Uniform PtIr catalysts supported on carbon nanotubes prepared with assistance from phosphomolybdic acid, and their enhanced performance in the oxidation of methanol†

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Multiwalled carbon nanotubes (MWCNTs) are functionalized with phosphomolybdic acid (PMo) by ultrasonication. With the assistance of PMo, PtIr nanoparticles are homogeneously dispersed on the surface of MWCNTs. The size of PtIr nanoparticles can be controlled from 1.6 to 3.2 nm by tuning the composition of Pt catalysts. The composition of PtIr nanoparticles can be optimized at 4 : 1 Pt/Ir ratio, and as-prepared PMo/Pt4Ir1/MWCNT catalysts possess unique properties including a small size of PtIr nanoparticles, a high electroactive surface area and a large current density of methanol oxidation. For comparison, some Pt catalysts, Pt4Ir1/MWCNT and PMo/Pt/MWCNT, are also prepared in a controlled experiment. In the absence of PMo, PtIr nanoparticles are unevenly dispersed and aggregated on the surface of MWCNTs. Their average diameter is 3.1 nm, much larger than that of PtIr nanoparticles which are prepared in the presence of PMo (1.6 nm). This accounts for the difference in the catalytic activity of methanol and CO oxidation between Pt4Ir1/MWCNT and PMo/Pt4Ir1/MWCNT. On the other hand, the introduction of Ir makes PMo/Pt4Ir1/MWCNT catalysts superior to PMo/Pt/MWCNT catalysts in terms of a better CO-tolerance and a higher catalytic efficiency of methanol oxidation.

1. Introduction

As an alternative power source for vehicles and portable devices, the direct methanol fuel cell (DMFC) has attracted considerable attention because of its great specific energy density, high energy conversion efficiency, low operating temperature and near zero pollution emission.1 In the past few decades, many improvements have been achieved in DMFCs. Nevertheless, the cost of DMFCs is still expensive, and the activity and durability of electrocatalysts still fail to meet the requirements of commercialization.2 Thus it is a long-standing research goal to develop active, robust and low cost electrocatalysts.3

A typical electrocatalyst in DMFCs is generally made up of Pt or Pt alloy composites supported on the surface of carbon materials. Methanol oxidation takes place on the surface of Pt metal. However, this reaction kinetics was sluggish, because it involves several electron transfers. What’s worse, Pt is susceptible to CO poisoning because the intermediate species, such as CO, will adsorb strongly on the Pt surface, which may block the pathway of methanol to the active sites of Pt crystal plane during the process of methanol oxidation.4 Multi-component Pt alloy catalysts have been developed in order to improve the performance of DMFC with economical use of the Pt content. Among these Pt alloys, PtRu alloy is a superior electrocatalyst in DMFCs, because Ru can react with water to produce Ru–OH species, which will combine with Pt–CO species to remove surface-adsorbed CO at the potential lower than pure Pt. However, Ru component is instable, it will be dissolved in acidic solutions for its low oxidation potential (0.89 V (Ru3+/Ru)).5 Other metals than Ru, such as Pd,4 Co,6 Ni,7 Sn8 or Ir,9 have been introduced in Pt catalysts to enhance the performance of Pt catalysts. Ir is unique among them, because Ir has a relatively high oxidation potential of 1.156 V (Ir3+/Ir). Therefore, Ir can be used as a potent alternative promoter, and it possesses more resistance to metal dissolution under the fuel cell operating conditions. Furthermore, Ir can improve the performance of Pt-based catalysts in the methanol oxidation reaction.9

On the other hand, supports used in DMFCs also have a significant influence on the performance of Pt based catalysts.10 For this purpose, Pt and Pt alloy were incorporated in a variety
of carbon support materials including carbon black,\textsuperscript{10} graphene,\textsuperscript{11} graphite nanofibers and carbon nanotubes (CNTs).\textsuperscript{12} Amids these carbon support materials, CNT is a promising candidate owing to its high electronic conductivity, good chemical stability and large surface to volume ratio.\textsuperscript{13} However, without surface modification, most CNTs are short of adequate binding sites to anchor metal precursor or nanoparticles, which will result in poor dispersion and aggregation of nanocrystals.\textsuperscript{14} Therefore, surface functionalization of CNTs is a necessary step in the preparation of Pt/CNT hybrids. To do so, several approaches have been applied. These included: (1) oxidation processes, \textit{e.g.} strong acid treatment\textsuperscript{14} and ozonation;\textsuperscript{15} (2) grafting reactions, \textit{e.g.} covalent binding with ionic liquid\textsuperscript{13} and \textit{in situ} polymerization of vinylpyrrolidone;\textsuperscript{12} (3) non-covalent modification, \textit{e.g.} surface wrapping with sodium dodecyl sulfate\textsuperscript{16} and poly(sodium 4-styrenesulfonate).\textsuperscript{17} However, CNT functionalization can cause its damage, which may affect its electrical structure, reduce CNT conductivity, and slow the electron transfer between the interface of CNTs and Pt nanoparticles.\textsuperscript{17}

