Short communication

Synthesis of Pt/Fe$_3$O$_4$–CeO$_2$ catalyst with improved electrocatalytic activity for methanol oxidation

Haiyi Sun [a,b], Jinmao You [b], Minghui Yang [a,*], Fengli Qu [b,*]

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China
[b] Shandong Provincial Key Laboratory of Life-organic Analysis, College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu Shandong 273165, China

ARTICLE INFO

ABSTRACT

A novel catalyst of Pt/Fe$_3$O$_4$–CeO$_2$ is prepared by anchoring Pt nanoparticles onto Fe$_3$O$_4$ coated cerium (CeO$_2$) surface. The catalyst is characterized by TEM and tested for methanol electrooxidation in acid solution. The results demonstrated enhanced catalytic performance of Pt/Fe$_3$O$_4$–CeO$_2$ toward methanol oxidation. The catalytic current of Pt/Fe$_3$O$_4$–CeO$_2$ towards methanol is about 4 times higher than that of Pt–CeO$_2$, indicating the introduction of Fe$_3$O$_4$ significantly improved the catalytic activity of the catalyst. The incaresed catalytic activity can be ascribed to the increased conductivity of the catalyst.

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1. Introduction

Direct methanol fuel cells, as a clean and sustainable power source have attracted great research interest during the past decades because of the ever increasing demand of energies [1–3]. In the development of improved fuel cells, a large amount of work is focused on the synthesis of novel catalyst with high electrocatalytic activity for methanol oxidation [4–6]. Considering of the CO poisoning issue, Pt based materials are still the most widely used catalyst. To enhance the performance of Pt based catalyst, Pt nanoparticles have been deposited onto a wide range of supporting matrix, such as TiO$_2$, carbon nanotube and polyaniline [7–9]. It is important to select an appropriate supporting matrix, which need be stable, cheap and could possibly enhance the electrocatalytic activity of Pt.

Recently, CeO$_2$ nanoparticle has found wide applications in different areas due to its low cost, high oxygen storage capability and high oxygen mobility [10–12]. CeO$_2$ has a Ce$^{3+/4+}$ redox cycle, however, due to its poor conductivity, it is necessary to modify the CeO$_2$ nanoparticle to increase its conductivity and subsequently the catalytic activity. Carrettin et al. synthesized the Au/CeO$_2$ hybrid nanostructure in aqueous solution and increased the activity of Au for CO oxidation by two orders of magnitudes [13]. Wang et al.

investigated the adsorption of Pt nanoparticles onto CeO$_2$ coated CNTs and the results indicated that CeO$_2$ can enhance the catalytic activity of Pt for methanol electro-oxidation [14].

In this work, we successfully prepared Pt/Fe$_3$O$_4$–CeO$_2$ catalyst through a simple method by depositing Pt nanoparticles onto Fe$_3$O$_4$ coated CeO$_2$ surface. The results indicate that the Pt/Fe$_3$O$_4$–CeO$_2$ catalyst exhibits improved catalytic activity, stability and anti-poisonous ability towards methanol oxidation.

2. Experimental

2.1. Reagents and apparatus

Ceria nanoparticles (10–20 nm) and H$_2$PtCl$_4$ were purchased from Sigma–Aldrich. Methanol was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All other reagents were of analytical grade and deionized water was used throughout the study.

All electrochemical measurements were performed on a CHI 650D electrochemical workstation (Shanghai CH Instruments Co., China). A conventional three-electrode system was used for all electrochemical measurements: a glassy carbon electrode (GC, 3 mm in diameter) as the working electrode, a saturated calomel electrode as the reference electrode, and a platinum wire electrode as the counter electrode. Transmission electron microscope (TEM) images were obtained from a JEOL JEM-2010 microscope (Japan).

* Corresponding authors. Tel.: +86 731 88836376; fax: +86 731 88836376.
E-mail addresses: yangminghui@csu.edu.cn, ymhhaohao@gmail.com (M. Yang), qflhn@126.com (F. Qu).
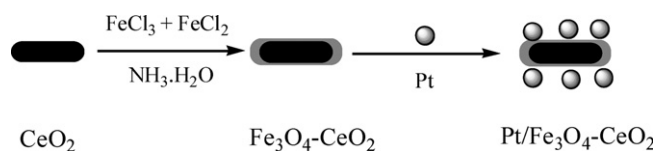
Scheme 1. Schematic representation for the preparation of Pt/Fe$_3$O$_4$–CeO$_2$.

