



Short Communication

A novel co-precipitation method for preparation of Pt-CeO₂ composites on multi-walled carbon nanotubes for direct methanol fuel cells

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ABSTRACT

Ceria (CeO₂) as co-catalytic material with Pt on multi-walled carbon nanotubes (Pt-CeO₂/MWCNT) is synthesized by a co-precipitation method. The physicochemical characterizations of the catalysts are carried out by using transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) techniques. Electrocatalytic activities of the catalysts for methanol oxidation is examined by cyclic voltammetry and chronoamperometry techniques and it is found that Pt-CeO₂/MWCNT catalysts exhibited a better activity and stability than did the unmodified Pt/MWCNT catalyst. CO-stripping results indicate the facile removal of intermediate poisoning species CO in the presence of CeO₂, which is helpful for CO and methanol electro-oxidation.

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1. Introduction

Cerium oxide is widely used as a support for many oxidation catalysts. These catalysts are active in oxidation of CO [1], elimination of CO and NO_x contaminants from automotive exhaust gases [2], water-gas shift reactions [3], combustion of hydrocarbons [4], etc. The industrial applications of CeO₂ as a catalyst support are due to its high oxygen transport and storage capacities [5]. Several authors have reported different kinds of interaction between noble metals and ceria and their effects on catalytic activities [6–13]. These studies have shown that the nature and extent of interaction depend on particular noble metal, catalyst pretreatment, preparation technique, size of CeO₂ crystallite, lattice oxygen, and so on. The promoting effect of CeO₂ was attributed by authors [14,15] to the strong Pt²⁺-CeO₂ interaction creating the Ce_{1-x}Pt_xO_{2-δ} species responsible for the higher catalytic activity. In short, noble metal (NM)/ceria-based catalysts exhibit strong metal-support interaction effects to give high activity for hydrogenation reactions, water-gas shift reactions, CO and hydrocarbon oxidation, etc. So the insertion of Pt into the mesoporous CeO₂ oxides or encapsulated metal in ceria is the most important. Traditional supported metal catalysts are comprised of small metal particles dispersed on the surface of an oxide support.

It is known that Ce³⁺ will be oxidized to form Ce⁴⁺ hydroxyl species in the presence of cationic surfactants under alkaline environments and O₂ [16]. This oxidation is coupled with reduction of Pt⁴⁺ to Pt⁰. A similar redox co-precipitation of Ce³⁺ and Pt⁴⁺ in NaOH solution was previously reported such that Pt⁰ can be obtained without H₂ pre-reduction [17,18], where cerium(III) nitrate is used as the metal oxide precursor and as the reducing agent, converting any Pt⁴⁺ in its immediate vicinity to Pt⁰, while itself being oxidised to Ce⁴⁺. The small Pt⁰ particles formed are left embedded in the CeO₂ that is formed. In summary, Pt ions should have been reduced by Ce³⁺ during the co-precipitation step of Pt-Ce preparation through the following redox reaction: Pt⁴⁺ + 4Ce³⁺ → Pt + 4Ce⁴⁺. As a result, the reduced Pt crystallites should have been finely dispersed and adhered to ceria particles deposited on carbon support.

On the other hand, Pt and Pt-based electro-catalysts should be supported on carbon surface in practice, and supported electro-catalysts show a higher electrocatalytic activity and utilization efficiency than unsupported ones because of their large surface area on the supports [19]. Carbon nanotubes (CNTs), as a new form of carbon, have been considered as new supports for metal catalysts due to their small size, high chemical stability and large surface area to volume ratio [20,21]. If the Pt-ceria nanoparticles are supported on the carbon nanotube surface, the electrocatalytic performance and utilization efficiency could be further improved. Therefore, herein we synthesized carbon nanotube supported Pt-ceria composite electro-catalysts by a co-precipitation method in aqueous solution. The electrocatalytic activity of Pt-ceria/MWCNT composites for methanol oxidation was also investigated in detail.

