



# Platinum nanoparticles decorated robust binary transition metal nitride–carbon nanotubes hybrid as an efficient electrocatalyst for the methanol oxidation reaction



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## H I G H L I G H T S

- CNTs@TiCoN hybrid support with tunable composition was successfully synthesized.
- Pt nanoparticles with small size were well dispersed on CNTs@TiCoN support.
- CNTs@TiCoN combines high conductivity and superb corrosion resistance.
- The catalyst shows remarkably enhanced methanol oxidation activity and durability.

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## A B S T R A C T

Titanium cobalt nitride (TiCoN)–CNTs hybrid support is prepared by a facile and efficient method, including a one-pot solvothermal process followed by a nitriding process, and this hybrid support is further decorated with Pt nanoparticles to catalyze the oxidation of methanol. The catalyst is characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and electrochemical measurements. Notably, Pt/CNTs@TiCoN catalyst exhibits a much higher mass activity and durability than that of the conventional Pt/C (JM) for methanol oxidation. The experimental data indicates that the CNTs@TiCoN hybrid support combines the merits of the CNTs's high conductivity and the superb corrosion resistance of external TiCoN coating.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) have attracted much attention because of their high power density, low operating temperature, and reduced pollution as a new power source for portable electronic devices and automobiles [1–6]. Moreover, liquid methanol can be safely and inexpensively stored and transported, as compared with the gaseous hydrogen used for the proton exchange membrane fuel cells (PEMFCs). Thus, not surprisingly, DMFCs are suitable for a large scope of power applications [5,7,8]. However, to make PEMFCs economically viable, one of the main problems to be

solved is finding catalysts with sufficient activity and stability for the methanol oxidation reaction (MOR). Up to now, platinum (Pt) based catalysts are still the most effective for PEMFCs [9]. However, the Pt catalysts are severely poisoned by carbonaceous intermediates generated during the MOR process [10]. Furthermore, carbon black is still the most widely used catalyst support for noble materials in DMFCs. Unfortunately, it has been argued that the loss of performance for Pt/C catalyst is mainly ascribed to the corrosion of carbon supports, which further results in migration, aggregation, and Ostwald ripening of Pt NPs [11–19]. Therefore, the design and synthesis of highly active MOR catalysts with strong durability is extremely desirable.

The introduction of novel support materials with co-catalytic functionality has proven to be a very effective approach for improving both the catalytic activity and the durability of Pt-based

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catalysts for MOR [20–23]. Transition metal nitrides (TMNs) are definitely suited to support noble metals in DMFCs because of their excellent electrical conductivity, thermal stability, exceptional hardness, corrosion resistance, and electrochemical durability in a wide range potential under fuel cell operations [23–31]. Pt or Pd supported on CrN [32] and TiN [29,31,33–35] as electrocatalyst in DMFCs has been reported, which showed higher performance and better stability than that of commercial Pt/C catalyst. In particular, bimetallic transition metal nitrides (BTMNs) demonstrate good synergistic effect with Pt on catalysis towards MOR activities. DiSalvo et al. reported  $\text{Ti}_{0.5}\text{Cr}_{0.5}\text{N}$  supported PdAg catalyst outperformed commercial Pt/C catalyst in terms of MOR activity while exhibiting high durability [36]. Recently, through the combination of solvothermal and post-nitriding process, we developed a Pt/TiMoN hybrid material, which shows much higher MOR performance and durability than that of Pt/TiN and commercial Pt/C catalyst in acid solutions [21].

A significant advance of the BTMNs supported Pt catalysts was that the hybrid materials exhibit excellent stability due to the strong metal support interactions (SMSI) instead of the weak interactions between the carbon black and the Pt NPs. However, a drawback is that the discontinuity caused by the existence of defects and abundant grain boundaries of nanoparticles could lower its electronic conductivity and make the electron transport inefficient. Thus, catalytic performance of the catalysts was weakened. We assume that the combination of BTMN NPs and few-walled carbon nanotubes (CNTs) could overcome this issue as the hybrid materials with a BTMN shell and CNTs core are expected to offer many advantages, such as: i) combination of the robust BTMNs with good synergistic effect and the high conductivity of CNTs, ii) creating an interactive porous three-dimensional (3D) structure and constructing a high conductive electron pathway, and iii) the avoidance of direct contact between CNTs and the electrolyte to protect the core CNTs from corrosion.

Herein, we report a facile method for the synthesis of titanium cobalt nitride/CNTs hybrid material (CNTs@TiCoN) as efficient support to anchor the Pt NPs. The resulting CNT@TiCoN supported Pt (Pt/CNTs@TiCoN) catalyst showed much higher MOR current density than our recently reported Pt/TiMoN and Pt/CNT@TiMoN prepared in the same method. This hybrid material affords a high potential for electrocatalyst support towards the MOR than did the carbon and BTMNs NPs.