Polyoxometalate can be spontaneously adsorbed on the surface of CNTs by ultrasonication.\textsuperscript{18} This strategy retains the structural integrity of CNTs. In addition, functionalization of CNTs with polyoxometalate is beneficial to the preparation of Pt/CNT catalysts and the catalysis of methanol oxidation as follows: (1) polyoxometalate can be used as a stabilizer for preparation of noble metal nanoparticles.\textsuperscript{19,20} (2) Polyoxometalate is capable of fast reversible electron transfer under mild conditions.\textsuperscript{21} (3) Polyoxometalate has strong Bronsted acidity and high proton conductivity.\textsuperscript{22} These unique properties can make polyoxometalates very useful in DMFCs.

Herein, we expatiate on the preparation of PtIr nanoparticles supported on multiwalled carbon nanotubes (MWCNTs) in the presence of phosphomolybdic acid (PMo) for the first time. MWCNTs were modified with a layer of PMo, which supply binding sites to deposit PtIr nanoparticles. Furthermore, PMo can stabilize and protect PtIr nanoparticles from aggregation. With the assistance of PMo, PtIr nanoparticles can be homogeneously deposited in high density on the surface of CNTs. It is expected that these PMo/PtIr/MWCNTs catalysts will exhibit superb activity in the electrochemical catalysis of methanol. In this study, the composition of PtIr nanoparticles is also optimized to upgrade the performance on methanol oxidation. On the other hand, as a comparison, PtIr/MWCNT and PMo/Pt/MWCNT catalysts were synthesized. A comparative investigation was carried out on the electro-oxidation of methanol at PMo/PtIr/MWCNT, PtIr/MWCNT, PMo/Pt/MWCNT catalysts modified electrode.

2. Experimental

2.1. Chemicals and materials

All chemicals and materials were purchased from Acros. HNO\textsubscript{3} and HCl were trace metal grade. H\textsubscript{2}PtCl\textsubscript{6}, IrCl\textsubscript{3} and H\textsubscript{2}PMo\textsubscript{12}O\textsubscript{40} were analytic pure. Water was purified by a Milli-Q system.

MWCNTs were obtained from Chengdu Organic Chemicals Co., Ltd. (purity >95% out diameter 10~20 nm, length ~30 \textmu m).

MWCNTs were purified as follows: the raw MWCNTs were dispersed by ultrasonication in de-ionized water for 30 minutes. A H\textsubscript{2}O\textsubscript{2} (18%) solution was added into this solution to decompose amorphous carbon by boiling for 6 hours. Then, a concentrated HCl (63%) solution was introduced to dissolve the metal particles inside the raw MWCNTs by refluxing for 8 hours. After the solution was filtered through a 0.45 \textmu m PTFE filter membrane, the filtered mass was collected and dried at 100 °C in vacuo.

2.2. Preparation of PMo/MWCNT hybrids

PMo/MWCNT hybrids were prepared by sonication according to ref. 18: 5 mg of MWCNTs and 10 mg PMo were dispersed in 10 mL of de-ionized water by sonication for 24 hours with a set frequency of 45 Hz at room temperature. The as-prepared sample was collected by centrifugation and thoroughly rinsed with de-ionized water to remove non-adsorbed PMo until the washing solution became colorless. Then PMo/MWCNT hybrids were dried at 80 °C in vacuo for characterization.