2.2. Synthesis of Pt/Fe$_3$O$_4$–CeO$_2$

For the synthesis of Pt/Fe$_3$O$_4$–CeO$_2$, first, Fe$_3$O$_4$–CeO$_2$ was prepared. At room temperature, CeO$_2$ was dispersed into water to reach a concentration of $1\,mg\,mL^{-1}$. The solution was sonicated and purged with N$_2$ for 30 min. Then into 20 mL of CeO$_2$ solution, 216 mg of FeCl$_3$·6H$_2$O and 80 mg of FeCl$_2$·4H$_2$O was added, followed with the addition of 0.4 mL of high concentrated HCl. After sonication, and under vigorous stirring, 100 mL of 1 M NH$_3$·H$_2$O was slowly added into the solution. The mixture was stirred for another 30 min, and the Fe$_3$O$_4$–CeO$_2$ was separated by magnet and washed extensively. For the synthesis of Pt/Fe$_3$O$_4$–CeO$_2$, Fe$_3$O$_4$–CeO$_2$ was mixed with H$_2$PtCl$_4$ solution (1%, w/w) and H$_2$PtCl$_4$ was reduced to metal Pt with the addition of NaBH$_4$ (5%, w/w).

3. Results and discussions

Scheme 1 shows the schematic illustration for preparation of the Pt/Fe$_3$O$_4$–CeO$_2$ catalyst. CeO$_2$ was first coated with Fe$_3$O$_4$ and then Pt nanoparticles were deposited onto Fe$_3$O$_4$–CeO$_2$ surface. The synthesized Pt/Fe$_3$O$_4$–CeO$_2$ catalyst was first characterized by TEM. Fig. 1 shows the TEM images of the Fe$_3$O$_4$–CeO$_2$ and Pt/Fe$_3$O$_4$–CeO$_2$ nanostructures. It can be seen from Fig. 1A that CeO$_2$ shows a cubic structure with the size around 20 nm. The CeO$_2$ are surrounded by the synthesized Fe$_3$O$_4$, which displays amorphous structure. With the further deposition of Pt onto Fe$_3$O$_4$–CeO$_2$, it can be seen that Pt nanoparticles, appears as black dot, with the size around 5–10 nm, are deposited on the periphery interface of Fe$_3$O$_4$ and CeO$_2$ (Fig. 1B). Fig. 1C displays the detailed structure of Pt/Fe$_3$O$_4$–CeO$_2$, in which the Fe$_3$O$_4$ are adsorbed onto the periphery of CeO$_2$, and Pt nanoparticles are mainly deposited onto Fe$_3$O$_4$ surface. The percentage of Pt in the catalyst is about 29%.

Fig. 2A shows the cyclic voltammetry (CV) curves of CeO$_2$, Pt–CeO$_2$ and Pt/Fe$_3$O$_4$–CeO$_2$ modified electrodes in 0.5 M H$_2$SO$_4$. It is observed that for CeO$_2$ modified electrode, no current peaks were observed (curve a). For Pt–CeO$_2$ modified electrode, small current peaks were observed above 0.4 V, which can be ascribed to the platinum oxide formation/reduction at the potential range (curve b). Compared to Pt–CeO$_2$, Pt/Fe$_3$O$_4$–CeO$_2$ modified electrode displays more obvious reduction peaks at around 0.55 V and oxidation peaks above 0.6 V, characteristic of Pt based material (curve c) [15,16]. From the above data, it suggests that the coating of Fe$_3$O$_4$ onto CeO$_2$ increased the electroactivity of the Pt nanoparticles.

