

N, P-codoped Mesoporous Carbon Supported PtCox Nanoparticles and Their Superior Electrochemical toward Methanol Oxidation

Hangjun Cui, Yueming Li* and Shimin Liu

¹ State Key Laboratory of Metastable Materials Science and Technology, College of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, China

* E-mail:liyueing@ysu.edu.cn.

Abstract. In this report, a novel strategy by using the N, P co-doped mesoporous carbon structure as catalyst support to enhance the electrochemical catalytic activity of Pt-based catalysts is proposed. The as-synthesized PtCox@N, P-doped mesoporous carbon nanocomposites have been studied as an anode catalyst toward methanol oxidation, exhibiting greatly improved electrochemical activity and stability compared with Pt@mesoporous carbon. The synergistic effects of N, P dual-doping and porous carbon structure help to achieve better electron transport at the electrode surface, which eventually leads to greatly enhanced catalytic activity compared to the pristine Pt/mesoporous carbon....

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted much attention over the past few decades due to high energy efficiency, low operation temperature and non-toxic pollution emission.[1] However, there are several key issues including sluggish kinetics of methanol oxidation reaction (MOR), methanol crossover through the membrane, low electrocatalytic activity of the electro-catalysts for DMFC. [2, 3] Currently, the most efficient catalysts toward MOR are Pt-based electro-catalysts, which are rare and expensive.

The mesoporous carbons with large specific surface area and plenty of pores can be used as catalyst support, exhibiting superior electrocatalytic activity than conventional carbon black.[4] The ordered mesoporous carbon (OMC) has large surface area and uniform pore structure, which not only limit the particle size of catalysts and facilitate mass diffusion, but also prevent the detachment, aggregation and even dissolution for the catalysts nanoparticles.[5] However, the corrosion tolerance for mesoporous carbon should be further improved.

Heteroatoms doping is found to be very effective to modify the electrochemical performance for carbon-based support carrier. It is found that the nitrogen doping has a remarkable effect on the surface chemical activity, the surface properties such as polarity and adsorption ability and the corrosion tolerance. [6] [7-9] It is believed that the nitrogen-containing groups in presence of Brønsted acid and Lewis base sites help to anchor Pt nanoparticles due to the strong interactions between the functional groups and Pt particles.[10] Except the single heteroatom doping, it is found that N and P dual-doped carbon material exhibit better electrochemical performance than N single doped one.[11]

The study of multiple heteroatoms doped mesoporous carbon as support is rather limited. In the present work, N, P co-doped hierarchical mesoporous carbon structure is prepared as the support of PtCox nanoparticles to combine the both advantage of porous structure and co-doping. Compared to



mesoporous carbon supported Pt, PtCox with N,P-codoped mesoporous carbon shows greatly improved catalytic activity toward methanol oxidation.

2. Experimental

The mesoporous carbon (MC) were synthesized by mesoporous silica (SBA-15) assisted method. The ordered mesoporous carbon was prepared according to our previous literature.[12] To get N-doped mesoporous carbon, the prepared mesoporous carbon was mixed with urea in ratio of 1: 1 and heated at 400 ° C for 2 hours under nitrogen atmosphere, denoted as NMC. The as prepared NMC was added into an aqueous solution of 113mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, followed by drying at 100 ° C for 2 h. The as-obtained product was mixed together with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (125mg) and heated in a tube furnace at 600 ° C for 1h under nitrogen atmosphere, yielding black powder. (NPMC-Co).

To prepare N,P co-doped mesoporous carbon supported catalyst, 50 mg NPMC-Co powder was added in 150 mL ethylene glycol (EG) solution under ultra-sonication for 30 min. Then 6.5 mL H_2PtCl_6 solution (5mg/mL) was added into the suspension for 1h. Sodium hydroxide was used to adjust the pH value to ~ 13, and then the solution was fluxed at 140 ° C for 4h under argon atmosphere. The black precipitate was filtered, washed with DI water, and dried in an oven at 80°C overnight. For comparison, Pt@MC, Pt@PMC and Pt@NPMC were prepared with a similar procedure using undoped MC, NMC and MC-Co as supports, respectively. The mass loading of Pt is about 25 wt % for all samples.

