

Substitute of Expensive Pt with Improved Electrocatalytic Performance and Higher Resistance to CO Poisoning for Methanol Oxidation: the Case of Synergistic Pt-Co₃O₄ Nanocomposite

Hongxiao Zhao^{1,*}, Zhi Zheng^{1,*}, Jing Li¹, Huimin Jia¹, Ka-wai Wong², Yidong Zhang¹, Woon Ming Lau²

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Abstract: In this paper, Pt-Co₃O₄ nanocomposite was synthesized by a sol-gel process combined with electrodeposition method. Its electrocatalytic activity towards methanol oxidation was investigated at room temperature using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and current density-time curve. It is found that the resultant Pt-Co₃O₄ catalysts with minute amount of Pt exhibit attractive electrocatalytic activity for methanol oxidation reaction (MOR) but with a high resistance CO poisoning due to the synergistic effects from Pt and Co₃O₄. Together with the low manufacturing cost of Co₃O₄, the reported nanostructured Pt-Co₃O₄ catalyst is expected to be a promising electrode material for direct methanol fuel cells (DMFC).

Keywords: Pt-Co₃O₄ nanocomposite; MOR; Electrocatalytic activity

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Introduction

Methanol oxidation reaction (MOR) has attracted extensive interest due to its potential application in direct methanol fuel cells (DMFCs) [1-2], which are promising systems for portable and residential power applications. However, the technically critical drawbacks of DMFC are the low catalytic activity and efficiency in methanol electro-oxidation, and severe poisoning of the anode by intermediates, in particular CO. Thus, an electrocatalyst for MOR with a higher activity at room temperature is imperatively needed to enhance DMFC's performance for commercial applications [3]. Tremendous research has been made towards different

electrocatalysts for MOR in recent years [4-7], especially those on Pt-base electrocatalysts. It is well known that Pt-containing electrocatalyst has two main disadvantages of (i) high material cost, and (ii) severe poisoning by the intermediates or CO-like species. Some metals, such as palladium and osmium [8-11], have been proposed as alternatives. However, they are also precious metals and use of them does not help reduce the manufacturing cost. On the other hand, the activity of the electrocatalyst other than noble metal is generally lower than that of the Pt-based catalysts [12]. Therefore, Pt-based catalysts still remain as the most optimal electrocatalysts for MOR [13-14]. Recently, promising results have been achieved by blending Pt with metal

¹Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, Xuchang University, Henan 461000 China

²Chengdu Green Energy and Green Manufacturing R&D Center, Sichuan 610207 China

*Corresponding author. E-mail: zhaoxiao124@126.com

oxides such as CeO_2 and MnO_2 . For example, Takahashi et al [15] found that the electrocatalytic activity of Pt- CeO_2 /carbon black (CB) for MOR and its performance as anode was superior to commercially available Pt-Ru/C materials. Yang et al [16] found that Pt nanoparticles on Mn_3O_4 -modified MWCNTs showed excellent electrocatalytic properties and excellent stability toward MOR, implying that metal oxides can play a key role in enhancing MOR.

Among various metal oxides, Co_3O_4 was considered as the most active catalyst for CO oxidation [17-19]. Therefore, addition of Co_3O_4 into the Pt-based electrodes is expected to be able to improve the catalytic performance by effectively reducing the amount of CO as a poisoning species. Recently, Xu et al [20] observed that Co_3O_4 promoted electro-oxidation reactions of methanol, ethanol, ethylene glycol and glycerol on Pd/C in alkaline media. However, a substantial amount of noble metal was still required. In this paper, Pt- Co_3O_4 nanocomposites with a low Pt content are obtained by a two-step method. The resultant nanocomposite as the catalyst for MOR as well as their electrochemical performance, chemical composition, crystallinity and morphology are evaluated by electrochemical technique, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses. Electrocatalytic activities of electrodes based on such Pt- Co_3O_4 nanocomposites for methanol electro-oxidation are investigated by CV, EIS and current density-time experiments. It is observed that the prepared Pt- Co_3O_4 nanocomposites exhibited excellent electrocatalytic activities towards MOR.

Experimental

Synthesis of Co_3O_4 nanoparticles

All solutions were prepared by using analytical grade chemical reagents and double distilled water. In the present study, Co_3O_4 nanoparticles were synthesized by a sol-gel method. The reaction mixture included $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and citric acid in a molar ratio of 1:2, and the pH of the solution was adjusted to 5. The precursor formed was calcinated at 600°C for 3 h and then crushed into fine powder. The Co_3O_4 nanoparticles collected were dispersed with polytetrafluoroethylene (PTFE) as a binder in anhydrous ethanol. The mixture was then daubed on the kryptol, and then dried in a vacuum oven.