2.3. Preparation of PMo/PtIr/MWCNT catalysts

PMo/Pt\textsubscript{4}Ir\textsubscript{1}/MWCNT (x = 1, 2, 4, 8) catalysts were synthesized by polyol reduction in the mixture solution of water and ethanediol with a volume ratio of 1 : 1. In brief, 5 mg of MWCNTs and 10 mg PMo were dispersed in 10 mL de-ionized water by sonication for 24 hours under 45 Hz frequency at room temperature. Then, a fixed total amount (100 \textmu mol) of H\textsubscript{2}PtCl\textsubscript{6} and IrCl\textsubscript{3} with a different molecular ratio of PtIr (Pt/Ir = x) was added in batches. This mixture solution was diluted with 10 mL ethanediol, and sonicated for 0.5 hours. Subsequently, it was transferred into a 100 mL flask charged with a magnetic bar, and this flask was placed in a thermostatted oil bath. To prepare PMo/Pt\textsubscript{4}Ir\textsubscript{1}/MWCNT catalysts, the mixture solution was deoxygenated by nitrogen for 15 minutes, and refluxed for 10 hours at 140 °C. Finally, the as-prepared samples were collected by centrifugation and thoroughly rinsed with de-ionized water to remove non-adsorbed PMo until the washing solution became colorless. These PMo/Pt\textsubscript{4}Ir\textsubscript{1}/MWCNT catalysts were dried at 80 °C in vacuo for characterization.

For comparison, Pt\textsubscript{4}Ir\textsubscript{1}/MWCNT and PMo/Pt/MWCNT catalysts were prepared. The strategy used in the synthesis of such Pt catalysts is identical to the preparation of PMo/Pt\textsubscript{4}Ir\textsubscript{1}/MWCNT catalysts except for some modification. For Pt\textsubscript{4}Ir\textsubscript{1}/MWCNT catalysts, they were synthesized in the absence of PMo. For PMo/Pt/MWCNT catalysts, they were prepared with 100 \textmu mol of H\textsubscript{2}PtCl\textsubscript{6}.

2.4. Characterization

Raman spectroscopy was performed by using a Renishaw InVia Raman spectrometer with 514.5 nm excitation. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB-MKII spectrometer with an unmonochromated Al KR X-ray source (1486.6 eV) for excitation. High-resolution spectra were obtained at a perpendicular takeoff angle, using the pass energy of 20 and 0.05 eV steps. Transmission electron microscopy (TEM) observation was performed on a JEOL 2010 microscope equipped with an
energy dispersive spectroscopy (EDS), operating at 200 kV with a high-brightness LaB6 electron gun. The composition of different Pt catalysts was determined by its EDS at 150 kV.

Inductively coupled plasma-atom emission spectroscopy (ICP-AES) was performed on Agilent 7500ce quadrupole ICP-AES. Different catalysts, PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT (\textit{x} = 1, 2, 4, 8), PMo/Pt/MWCNT, and Pt/MWCNT, were sampled by treatment with aqua regia. MWCNTs cannot be dissolved, and can be discarded by centrifugation. The elements, Pt, Ir and Mo were dissolved, and left in solution for ICP-AES analysis.

2.5. Electrochemical investigation

We used a 15 mL glass electrochemical cell containing three electrodes: a glassy carbon disk working electrode (3 mm in diameter) embedded in Teflon, a platinum wire counter electrode (1 mm in diameter, 5 cm in length), and a saturated KCl Ag/AgCl electrode as the reference electrode. Before use, the glassy carbon electrodes were polished with 0.5 μm alumina slurry, washed with the de-ionized water, then immersed for 20 minutes in a sonicator bath, and finally washed with the de-ionized water.

To modify the glassy carbon electrode with as-prepared hybrids, 4.0 mg of these carbon nanotube materials (PMo/MWCNT, PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT (\textit{x} = 1, 2, 4, 8), PMo/Pt/MWCNT or Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT) were dispersed in 400 μL de-ionized water by sonication to form a homogeneous catalyst ink, and then 5 μL of this catalyst ink was mixed with 2.5 μL of 0.5% Nafion® 117 ethanol solution. The mixture was spread and air-dried on a glassy carbon electrode at room temperature.

A three-electrode setup was configured with CHI 660C interfaced to a personal computer at room temperature for the electrochemical characterization of the as-prepared modified glassy carbon electrodes. The electrolytic solution was bubbled with nitrogen for 15 minutes before the electrochemical experiment.