Fig. 2B shows the CV curves for methanol electro-oxidation in 0.5 M H$_2$SO$_4$ containing 1 M methanol at the scan rate of $100\,mV\,s^{-1}$. Different materials for the oxidation of methanol were investigated in detail. For CeO$_2$ or Fe$_3$O$_4$ modified electrode, there is no current peaks, indicating CeO$_2$ and Fe$_3$O$_4$ have no electro-catalytic activity towards methanol oxidation (curve a and b). For Pt–CeO$_2$ and Pt–Fe$_3$O$_4$ modified electrode, two oxidation peaks appeared at around 0.4 and 0.65 V (curves c and d). However, the catalytic activity of Pt–CeO$_2$ and Pt–Fe$_3$O$_4$ toward methanol oxidation is still rather low. On the contrary, Pt/Fe$_3$O$_4$–CeO$_2$ displays two sharp oxidation peaks (curve e). In the forward scan, the catalytic current of Pt/Fe$_3$O$_4$–CeO$_2$ is about 4 times higher than that of Pt–CeO$_2$. In addition, for both of the catalyst of Pt–CeO$_2$ and Pt/Fe$_3$O$_4$–CeO$_2$, there is no obvious change of the onset of the potential for the oxidation of methanol, indicating the
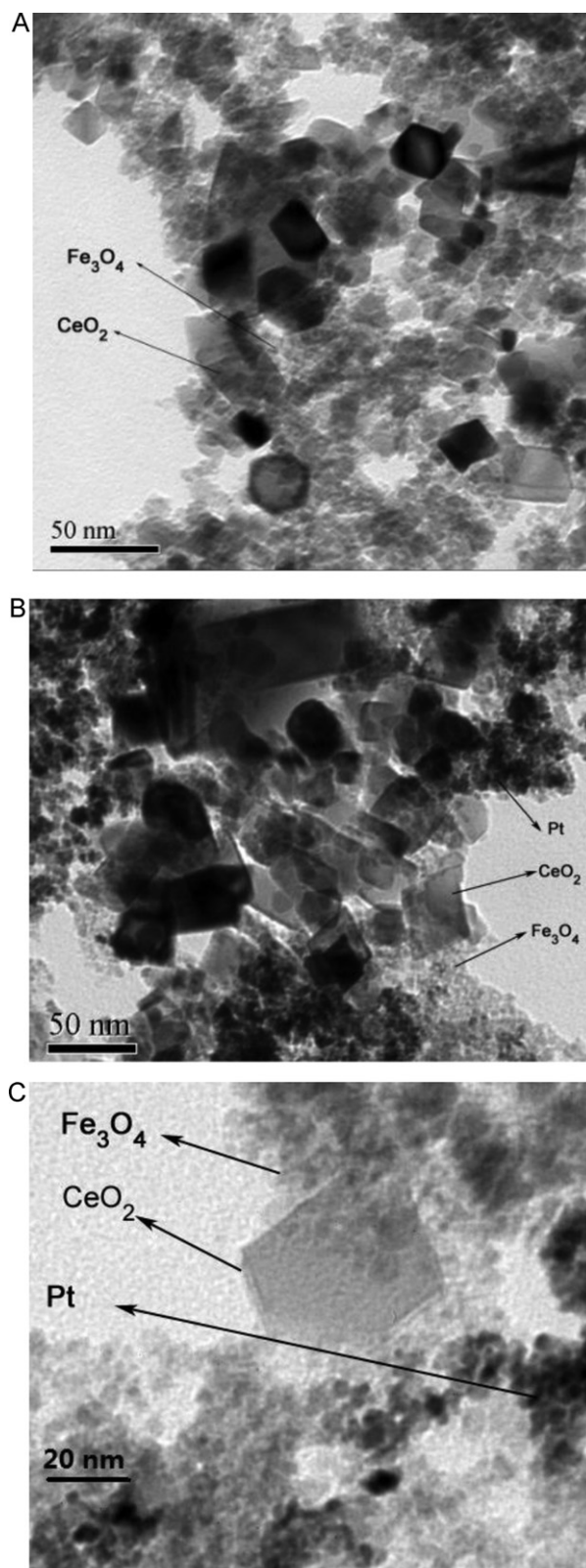

Fig. 1. TEM images of (A) Pt–CeO$_2$ and (B and C) Pt/Fe$_3$O$_4$–CeO$_2$.