Synthesis of Pt- Co_3O_4 nanoparticles

Prior to all electrochemical experiments, the solution

in the electrochemical cell was degassed by bubbling N_2 for 20 min. Upon the prepared electrode with Co_3O_4 nanoparticles, Pt was electrodeposited at the potential range from -0.3 V to 0.2 V at 50 mV/s for certain segments in a solution of 5 mM H_2PtCl_6 and 0.5 M H_2SO_4 . As a control, pure Pt electrode was prepared under the same conditions on the bare kryptol. The resultant Pt- Co_3O_4 nanocomposite and Pt electrode were then directly used as the working electrode for MOR.

Analysis and measurement

Electrochemical experiments were carried out in a conventional three-electrode cell with a CHI 660D electrochemical workstation. The working electrode was kryptol. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes respectively. The electrocatalytic properties of Pt- Co_3O_4 nanocomposite was studied in CH_3OH solution of H_2SO_4 since H_2SO_4 is extensively used as electrolyte in DMFCs. The impedance data were collected with a frequency range from 1 Hz to 100 kHz of AC amplitude of 5 mV. The electrochemical active surface area (ECSA) of the Pt and Pt- Co_3O_4 nanocomposite were measured in a nitrogen saturated 0.5 M H_2SO_4 aqueous solution, and the potential was scanned from -0.2 to 0.8 V (vs SCE) at a sweep rate of 10 mV/s. CVs were obtained after 50 cycles. All experiments were carried out at room temperature.

XRD measurement was performed by a Rigaku D/MAX-RB diffractometer with a $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15418$ nm). XPS measurements were performed with a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh vacuum (UHV) chambers. All binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The morphology of the synthesized nanomaterials was studied using a SEM operating at 15 kV, a transmission electron microscope (TEM, Philip CM-120) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2100) operated at 200 kV.

Results and discussion

XRD and XPS analysis

The XRD spectra of the prepared Co_3O_4 and Pt- Co_3O_4 samples are shown in Fig. 1. Co_3O_4 can be readily identified in both the pure nanoparticles and Pt- Co_3O_4 nanocomposite because all diffraction peaks can be indexed to Co_3O_4 and matched well with the cubic crystal structure (JCPDS file No. 42-1467, Fd3m). However, the typical diffraction peaks for Pt cannot be observed in the XRD pattern of Pt- Co_3O_4 nanocomposites (Fig. 1(b)), implying that the Pt content in Pt- Co_3O_4 nanoparticles is very low. By using the Scher-

rer's equation, the average diameter of as-prepared Co_3O_4 particles is about 35 nm.

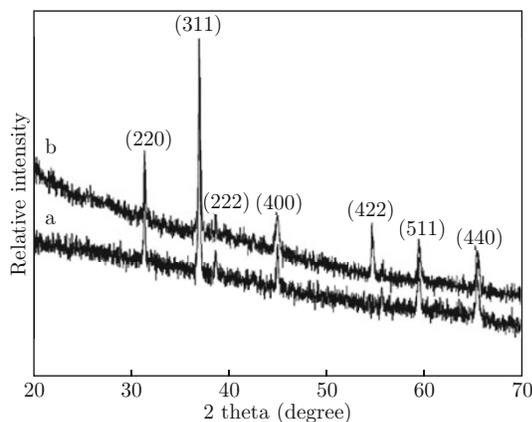


Fig. 1 XRD spectra of (a) Co_3O_4 nanoparticles; (b) $\text{Pt-Co}_3\text{O}_4$ nanocomposite.

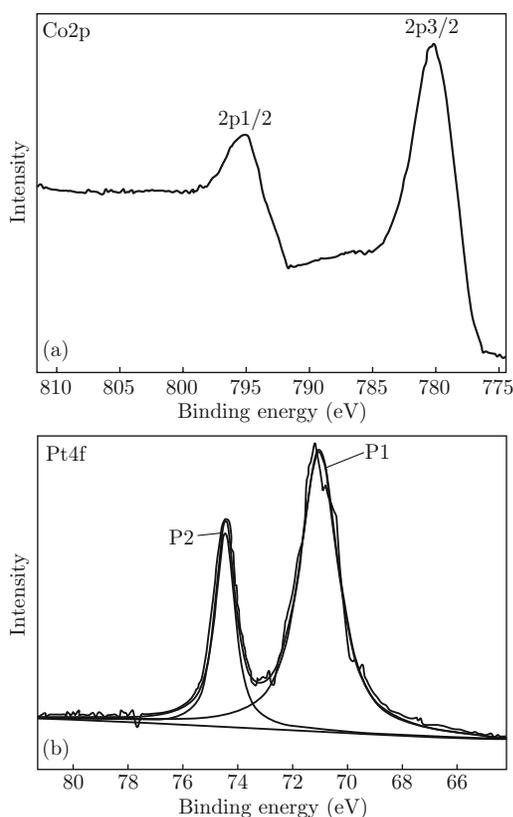


Fig. 2 XPS Co 2p and Pt 4f core level emission of $\text{Pt-Co}_3\text{O}_4$ nanocomposite.