3. Results and discussion

3.1. Characterization of PMo/MWCNT hybrids

The morphology of PMo/MWCNT hybrids was shown in Fig. S1. PMo is covered on the surface of MWCNTs to form a membranous structure with a thickness of 10–20 nm, whereas purified MWCNTs are clean and free of particles deposited. The presence of PMo on the surface of MWCNTs was confirmed by cyclic voltammetry. Fig. S2 shows cyclic voltammograms (CVs) of the electrode modified with PMo/MWCNT hybrids in nitrogen-saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} solutions with a different scan rate. Three reversible redox peaks of PMo can be observed, which should be ascribed to multi-electron transfer of PMo adsorbed on the surface of MWCNTs. Take peaks I for instance, their peak currents (anodic peak current \textit{I\textsubscript{a}} and cathodic peak current \textit{I\textsubscript{c}}) increase linearly with the increase of scan rates while their peaks potentials remain invariant. The results reveal that the absorbed PMo follows a surface confined redox process in nitrogen-saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} solutions.

Raman spectra reveal that the process of PMo modification led to some structural damage of MWCNTs. The extent of the damage of PMo/MWCNT hybrids is much less than that of acid-oxidized MWCNTs (Fig. S3†). This result suggests that MWCNTs modified with PMo will retain higher conductivity than those oxidized by acid, which is propitious to the electrochemical performance of Pt-based catalysts supported on CNTs.

3.2. Characterization of PMo/PtIr/MWCNT catalysts

Fig. 1 shows TEM images of PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT catalysts (\textit{x} = 1, 2, 4, 8) prepared with a 100 μmol of metal precursors H\textsubscript{2}PtCl\textsubscript{6} and IrCl\textsubscript{3} at different ratios of Pt/Ir. All PtIr nanoparticles were uniformly deposited onto the surface of MWCNTs without aggregation. As shown in Fig. S4† the size distribution was evaluated statistically through measuring the diameter of 200 PtIr nanoparticles in the selected TEM images. The sizes of PtIr nanoparticles distribute between 1 and 4 nm. The average diameters of PtIr nanoparticles vary according to Pt/Ir ratio. When the PtIr nanoparticles were prepared at Pt/Ir ratio = 1 (PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT), their diameters averaged 3.2 nm. With an increase of Pt content in PtIr nanoparticles, the average diameter of PtIr nanoparticles changes observably. For example, the average diameter of PtIr nanoparticles was 2.4 nm when prepared at a ratio of Pt/Ir = 2 (PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT), and 2.0 nm when prepared at a ratio of Pt/Ir = 8 (PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT). Among these PtIr nanoparticles, these PtIr nanoparticles prepared at Pt/Ir ratio of 4 : 1 have a smallest average diameter, which is 1.6 nm (PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT).

The composition of PMo/Pt\textsubscript{x}Ir\textsubscript{y}/MWCNT catalysts was investigated by EDS. As shown in Fig. 2, it reveals C, O, Mo, Pt
and Ir signals from MWCNTs and PtIr nanoparticles. The Cu and Si signals come from the copper grid. Mo L signal is presented at all EDS curves at 2.3 keV. Both Pt M and Ir M signals occur at about 2.0 keV. But the Pt L signal is different from the Ir one. For the Pt L signal, it appears at 9.5 keV for Pt La and 11.1 keV for Pt Lb. For the Ir L signal, it occurs at 9.1 keV for Ir La and 10.6 keV for Ir Lb. The molar ratio of Pt/Ir for PMo/Pt$_x$Ir$_1$/MWCNT catalysts can be estimated by normalizing the intensity of the Pt L and Ir L signals on the EDS curves, which was listed in Table S1.† The results were consistent with those of ICP-AES. Besides, the content of Mo in PMo/Pt$_x$Ir$_1$/MWCNT catalysts was also presented in Table S1.† From Table S1,† it is clear that the amount of adsorbed PMo will mainly depend on the surface area of PtIr nanoparticles with a view to a constant mass of MWCNTs in the matrix of PMo/Pt$_x$Ir$_1$/MWCNT. The smaller the size of PtIr nanoparticles, the higher their specific surface area, and thus the more the PMo adsorbed.

