finally, the powder was nitrided in a furnace at 750 °C in the presence of NH_3 gas flow (100 sccm) for 2 h, and then the powder was cooled to room temperature under the protection of an argon gas flow. The sample was labeled as $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs. The TiN NTs was prepared following the same processes as $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs but the only difference was that $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was not added to the precursor.

2.2. Synthesis of catalysts

The Pt loading of Pt/ $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs and Pt/TiN NTs catalysts was controlled at 20 wt%. At great length, 80 mg of non-carbon support and 60 mg of sodium citrate were dispersed in 30 mL of

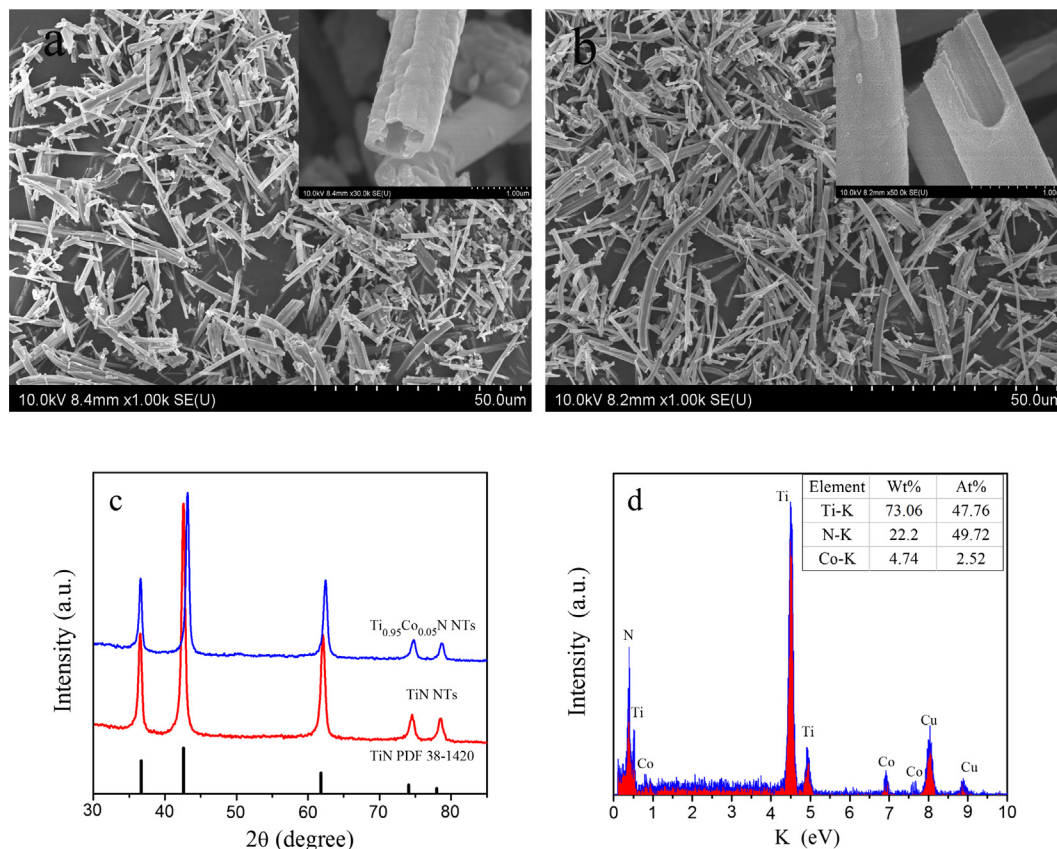


Fig. 1. The SEM images of (a) TiN NTs and (b) $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs and the insets are the typical enlarged SEM images, respectively; (c) XRD patterns of as-prepared TiN and $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs and (d) EDS profile of $\text{Ti}_{0.95}\text{Co}_{0.05}\text{N}$ NTs.

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