Considering Pt is electrodeposited when Co_3O_4 is formed, it may be attached on Co_3O_4 surface. The XPS characterization of the samples is further performed to identify the presence of Pt in $\text{Pt-Co}_3\text{O}_4$ particles. Figure 2 shows the XPS spectra of the Co 2p and Pt 4f core level. The XPS Pt 4f core level (Fig. 2(b)) was observed at the binding energies of around 71.0 eV (Pt

4f7/2) and 74.4 eV (Pt 4f5/2), which is in good agreement with that in elemental Pt. The XPS Co 2p core level spectrum (Fig. 2(a)) also showed respectively two peaks at binding energy of 780.0 eV and 795.1 eV, suggesting the presence of Co in metal oxide form. The atomic ratio of Pt to Co of the particle surface was calculated to be around 3:97 by XPS, which was confirmed by energy dispersive X-ray analysis (EDX, Fig. 3(b)). It also confirms a relative low content of Pt.

SEM, TEM and HRTEM images

The SEM and TEM micrographs of the synthesized $\text{Pt-Co}_3\text{O}_4$ nanocomposites are shown in Fig. 3. The as-prepared samples were aggregated severely so that the particles were difficult to be identified in SEM (Fig. 3(a)). However after sonication, spherical nanoparticles could be clearly seen in TEM and the average diameter of these nanoparticles were estimated to be 50-60 nm (Fig. 3(c)), which is comparable to the value determined by XRD. The inset of Fig. 3(c) shows the selected area electron diffraction (SAED) pattern that was recorded from an individual $\text{Pt-Co}_3\text{O}_4$ nanoparticle that exhibits good crystallinity. The HRTEM images (Fig. 3(d)) show the clearly resolved lattice fringes, corresponding to the (222) planes of Pt and (440), (731) plans of Co_3O_4 , respectively. These substantiate that the presence of Pt particles in the products with high crystallinity.

CV for methanol electro-oxidation

Figure 4 showed the CVs of kryptol, Co_3O_4 electrode, bare Pt nanostructured electrode and $\text{Pt-Co}_3\text{O}_4$ nanocomposite electrode in 0.5 mol/L H_2SO_4 + 1 mol/L CH_3OH solution. The shapes of the CV curves were close to that previously reported with other anode materials [21]. The anodic peaks for MOR appeared on both anodes in forward and reverse sweeps. Peak "f" was obtained from the positive direction scan (forward scan) and Peak "b" from the reverse direction (reversed scan).

The ratio of the forward anodic peak current density to the reverse anodic peak current density (I_f/I_b) can be used to describe the catalyst tolerance to carbonaceous species accumulation [16,22-23]. We assigned the ratio of I_f/I_b as k . The current density at the peak potential was taken as one main parameter of the activity of the electrocatalysts for MOR [24]. According to Fig. 4, it is noticed that there was no methanol oxidation on pure Co_3O_4 electrode while methanol oxidation on $\text{Pt-Co}_3\text{O}_4$ nanocomposite electrode can be observed and the peak current density (I_f) was higher than Pt nanostructured electrode, though only minute amount of Pt was introduced (atomic ratio of Pt:Co is 3:97 as determined by XPS). The k value of $\text{Pt-Co}_3\text{O}_4$ electrode ($k = 1.33$) is around 25 % higher than that