3.3. Electrochemical investigation of PMo/PtIr/MWCNT catalysts

The electrochemical behavior of PMo/Pt$_x$Ir$_1$/MWCNT catalysts ($x = 1, 2, 4, 8$) was conducted by cyclic voltammetry. Fig. 3 shows the CVs of the modified electrodes with PMo/Pt$_x$Ir$_1$/MWCNT catalysts in N$_2$-saturated 0.5 M H$_2$SO$_4$ solution. The PtIr nanoparticles show signatures of polycrystalline Pt in the potential interval between $-0.2$ and 0.1 V, which was divided into the reductive adsorption region of protons in the reverse cathodic scan and the oxidative desorption region of hydrogen atom in the forward anodic scan. This potential region is defined as the hydrogen area, which can be used to calculate the electrochemical surface area (ESA) of Pt based catalysts. In addition, a couple of reversible redox peaks ($I$) occur at 0.2 V, which are assigned to multiple electrons transfer of Keggin PMo. As shown in Fig. S5,† the currents of peaks ($I$) obtained at the electrode modified with PMo/Pt$_x$Ir$_1$/MWCNT catalysts are linear to their scan rates of CVs, indicating a surface-confined redox process for PMo adsorbed on the surface of Pt nanoparticles and MWCNTs in N$_2$-saturated 0.5 M H$_2$SO$_4$ solution. Another three couples of redox peaks from PMo should be presented at about 0, $-0.15$ V and 0.4 V. Since they are overlapped in the hydrogen area or blurred by the oxygen desorption on the platinum surface, they are inconspicuous on the CVs of PMo/Pt$_x$Ir$_1$/MWCNT catalysts.
the electrode modified with PMo/PtIr/MWCNT catalysts. As expected, Fig. 3 shows that the peak (I) current of PMo on the CVs of the modified electrode increased with the amount of PMo adsorbed in PMo/PtIr/MWCNT catalysts. On the other hand, as discussed above, the hydrogen region of PMo/PtIr/MWCNT catalysts was superimposed with the redox peaks from PMo; thus, it is difficult to accurately measure their ESAs from the hydrogen region of CVs.

Without regard to the contribution from PMo, the ESAs of PMo/PtIr/MWCNT catalysts are estimated by integrating the hydrogen region, which were listed in Table S2. It is clear from Table S2† that the ESAs of PMo/PtIr/MWCNT catalysts are mostly dependent on the composition of PtIr nanoparticles supported on MWCNTs. As suggested by the ESA definition, more Pt contents that PtIr nanoparticles have, and larger ESAs that they possess. Besides, the size of PtIr nanoparticles has significant influence on their ESAs. Given the mass of PtIr nanoparticles, as discussed above, a decrease of their average diameter will give rise to an increase of their specific surface areas. Therefore, the ESA sequence of PtIr nanoparticles among PMo/PtIr/MWCNT catalysts follows this order of decrease: PMo/PtIr1/MWCNT, PMo/Pt8Ir1/MWCNT, PMo/Pt2Ir1/MWCNT and PMo/Pt4Ir1/MWCNT.

The electrocatalytic oxidation of methanol was studied at the PMo/PtIr/MWCNT catalysts modified electrodes by cyclic voltammetry in N2-saturated 0.5 M H2SO4 solution containing 0.5 M methanol. As shown in Fig. 4, the faradic current exhibits a well-known dependence on the electrode potential for the methanol oxidation on carbon-supported Pt catalysts. The forward peak at about 0.7 V is due to oxidation of methanol. Its peak current and peak potential is designated as IMeOH and EMMeOH. The backward peak at about 0.5 V can be regarded as the oxidation of adsorbed byproduct, mainly made up of CO, which results from incomplete oxidation of methanol in the forward scan. Thus, its peak current and peak potential is defined as ICO and ECO. From Fig. 5, it can be observed that the IMeOH of PMo/PtIr/MWCNT catalysts decrease in accordance with the following sequence: PMo/PtIr1/MWCNT, PMo/Pt8Ir1/MWCNT, PMo/Pt2Ir1/MWCNT, PMo/Pt4Ir1/MWCNT, PMo/Pt2Ir1/MWCNT, PMo/Pt4Ir1/MWCNT, PMo/Pt8Ir1/MWCNT and PMo/Pt4Ir1/MWCNT.

![Fig. 5 TEM images of (A and B) Pt4Ir1/MWCNT, (C and D) PMo/Pt/MWCNT catalysts.](image)

Fig. 5 TEM images of (A and B) Pt4Ir1/MWCNT, (C and D) PMo/Pt/MWCNT catalysts.