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2. Experimental

2.1. Preparation of Pt-CeO₂/MWCNT composites

Multi-walled carbon nanotubes (MWCNTs) were obtained from Chemical Engineering Department, Tsinghua University. The MWCNTs were treated by boiling the as-received MWCNTs in HNO₃ for 3 h, rinsed with copious water, dried and ground. For Pt-ceria catalysts supported on multi-walled carbon nanotubes (MWCNTs), the preparation procedures are as follows: 40 mg MWCNTs were dispersed into 20 mL distilled water and agitated with a magnetic agitator. Then, the Pt precursor salt solution with ceria was prepared by dissolving appropriate of H₂PtCl₆ and 40 mg cerium (III) nitrate into 100 mL of DI water. The aqueous solution of Pt precursor with ceria was added drop wise to the MWCNT solution. A solution of $1 \times 10^{-3} \text{ mol L}^{-1}$ KOH was added into the reaction mixture until the pH value reaches 9. Then, the reaction mixture was allowed to age for 6 days with a constant stirring (the aging process is essential to form metal encapsulation in ceria). After the ageing step, the reaction mixture was centrifuged to collect the product. The product was washed with ethanol and DI water. Finally, the solid product obtained was dried in air for overnight and then the powder was calcined at 400 °C for 1 h to obtain 10 wt% Pt-CeO₂/MWCNT nanoparticles. For comparison, Pt/MWCNT catalysts with the same contents of Pt were obtained directly by reducing the Pt precursors in a carbon nanotube suspension using the drop wise addition of NaBH₄ at room temperature with stirring.

2.2. Measurement

Electrochemical reactivity of the catalysts was measured by cyclic voltammetry (CV) using a three-electrode cell at the Solartron electrochemical workstation (Solartron 1287BZ). The working electrode was a gold plate covered with a thin layer of Nafion-impregnated catalyst. As a typical process, about 1 mg catalyst sample was ultrasonically mixed with Nafion EG solution to form homogeneous ink which was cast on the gold plate. Pt gauze and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials in this report are quoted versus SCE. CV test was conducted at 50 mV s^{-1} in a solution of 1 M HClO₄ with and 1 M CH₃OH, potential ranging from -0.2 to 1.0 V. CO-stripping experiments were performed as follows: after purging the solution with N₂ gas for 20 min, gaseous CO was bubbled for 20 min to allow adsorption of CO onto the electro-catalysts while maintaining a constant voltage of 0.1 V versus SCE. Excess CO dissolved in solution was purged out with N₂ for 20 min and CO-stripping voltammetry was recorded in 1 M HClO₄ solution at a scan rate of 10 mV s^{-1} . The electrochemical measurements were conducted under 25 °C.

The morphology of Pt-CeO₂/MWCNT composites was investigated using transmission electron microscopy (TEM, JEOL model JEM-1200EX). The X-ray diffraction (XRD) analysis was performed using the Rigaku X-ray diffractometer with Cu K_α radiation source. The 2θ angular regions between 20° and 90° were explored at a scan rate of 6° min^{-1} with step of 0.02° .

3. Results and discussion

3.1. TEM analysis of Pt-CeO₂/MWCNT composites

Fig. 1 shows a high resolution TEM image and EDS spectrum of the nanoparticles decorated MWCNTs. The HRTEM shows that Pt and CeO₂ grow on the out surface of MWCNTs, the distance