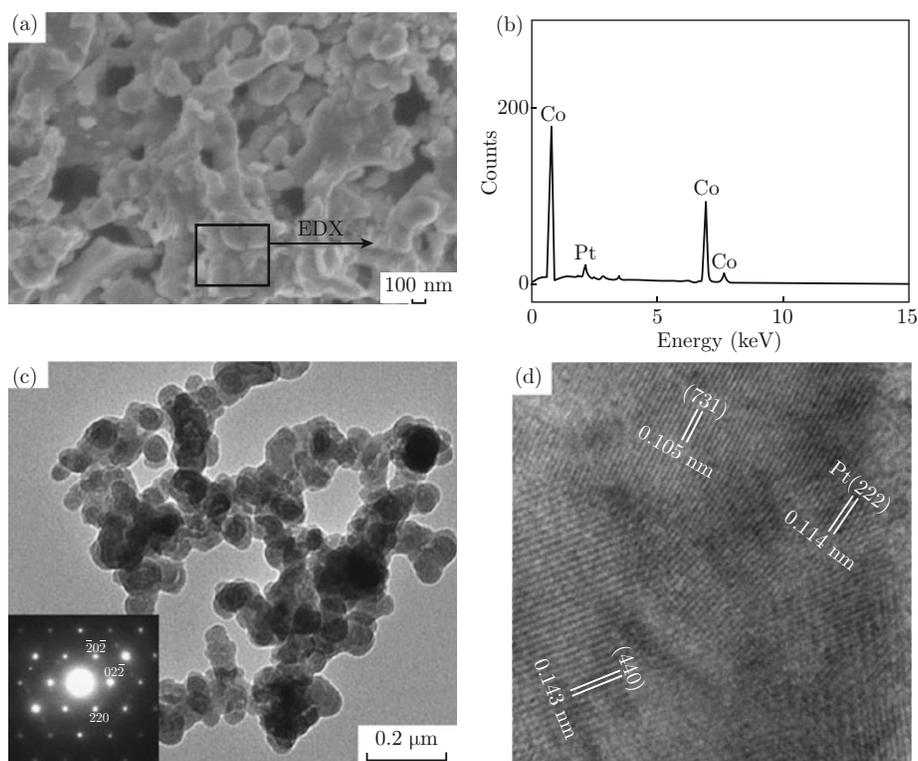


Fig. 3 (a) SEM; (b) EDX; (c) TEM and (d) HRTEM morphologies of Pt-Co₃O₄ nanoparticles (Inset is SAED pattern of Pt-Co₃O₄ nanoparticles).

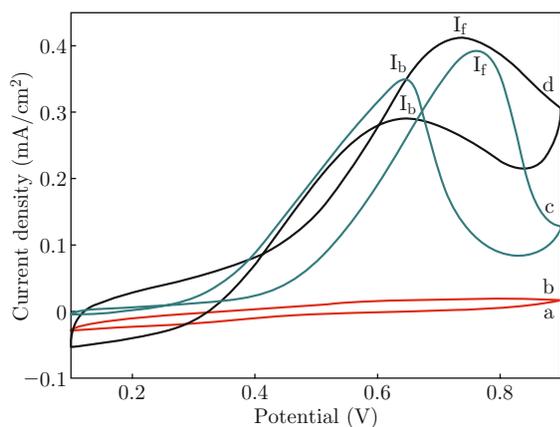
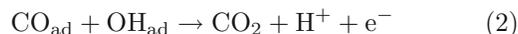
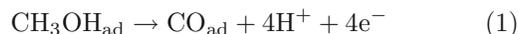


Fig. 4 Cyclic voltammograms for (a) kryptol; (b) Co₃O₄ electrode; (c) Pt electrode and (d) Pt-Co₃O₄ electrode in 0.5 mol/L H₂SO₄ + 1 mol/L CH₃OH solution obtained at 0.05 V/s.

of pure Pt nanostructured electrode ($k = 1.07$). It is proposed that though the pure Co₃O₄ is not catalytically active towards MOR, the presence of Co₃O₄ can enhance the catalytic activity of Pt by oxidizing the intermediate carbonaceous species to carbon dioxide on Pt-Co₃O₄ electrode.

It has been reported that the mechanism of MOR on Pt nanostructured electrode in acidic medium involves parallel and consecutive oxidation reactions [25], in which “ad” denotes species in adsorbed state, as fol-

lows:



Further oxidation to carbon dioxide is usually difficult on pure Pt electrodes at room temperature because of the lack of active oxygen on the surface. Both CO as a poisoning agent and CO₂ have been clearly observed by infrared reflectance spectroscopy and gas chromatography [26-27]. The oxidation current density at the peak potential increased when Co₃O₄ was added, it appears that the presence of Co₃O₄ facilitates the oxidation of freshly chemisorbed species and leads to an enhanced activity for methanol electro-oxidation, in which Co₃O₄ provides active oxygen for removal of intermediates such as CO on the Pt surface effectively. The mechanism of MOR on Pt-Co₃O₄ electrocatalyst is proposed. The methanol is initially adsorbed on Pt, while simultaneously loses its methanolic proton to a basic oxide ion. Then the methoxy species formed get oxidatively decomposed to CO species and this strongly bound intermediate is expected to be removed from the electrocatalyst surface by the reaction with Co₃O₄. CO was suggested to be adsorbed on oxidized cobalt site, probably Co³⁺ [28], and the adsorbed CO reacts with oxygen linked to the active Co³⁺. CO₂ is formed and desorbed quickly [29]. This process can be described by

the following equation:



EIS for methanol electro-oxidation

Figure 5 shows the electrochemical impedance spectroscopy of Pt and Pt-Co₃O₄ electrode in 1 mol/L CH₃OH + 0.5 mol/L H₂SO₄ aqueous solution. The impedance spectra display a depressed semi-circle in the high frequency region and a straight line with a slope of nearly 45° in the low frequency region. In comparison with the impedance spectra shown in Fig. 5(a), it is found that the diameter of the semi-circle in Fig. 5(b) declines greatly. In other words, the charge transfer resistance (*R_{ct}*) of the Pt-Co₃O₄ (1.607 Ω) is much lower than that of Pt (34.55 Ω). This means that the presence of Co₃O₄ nanoparticles in Pt-Co₃O₄ electrode leads to a faster charge transfer in the Pt-Co₃O₄-solution electrode-solution interface than at the Pt-solution interface for Pt nanostructured electrode, contributing to the enhanced MOR exhibited by Pt-Co₃O₄ nanocomposite.

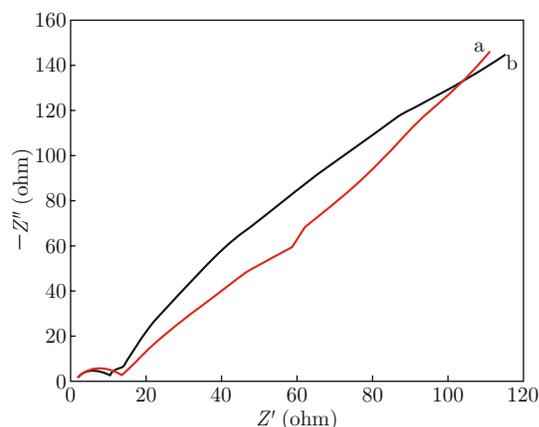


Fig. 5 EIS of (a) Pt; (b) Pt-Co₃O₄ electrode in 1 mol/L CH₃OH + 0.5 mol/L H₂SO₄ aqueous solution.

Current density-time curves for methanol electro-oxidation

Figure 6 shows the typical current density-time curves obtained in 1 M CH₃OH + 0.5 M H₂SO₄ solution at an anodic potential of 0.7 V for Pt and Pt-Co₃O₄ electrodes. This applied potential was chosen because it was close to the oxidation potential as revealed from CVs (Fig. 4). It can be seen that both samples show current density decay in current density-time measurements. There is an initial current density drop, followed by a slower decay. However, the current density values obtained from Pt-Co₃O₄ are higher than that from Pt electrode, indicating that Pt-Co₃O₄ electrode has a better CO resistance than pure Pt. This result is consistent with the above CV results.

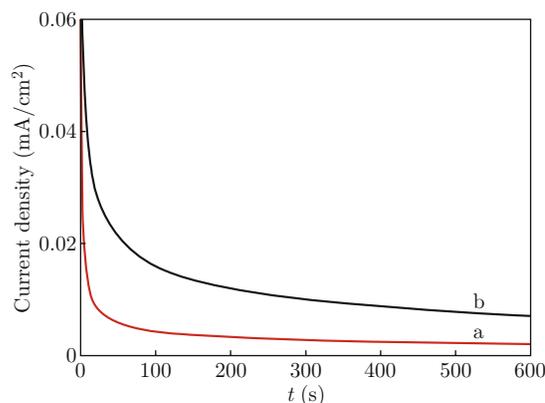


Fig. 6 Current density-time curves at 0.7 V for (a) Pt; (b) Pt-Co₃O₄ electrode in 1 M CH₃OH and 0.5 M H₂SO₄.

Conclusions

The Pt-Co₃O₄ nanocomposite electrode was successfully prepared by a two-step method. The results of CV measurement imply a higher electrocatalytic activity for MOR on Pt-Co₃O₄ nanocomposite electrode than pure Pt nanostructured electrode. The current-time experiment demonstrated that Pt-Co₃O₄ nanocomposite electrode showed good resistance to CO poisoning due to the presence of Co₃O₄. The impact of the current research work is that the obtained Pt-Co₃O₄ nanocomposite electrode can not only enhance the electrochemical activity and resistance to catalysts poisoning, but also reduce the cost of the electrodes because of the introduction of low-cost Co₃O₄. These two advantages are crucial to the realistic application of DMFC. The Pt-Co₃O₄ nanocomposite electrode is thus expected to be a promising candidate as electrode material of DMFC.

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