3.4. Comparative investigation of PMo/PtIr/MWCNT, Pt4Ir1/MWCNT and PMo/Pt/MWCNT catalysts

As noted above, among PMo/PtIr/MWCNT catalysts (x = 1, 2, 4, 8), PMo/Pt8Ir1/MWCNT catalyst has a highest current response towards electro-oxidation of methanol. Control catalysts are prepared according to the procedures of PMo/PtIr1/MWCNT catalysts for comparison, which were specified as PtIr1/MWCNT and PMo/Pt/MWCNT catalysts, respectively. These catalysts were characterized by TEM and XPS. And their performance in electro-oxidation of methanol was investigated by cyclic voltammetry and chronoamperometric technique.

Fig. 5 shows the morphology of Pt8Ir1/MWCNT and PMo/Pt/MWCNT catalysts. In the absence of PMo, the PtIr nanoparticles are unevenly dispersed and aggregated on the surface of MWCNTs. Their average diameter is about 6 nm with a size distribution of 3 to 10 nm (Fig. S4†). Obviously, PtIr nanoparticles in Pt8Ir1/MWCNT catalysts have a larger average diameter and a wider size distribution than those in PMo/Pt4Ir1/MWCNT catalysts. In the presence of PMo, Pt nanoparticles can be uniformly dispersed on the surface of MWCNTs without conglomeration. As shown in Fig. S4,† the diameter of Pt nanoparticles is 2.4 nm. The size distribution of Pt nanoparticles is 1–3 nm. Obviously, PMo makes a difference in the synthesis of Pt and Pt alloy nanoparticles on the surface of MWCNTs. The reason is discussed below: for the purified MWCNTs, there are some defects on the surface of MWCNTs originated from purification. These defects supply sites for the deposition of Pt and Pt alloy nanoparticles. However, they are uneven and insufficient, especially for loading high-density Pt and Pt alloy nanoparticles, which will result in a poor dispersion of Pt or Pt alloy nanoparticles on the surface of the MWCNTs. When MWCNTs were functionalized with PMo, a PMo layer will be formed. This PMo layer produces a uniform distribution of OH and Mo–O groups. The oxygenic group can act as a coordination site to bond with Pt in the form of PtOx at the outermost perimeter of Pt nanoparticles. Therefore, a much more uniform distribution of PtIr
Nanoparticles can be observed on the surface of PMo/MWCNT catalysts. On the other hand, PMo possess 3–4 negative charges, which makes PMo available for use as a stabilizer to protect against aggregation and overgrowth of PtIr alloy nanoparticles. In the absence of PMo, PtIr alloy nanoparticles will be unstable, small PtIr alloy nanoparticles will aggregate into a larger one.

Fig. 6A shows the XPS survey profiles of different Pt and PtIr alloy catalysts. It is clear that the Pt 4f signal occurs at 77 eV and C 1s at 285 eV. As calculated from the intensity of XPS curves, the Pt/C ratios for all catalysts do not have a large difference, ranging from 0.15 to 0.18, which was in agreement with ICP-AES data (Table S1†). Ir 4f signal can be observed on the XPS curves of PMo/Pt4Ir1/MWCNT and Pt4Ir1/MWCNT catalysts at about 63 eV (Fig. 6B), while no Ir 4f signal appears on those of PMo/Pt/MWCNT catalysts. Mo 4f signal presents itself at about 235 eV, when Pt catalysts were prepared with PMo (Fig. 6D). However, no Mo 4f signal can be seen on the XPS curves of Pt4Ir1/MWCNT catalysts. Moreover, the position of the O 1s signal of the catalysts prepared with PMo (Fig. 6E) is different from that synthesized without PMo. For example, the O 1s signal of Pt4Ir1/MWCNT catalysts is mainly located in 533 eV, which derived from the purification of MWCNTs. But for PMo/Pt4Ir1/MWCNT catalysts, the O 1s signal is wider, and its peak position shifted more negative at 531 eV. The results may result from the adsorbed PMo.

Fig. 7A shows the CVs of the electrode modified with different Pt alloy catalysts in N2-saturated 0.5 M H2SO4 solution. A couple of reversible redox peaks attributed to PMo was presented on the CVs of PMo/Pt4Ir1/MWCNT and PMo/Pt/MWCNT catalysts at about 0.2 V, while Pt4Ir1/MWCNT catalysts have no obvious current of PMo redox. Irrespective of the contribution from PMo, the ESAs of these Pt catalysts are evaluated and listed in Table S2†. It is clear that PMo/Pt4Ir1/MWCNT catalysts have the largest ESA among these Pt catalysts due to their smaller PtIr nanoparticles.