introduction of Fe$_3$O$_4$ did not change the electron transfer process of methanol at the electrode surface. The increased catalytic activity of Pt/Fe$_3$O$_4$–CeO$_2$ can be ascribed to the improvement in electron conductivity of the catalyst after being coated by Fe$_3$O$_4$. With the immobilization of Pt and Fe$_3$O$_4$ onto CeO$_2$ surface, it conductivity
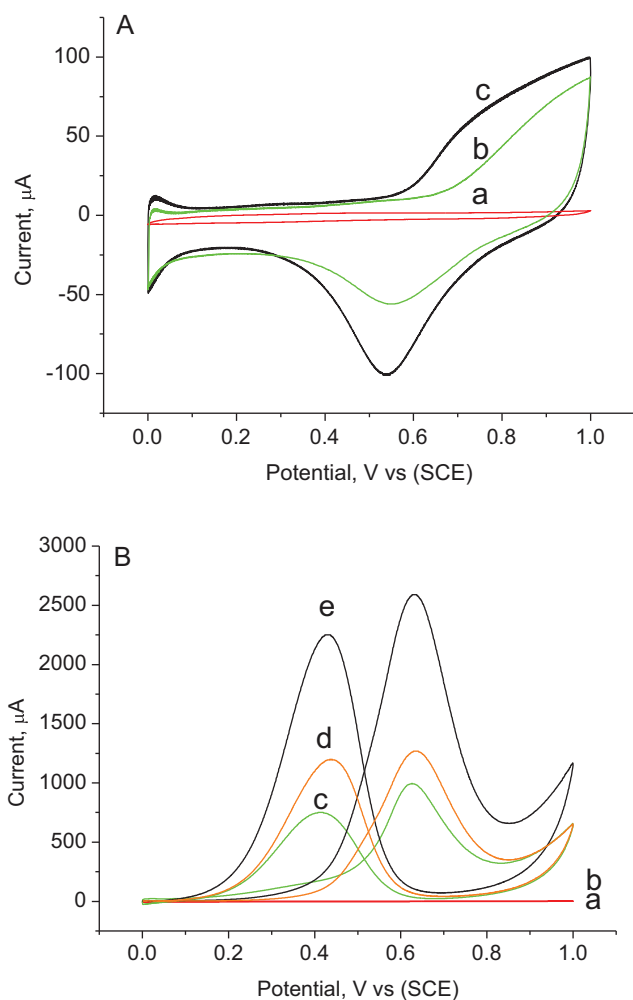
Fig. 2. (A) Cyclic voltammetry (CV) of (a) CeO$_2$, (b) Pt–CeO$_2$ and (c) Pt/Fe$_3$O$_4$–CeO$_2$ modified electrode in0.5 M H$_2$SO$_4$. (B) CV of (a) CeO$_2$, (b) Fe$_3$O$_4$, (c) Pt–CeO$_2$, (d) Pt–Fe$_3$O$_4$ and (e) Pt/Fe$_3$O$_4$–CeO$_2$ modified electrode in 0.5 M H$_2$SO$_4$ containing 1 M methanol.

Fig. 3. Electrochemical stability of the Pt/Fe$_3$O$_4$–CeO$_2$ catalyst for methanol oxidation. (A) The forward scan peak current as a function of scan numbers for 100 continued scans in 0.5 M H$_2$SO$_4$ containing 1 M methanol. (B) The first (a) and the last (b) CV curves of the 100 continued scans of the Pt/Fe$_3$O$_4$–CeO$_2$ catalyst in 0.5 M H$_2$SO$_4$ containing 1 M methanol.

was substantially increased, and as a result the electron transfer of methanol at Pt/Fe$_3$O$_4$–CeO$_2$ was greatly facilitated. The mass activity of the Pt/Fe$_3$O$_4$–CeO$_2$ catalyst toward methanol oxidation is 3.5 A mg Pt^{-1}, which is much higher than literature reported PtRu/C catalyst (about 0.6 A mg Pt^{-1}) [17].