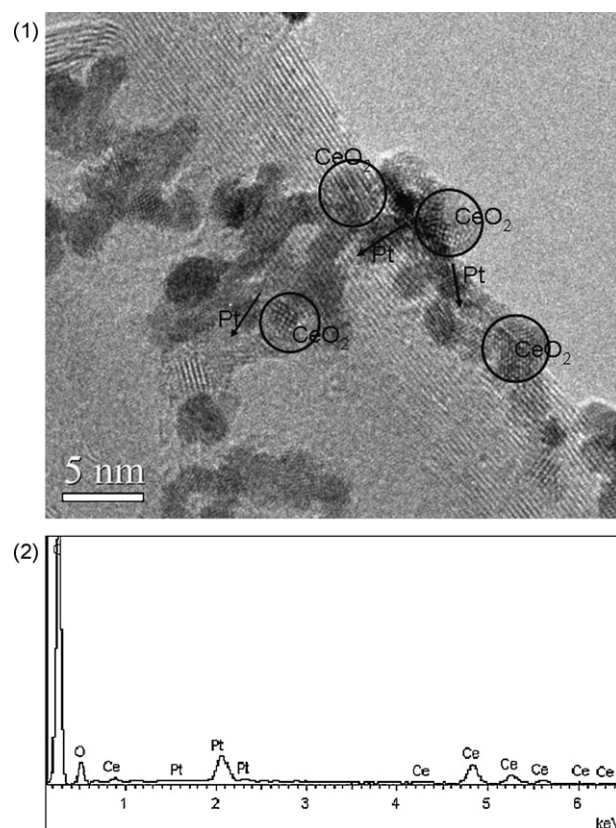


Fig. 1. The HRTEM analysis of the MWCNTs decorated with nanoparticles and EDS analysis of the nanoparticles decorated on MWCNTs.

of the crystal planes of the nanoparticle was determined to be 0.302 nm, consistent with that of the (1 1 1) plane of CeO₂. It can also be found that Pt and CeO₂ nanoparticles were closely adjacent to each other. The diameter of the Pt or CeO₂ nanoparticles is about 3–6 nm, and has a mean value at 4 nm. Furthermore, the EDS analysis of the nanoparticles decorated on the surface of MWCNTs detected Pt, Ce, O and C. Combining the facts of the crystal plane formation and a large amount of Pt and Ce detected, it can be inferred that the nanoparticles mainly consist of Pt and CeO₂.

3.2. XRD analysis of Pt-CeO₂/MWCNT composites

The XRD pattern of Pt-CeO₂/MWCNT catalyst is shown in Fig. 2. The structure of the ceria was characterized by XRD and showed that ceria is a cubic crystallite, five diffraction peaks of CeO₂ at 28.6°, 33.1°, 47.5°, 56.3° and 79.2° were identified as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (4 2 0), respectively. The average crystallite size of CeO₂ was estimated from Scherrer's equation to be 4.2 nm. It is clear from the diffraction pattern of Pt-CeO₂/MWCNT catalyst in Fig. 2 that both crystalline Pt and CeO₂ phases coexist. There was no shift of the position of Pt diffraction peaks in the Pt-CeO₂/MWCNT catalyst, indicating that the addition of CeO₂ has no effect on the crystalline lattice of Pt. The average crystallite size of Pt was 3.4 nm for the Pt-CeO₂/MWCNT catalyst.

3.3. Electrochemical properties of Pt-CeO₂/MWCNT composites

The electrocatalytic activity of the Pt-CeO₂/MWCNT catalysts toward the oxidation of methanol was tested and the results were compared with those obtained on Pt/MWCNT catalysts. The measurements were carried out in a 1 M HClO₄ aqueous solution

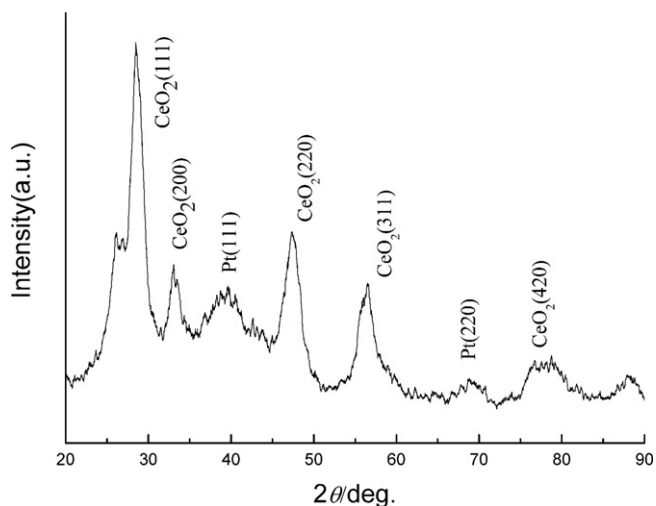
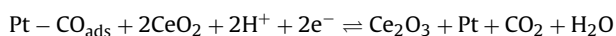
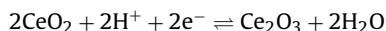