Fig. 7B shows the CVs of the electrode modified with different Pt alloy catalysts in N2-saturated 0.5 M H2SO4 solution containing 0.5 M methanol. Their IMOH, EMOH, ICO, ECO and IMOHICO are recorded in Table S3†. Obviously, EMOH is almost the same for PMo/Pt4Ir1/MWCNT and Pt4Ir1/MWCNT catalysts, and it is about 0.70 V. The overpotential is reduced by 0.04 V as compared to that of PMo/Pt/MWCNT catalysts. The results suggested that Ir can be used as a promoter of Pt catalysts on methanol oxidation. In addition, the IMOH of Pt4Ir1/MWCNT catalysts (104 mA mg−1) is lowest among these Pt alloy catalysts, which may be attributed to their larger size of PtIr nanoparticles in contrast with those of other two catalysts. Meanwhile, the IMOH sequence for Pt based catalysts is listed below in a decrease order: PMo/Pt4Ir1/MWCNT (288 mA mg−1) > PMo/Pt/MWCNT (178 mA mg−1). The results demonstrate a highest activity of PMo/Pt4Ir1/MWCNT catalysts towards methanol oxidation among these Pt catalysts, which is consistent with those of ESAs analysis. To see how Ir affects the properties of Pt, IMOH at Pt catalysts is normalized to their ESAs, which is denoted as IMOH/ESA, and listed in Table S3†. By this means, the contribution to IMOH from the size effect is eliminated. However, IMOH/ESA of PMo/Pt4Ir1/MWCNT catalysts (3.18 A m−2) is still greater than that of PMo/Pt/MWCNT catalysts (2.26 A m−2). This difference should be ascribed to the synergic effect of Ir and Pt by the incorporation of Ir into Pt catalysts.25 Moreover, it should be noted that IMOH of PMo/Pt4Ir1/MWCNT catalysts is higher than those of Pt catalysts reported
recently, such as PtRu nanoparticles supported on MWCNT functionalized with ionic liquid and poly(vinylpyrrolidone). Also, PMo/PtIr/MWCNT catalysts show a higher activity toward methanol oxidation than PMo/PtRu/MWCNT catalysts. On the other hand, a large ratio of \( \text{I}_{\text{MeOH}}/\text{I}_{\text{CO}} \) represents a more complete methanol oxidation, less accumulation of CO-like species on the catalyst surface, and thus a better CO-tolerance. From Table S3, \( \text{I}_{\text{MeOH}}/\text{I}_{\text{CO}} \) of PMo/PtIr/MWCNT and PMo/Pt/MWCNT catalysts is 1.08 and 0.68, respectively. This result suggests that Ir component of PMo/PtIr/MWCNT catalysts can improve CO-tolerance of Pt catalysts to some extent.

The poison tolerance of Pt alloy catalysts was tested by CO-stripping voltammetry, CO was adsorbed by the electrode modified with Pt alloy catalysts at 0.10 V vs. AgCl in a CO-saturated 0.5 M H\(_2\)SO\(_4\) for 20 min. This was followed by removal of CO from the solution by purging N\(_2\) for 20 min. As shown in Fig. 8a and b, only one well-defined CO ad oxidative wave is found on PtIr/MWCNT and PMo/PtIr/MWCNT catalysts, suggesting that the CO ad oxidation peak is not simply an addition of fraction contribution of Pt and Ir sites but a synergistic effect. The onset and peak potentials of CO ad on the bimetallic PMo/PtIr/MWCNT catalysts are 0.330 and 0.441 V, which is shifted negatively by 0.155 and 0.172 V as compared to PtIr/MWCNT. The results demonstrate that PMo/PtIr/MWCNT catalysts are more active for CO ad than PtIr/MWCNT catalysts. Obviously, PMo make some positive difference to improve CO tolerance for PtIr catalysts, which is well in agreement with a previous report on polyoxometalate-deposited Pt/C electrocatalysts at this point. On the other hand, PMo/Pt4Ir/MWCNT catalysts show a lower stripping potential of CO ad as compared to PMo/Pt/MWCNT catalyst, 0.086 V less for the onset potential and 0.125 V less for of the peak potential (Fig. 8a and c). The result is indicative of a faster oxidative removal of CO ad that occurs at the surface of PtIr nanoparticles. Given the amount of PMo adsorbed in the matrix of these two Pt catalysts as listed in Table S1, it is clear that the superior of PMo/Pt4Ir/MWCNT catalysts over PMo/Pt/MWCNT catalysts in CO tolerance is due to the introduction of Ir element into Pt catalysts. As is well known, Ir is similar to Ru, both of them has lower electron affinity than Pt (190 keV for Ir and 203 keV for Pt). When Ir is alloyed with Pt, electrons will transfer from Ir to Pt, resulting in a change in the adsorption energy of CO ad on the surface of the PtIr nanoparticles. In addition, the introduction of Ir can mediate the electronic structure of the bimetallic monolayer surfaces, which increases repulsive interaction between CO ad. All these factors will favor the oxidative removal of CO ad. In our case, Ir addition improves CO tolerance of Pt catalysts. The result is consistent with the CV data of methanol electrooxidation.