## 2. Experimental procedures

### 2.1. Synthesis of CNT@TiCoN hybrid

All chemicals were purchased commercially (analytical grade, Aladdin, China) and were used without further purification. CNTs (10–80 nm in diameter and 30–100  $\mu\text{m}$  in length) were treated with concentrated  $\text{HNO}_3$  in an ultrasonic bath at 80 °C for 6 h for surface functionalization, then followed by filtration and thoroughly washing with deionized water. 50 mg pre-treated CNTs were dispersed in a solution containing 30 mL ethanol, 5 mL deionized water and 5 mL benzyl alcohol under ultrasonication and stirring, then a uniformly mixed solution composed of 15 mL ethanol, 0.2 mL tetrabutyl titanate ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ , TBOT) and appropriate amount of cobalt acetate tetrahydrate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) was dipped into the CNTs suspension drop by drop and continuously stirred for 2 h, and then the mixture was transferred to a Teflon-lined autoclave and kept at 150 °C for 3 h. The precipitate was cooled down to the room temperature, followed by filtering, washing thoroughly with deionized water, and then drying in air at 80 °C overnight, which was labeled as CNTs@TiCoO<sub>2</sub>. Finally, appropriate amount of the powder precursors was placed in the

tubular furnace, annealed at 800 °C under an  $\text{NH}_3$  gas flow (100 sccm) for 2 h with a progressive heating rate (room temperature to 800 °C, 5 °C  $\text{min}^{-1}$ ), and the sample was labeled as CNTs@TiCoN. For comparison, CNTs@TiMoN was synthesized with the same process without the addition of  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , instead of  $\text{MoCl}_5$ , and the atomic ratio of Ti/M (Co or Mo) was maintained at 4:1 for both CNTs@TiCoN and CNTs@TiMoN.

### 2.2. Preparation of Pt/CNTs@TiCoN and Pt/CNTs@TiMoN

CNTs@TiCoN and CNTs@TiMoN supported Pt catalysts were synthesized by the ethylene glycol (EG) reduction method, labeled as Pt/CNTs@TiCoN and Pt/CNTs@TiMoN, respectively, and the total Pt content was controlled ca. 20 wt%. Briefly, 80 mg of the support, 60 mg of sodium citrate and 1.35 mL of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution (40 mg  $\text{mL}^{-1}$ ) were mixed with 30 mL of EG, followed by vigorous stirring and ultrasonic for 30 min. Then the mixture was transferred to a flask and heated at 160 °C for 3 h. Subsequently, the suspension was filtered and washed thoroughly with deionized water, and then dried at 60 °C in a vacuum drying oven overnight. The commercial Johnson Matthey Pt/C (JM Pt/C, 3.3 nm on Vulcan XC-72R carbon, 20 wt%) was used for comparison in this work.

### 2.3. Materials characterization

X-ray diffraction (XRD) was operated on a Rigaku-Ultima III X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) in the Bragg angle ranging from 20° to 86°. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed with a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high-resolution Transmission electron microscopy (HR-TEM) images were acquired with a JEOL 2100 microscope. X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra DLD X-ray photoelectron spectrometer employing a monochromated Al-K $\alpha$  X-ray source ( $h\nu = 1486.6 \text{ eV}$ ). The precise Pt loading was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES, Leeman PROFILE SPEC) measurements.

### 2.4. Electrode preparation

All electrochemical experiments were carried out on an Autolab electrochemical workstation (Model PGSTAT302N, Metrohm) at room temperature ( $25 \pm 1 \text{ }^\circ\text{C}$ ), using a three-electrode electrochemical cell. The cell consisted of a glassy carbon working electrode (GC electrode, 5 mm inner diameter, 0.196  $\text{cm}^2$ ), a platinum foil counter electrode and an Ag/AgCl (3 M NaCl) reference electrode. In this study, all potentials are referenced with respect to Ag/AgCl electrode. A thin film of the electrocatalyst was prepared as follows: 5 mg catalyst was dispersed ultrasonically in 1 mL ethanol for 30 min in ice water bath to form a uniform catalyst ink (1 mg Pt  $\text{mL}^{-1}$ ). A total of 5  $\mu\text{L}$  of well-dispersed catalyst ink was spread onto the pre-polished GC electrode. After drying at room temperature, the electrode was then covered by a drop of Nafion solution (0.1 wt % in ethanol solution) and dried in air before measurements. The loading amount of Pt for Pt/C, Pt/CNTs, Pt/TiCoN, Pt/CNTs@TiMoN and Pt/CNTs@TiMoN were controlled at 25  $\mu\text{g cm}^{-2}$  normalized to the geometric electrode area, and the actual loadings are confirmed by ICP-OES.

Cyclic Voltammetry (CV) performance of the catalysts was carried out in  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution in the potential range from 0 to 1 V at a scan rate of 50  $\text{mV s}^{-1}$ . Before the ORR activity test, all of the electrodes were pretreated by cycling the potential between 0 and 1.2 V at a sweep rate of 50  $\text{mV s}^{-1}$  for 20 cycles so as to remove any surface contamination. The

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