3. Results and discussions

As shown in Figure 1, the strong diffraction peaks at ~39.8, 46.2 and 67.6° in the XRD patterns of Pt@MC and Pt@NMC composites can be assigned to the (111), (200) and (220) plane of the cubic Pt crystal (JCPDS No. 04-802), while the broad peaks at ~ 23° can be assigned to amorphous carbon. The peaks corresponding to (111) plane for Pt@PMC and Pt@NPMC slightly shift toward the high angle comparing to that of Pt/MC, suggesting the formation of PtCox alloy. The formation of PtCo alloy is still not very clear, as the components of NPMC-Co are very complicated. During the reaction of NaH_2PO_2 with NMC/ $\text{Co}(\text{NO}_3)_2$ composites, multiple phases including CoPx, CoNx, metal Co and CoCx may form during this process. [13-15]

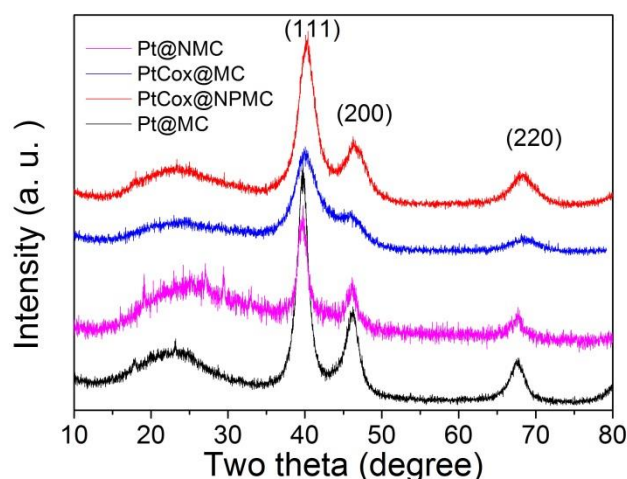


FIGURE 1 XRD patterns of Pt@MC, Pt@NMC, PtCox@MC and PtCox@NPMC

As shown in Figure 2, the small PtCox nanoparticles are uniformly anchored on both the surface of N, P doped mesoporous carbon. The formation of Pt alloy can be attributed to low valence Co species or soluble cobalt salt. As the content of NPMC-Co is very complicated, the exact formation reason for Pt alloy is still under investigation.

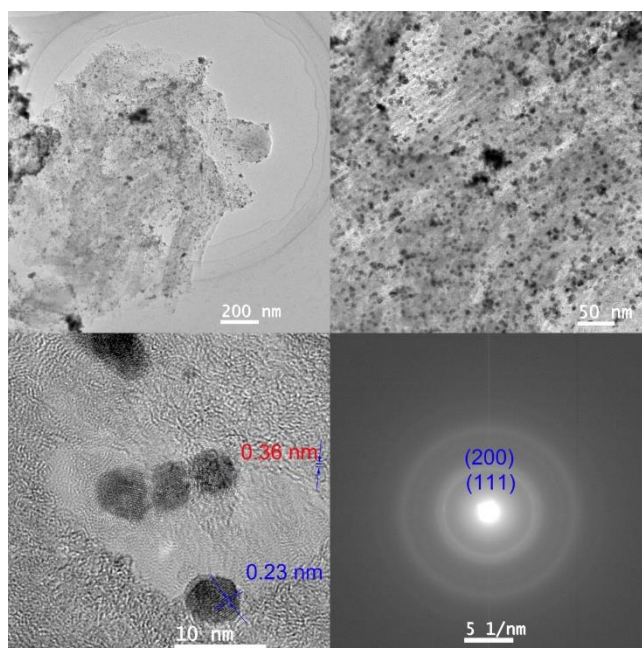


FIGURE 2 TEM image of PtCox@NPMC at lower magnification (a) and high magnification (b) and HRTEM image (c) and SAED (d) of PtCox@NPMC

It is believed that the doping is favourable for the dispersion of Pt nanoparticles because the introduction of N can enhance the interaction between the Pt and support carrier.[16] The HRTEM image of PtCox nanoparticles discloses a clear crystalline lattice fringe with d-spacing of ~ 0.23 nm, which can be indexed to (111) plane of face-centered cubic Pt lattice. The selected-area electron diffraction image shows the diffraction rings corresponding to Pt polycrystalline nature.