Fig. 9A shows the typical steady-state currents recorded by chronoamperometry at 0.6 V in N\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) solution containing 0.5 M methanol. The oxidative currents of methanol decrease for all catalysts at the beginning, which resulted from the deactivation of the Pt sites by adsorbed CO species generated from methanol oxidation process. When the processes of accumulation and removal of CO species at Pt sites reach a balance, the currents of methanol oxidation at all Pt catalysts will arrive at a stable stage. A faster current decay in the beginning was shown on the chronoamperometric curve of Pt4Ir/MWCNT catalysts by contrast with the other two catalysts. The results suggest that PtIr/MWCNT catalysts are more susceptible to the deactivation of Pt sites by adsorbed CO in the absence of PMo. On the other hands, Ir atoms in Pt alloy can promote oxidation of the surface-absorbed CO to CO\(_2\). leading to activity recovery of the Pt catalysts. Thus a significant
enhancement in oxidative current of methanol can be observed on the chronoamperometric curves of PMo/Pt4Ir1/MWCNT by comparison with PMo/Pt/MWCNT. The current of methanol oxidation at PMo/Pt4Ir1/MWCNT catalysts is 180 mA mg⁻¹ even after 3000 s continuous electrocatalysis at 0.6 V, being 3.6 times greater than that of Pt4Ir1/MWCNT catalysts. Fig. 9B indicates that the PMo/Pt4Ir1/MWCNT catalysts exhibit a better performance for methanol electrooxidation than those of Pt4Ir1/MWCNT and PMo/Plt/MWCNT catalysts at all applied potentials.

4. Conclusion

We develop a facile approach to synthesize PMo/Plt/MWCNT catalysts with the assistance of PMo. MWCNTs were modified with a layer of PMo by ultrasonication. This procedure does much less damage to MWCNTs than those of MWCNTs functionalization by oxidation with strong acid. In the presence of PMo, PtIr nanoparticles were uniformly deposited on the surface of MWCNTs. In the absence of PMo, PtIr nanoparticles were unevenly distributed and aggregated on the surface of MWCNTs. It was found that the PMo layer on the surface of MWCNTs supplies a uniform distribution of the coordination site for PtIr nanoparticles to deposit. Moreover, PMo in the reaction solution protects PtIr nanoparticles from aggregation. The preparation of PMo/Plt/MWCNT catalysts was optimized by tuning the Pt/Ir ratio while amount of the metal precursor H2PtCl6 and IrCl3 remains constant. Among PMo/PltIr/MWCNT catalysts (X = 1, 2, 4, 8), the average diameter of PtIr nanoparticles in PMo/Plt4Ir/MWCNT catalysts is smallest. It is 1.6 nm with a size distribution of 1−3 nm. The smaller size of PtIr nanoparticles enables PMo/Plt4Ir/MWCNT catalysts to possess higher ESAs and larger IₘOH in methanol oxidation. Moreover, PMo/Plt4Ir/MWCNT catalysts exhibit a higher performance on electrooxidation of methanol than those of Pt based catalysts, such as PtIr/MWCNT and PMo/Plt/MWCNT catalysts. For these Pt catalysts, the IₘOH of PMo/Plt4Ir/MWCNT catalysts is 288 mA mg⁻¹, being 2.5 times Pt4Ir1/MWCNT catalysts. On the other hand, PMo/Pt4Ir1/MWCNT catalysts show the highest CO-tolerance among these Pt catalysts, their IₘOH/IₘCO is 1.05, which is higher than that of PMo/Plt/MWCNT catalysts (0.76).

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Notes and references