To evaluate if a catalyst is suitable for methanol based fuel cell, one important issue is its resistance to poisoning. For Pt based catalyst, it is extremely susceptible to poisons such as CO-like species, which result in a dramatic decrease of the catalytic activity. In methanol electro-oxidation, the anodic peak current during the reverse scan (I_b) is for the removal of intermediate CO-like compounds produced during the forward scan (I_f). So, the ratio of two anodic current, I_f/I_b, is an important parameter to evaluate catalyst susceptibility to poisoning [17]. Low I_f/I_b ratio indicates poor oxidation of methanol to carbon dioxide during the forward scan and excessive accumulation of carbonaceous residues on the catalyst surface, which leads to catalyst poisoning. High I_f/I_b ratio indicates the other side. In this study, this ratio for Pt/Fe$_3$O$_4$–CeO$_2$ is 1.32, which is higher than that of Pt–CeO$_2$ in this work (1.20), some PtRu/C based catalyst (0.95 and 1.06) [17], commercial Pt/C (0.77) [18] and platinum-decorated nanoporous gold Leaf (1.23) [19]. These data indicates good anti-poisoning ability of Pt/Fe$_3$O$_4$–CeO$_2$.

The electrochemical stability of the Pt/Fe$_3$O$_4$–CeO$_2$ catalyst for methanol oxidation was also investigated by continued CV scans

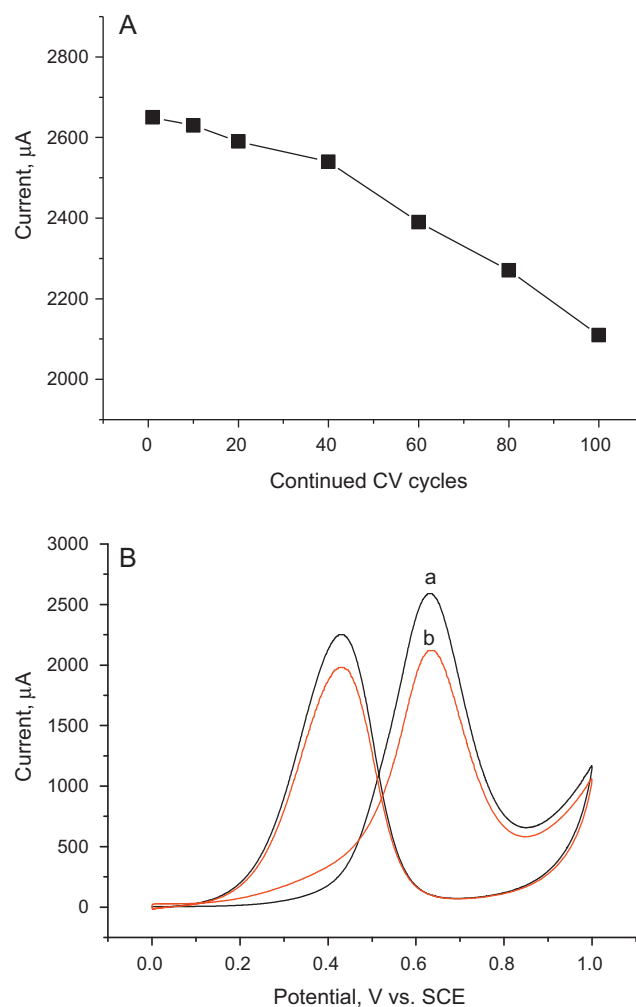in methanol solution. The forward scan peak current decreased continually with the successive CV cycles, and lost about 20% of it activity after 100 cycles (Fig. 3A), compared to almost 35% loss of activity for Pt–CeO$_2$. Fig. 3B shows the first (curve a) and the last (curve b) CV curves of the 100 cycles of Pt/Fe$_3$O$_4$–CeO$_2$ in methanol solution. It can be seen the I_f/I_b value also decrease with successive scans, indicating partial poisoning of the catalyst. After 100 cycles, the I_f/I_b value decreased to 1.08. The decreased catalytic activity has been reported by other groups [17], which can be ascribed to the poisoning of the catalyst and dissolution of Pt/Fe$_3$O$_4$–CeO$_2$ in acid solution.

4. Conclusions

In conclusion, we have reported a simple method to prepare Pt/Fe$_3$O$_4$–CeO$_2$ catalyst by anchoring the Pt nanoparticles on CeO$_2$ that coated with Fe$_3$O$_4$. The catalyst was tested for the electro-oxidation of methanol in acid solution and the results shows enhanced catalytic performance of Pt/Fe$_3$O$_4$–CeO$_2$ for methanol due to increased conductivity of the catalyst. The Pt/Fe$_3$O$_4$–CeO$_2$ catalyst presented in this paper shows great potential as cost effective electrocatalyst in direct methanol fuel cells.

Acknowledgements

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