Fig. 2. XRD patterns of Pt-CeO₂/MWCNT composites.

containing 1.0 M methanol shown in Fig. 3. From Fig. 3 we can see that the methanol electro-oxidizing current is significantly increased and the onset potential of methanol electro-oxidation shifted to a lower value on Pt-CeO₂/MWCNT electrode than on Pt/MWCNT electrode. On the other hand, the H region area has no large difference, as can be seen from Fig. 3. Such a result indicates that the CeO₂ can promote the electro-oxidation of methanol on Pt with no influence on electrochemical active surface of Pt.

The enhancement of the oxidation as assisted by ceria can be described to happen by some possibilities [22]: chemical enhancement of the oxidation of the adsorbed CO as assisted by ceria as an oxidation catalyst/oxygen donor, or by the effect of ceria's altering the electrode's morphology, physically inhibiting the CO adsorption. A mechanism for ceria's proposed enhancement of oxidation can be described by the following reactions:



which assist on the weakening of the Pt-CO bond, thus reducing the CO poisoning effect and promoting the oxidation of methanol. A mechanism for ceria's proposed enhancement of oxidation can also be described by the bifunctional mechanism, the OH_{ads} species

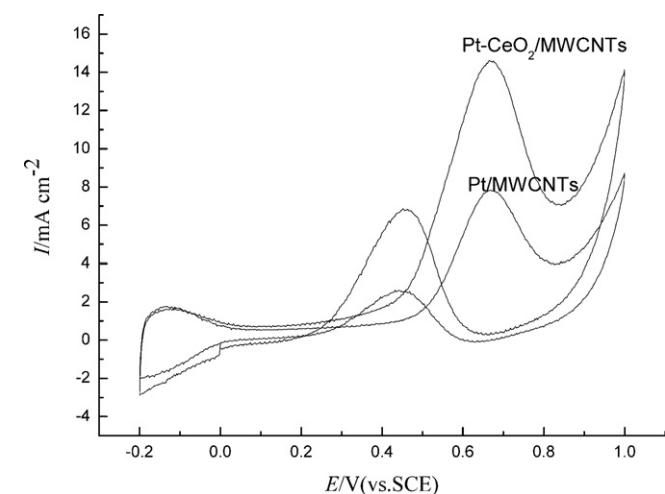


Fig. 3. Voltammetry curves for Pt-CeO₂/MWCNT and Pt/MWCNT catalysts in 1 M HClO₄ + 1 M CH₃OH solution with a scan rate of 50 mV s⁻¹.

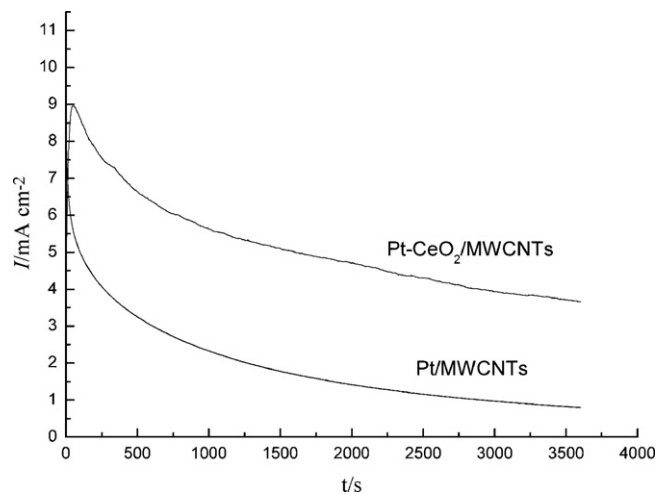
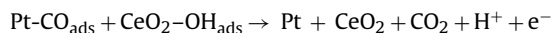


Fig. 4. Chronoamperometry test for Pt-CeO₂/MWCNT and Pt/MWCNT catalysts in 1 M HClO₄ containing 1 M methanol at 0.5 V.

on metal oxide can transform CO-like poisoning species (CO_{ads}) on Pt to CO₂, releasing the active sites on Pt for further electrochemical reaction [23–25].



The chronoamperometric technique is an effective method to evaluate the electrocatalytic activity and stability of electrode material. Fig. 4 shows typical current density–time responses for methanol oxidation measured at a fixed potential of 0.5 V (vs. SCE) of all catalyst electrodes in 1.0 M HClO₄ aqueous solution containing 1.0 M CH₃OH. As expected, the methanol oxidation current at Pt-CeO₂/MWCNT electrode was evidently higher than Pt alone electrode. The result indicates that the Pt-CeO₂/MWCNT catalyst has a higher activity than Pt/MWCNT catalyst. The methanol electro-oxidation current on Pt-CeO₂/MWCNT catalyst was greatly enhanced compared to Pt/MWCNT catalyst. Both the cyclic voltammetry and chronoamperometric data show that Pt-CeO₂/MWCNT catalysts are more effective for the methanol oxidation than Pt/MWCNT catalysts.

Since CO species are the main poisoning intermediate in electro-oxidation of methanol while employing platinum catalysts, a

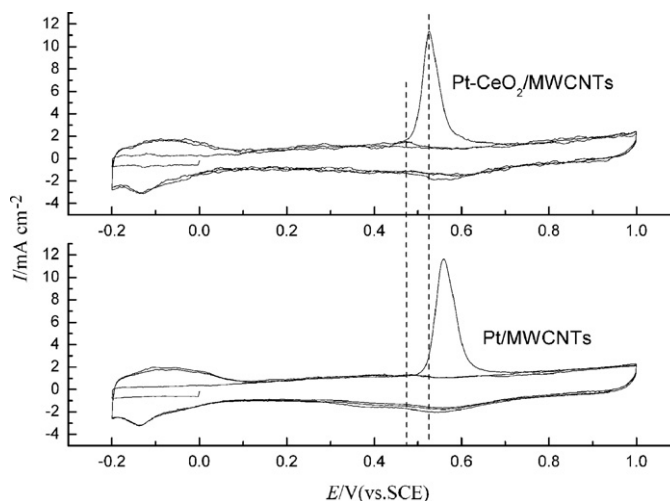


Fig. 5. CO-stripping curves for Pt-CeO₂/MWCNT and Pt/MWCNT catalysts in 1 M HClO₄ solution with a scan rate of 20 mV s⁻¹.

co-catalyst may assist the removal of the poisoning intermediate and thus offering excellent CO electro-oxidizing ability to the catalyst system, and this quality can also be studied by using CO-stripping tests. This information may help to analyze the mechanism behind the enhanced electro-catalyzing activity of Pt-CeO₂/MWCNT catalysts for methanol electro-oxidation. Fig. 5 presents the CO-stripping voltammograms of ceria free and ceria incorporated platinum supported on carbon nanotubes studied in this present investigation. The onset stripping potential and the peak maxima may directly reflect the CO oxidizing ability of the catalysts. It can be seen that in ceria incorporated platinum catalyst, the onset potential and peak maxima are shifted to lower potentials compared to ceria free Pt alone systems, as shown in Fig. 5.

4. Conclusions

In this study, Pt-CeO₂/MWCNT nanoparticles have been synthesized using a co-precipitation method. The XRD and TEM showed that the prepared catalysts had narrow particle size distribution. Compared with Pt/MWCNT, Pt-CeO₂/MWCNT exhibited higher catalytic activity for methanol electro-oxidation, and the corresponding CO-stripping potential and onset potential shifted to a lower value, indicating that CeO₂ can make CO electro-oxidation easier. The influence of ceria on platinum activity toward methanol oxidation may be due to both bifunctional as well as intrinsic mechanism. Pt-CeO₂ system appears to be a promising and less expensive methanol oxidation anode catalyst.

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