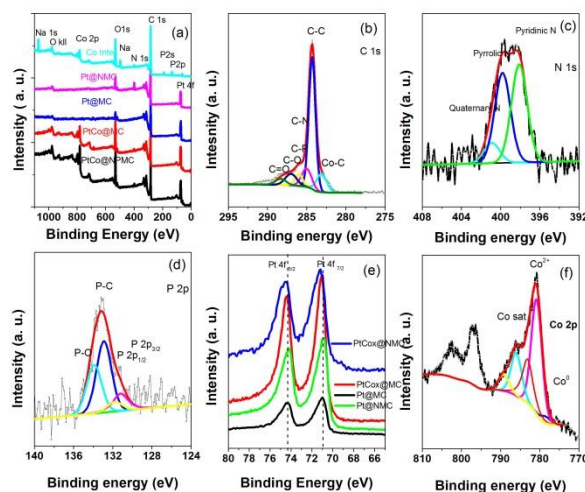


FIGURE 3 (A) XPS survey spectra of CoP@NC, Pt@MC, PtCo@MC, Pt@NMC and PtCox@NMC; (B) High resolution Pt 2f spectra of Pt@MC, PtCo@MC, Pt@NMC and PtCox@NMC; High resolution (C) C1s, (D) N1s, (E) P2p and (F) Co2p spectra of PtCox@NMC

The information on the valence states and elemental composition of as prepared samples was evaluated by X-ray photoelectronic spectroscopy (XPS). As shown in survey spectrum in Figure 3a, the peaks corresponding to Pt, C, Co, P, N and O can be clearly observed for PtCox@NPMC sample. The C1s spectrum (Figure 3b) can be fitted into five peaks located at 283.4, 284.2, 288 eV, corresponding to C-N, C-P, C-O, and C=O, respectively, disclosing the successful doping of N and P into the

framework of carbon. The peak at 283.4 eV can be attributed to Co-C bond, which formed owing to the reaction of Co species with carbon materials during annealing process.[14] The N1s spectrum (Figure 3c) can be fitted into three peaks located at 398.5, 400 and 400.9 eV, corresponding to pyridinic, pyrrolic and graphitic N, respectively, disclosing the successful doping of N into the framework of mesoporous carbon. Figure 3d shows the high-resolution P 2p XPS spectrum, which can be fitted into four peaks. The two peaks at 133.8 and 132.8 eV can be assigned P–O bond as well as P–C bond in as-prepared PtCox@NPMC, respectively, indicating the P doping into carbon materials. The doping of N and P heteroatoms to carbon materials help to improve the corrosion tolerance and dispersion of Pt nanoparticles due to the abundant dangling bonds. The N and P content are about 2.3 and 1.6 (at.) %, respectively. Figure 3e present the high resolution XPS of Pt 4f. The Pt 4f 7/2 spectra of PtCox@NMC can be observed to shift to higher binding energy (about 0.3 eV) compared to those of Pt@MC or Pt@NMC, which can be attributed to the electron loss or the work function change for Pt alloy. [17, 18]. The results exhibit that the doping of N and P atoms to hierarchical carbon structure for PtCox@NPMC. The other two weak peaks can be attributed to existence of the minor CoP phase.

Figure 3f shows the high resolution XPS spectrum of Co2p core level, which has been fitted by three peaks for Co 2p 3/2 region. The main peak at about 780 eV can be assigned to Co(II) species, while the weak peak at about 778 eV for Co 2p3/2 displays the existence of Co (0) species. In addition, the strong satellite peaks in Co2p spectra located at ~ 786.0 eV and 803.1eV can be assigned to shake up excitation of the high-spin Co(II) species. [56] As is known, the presence of Co(II) in PtCo alloy is common due to the susceptible oxidation in air.

Cyclic voltammogram (CV) experiments were used to analyze the electrocatalytic activity for as prepared sample. Figure 4a shows the representative set of CV curves of Pt@MC, Pt@NMC, PtCox@MC, and PtCox@NPMC in a solution containing 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹. The typical hydrogen adsorption and desorption peaks for Pt catalysts can be clearly observed in the potential range of ~ -0.2 to 0 V (vs Ag/AgCl). The electrochemically active surface areas (ECSA) can be evaluated by integrating the charges on the hydrogen desorption region assuming the adsorption of a monolayer of hydrogen on the polycrystalline Pt surface of 210 $\mu\text{C cm}^{-2}$. [19]

The ECSA value (58.8 m² g⁻¹) of Pt@NMC is larger than that (29.4 m² g⁻¹) of Pt@MC, indicating the introduction of N-doping can enhance the electrochemical activity of Pt catalyst. The ECSA value (62.2 m² g⁻¹) of PtCox/MC also increase sharply compared to Pt/MC, suggesting the alloying with Co can improve the electrochemical performance greatly. The PtCox@NPMC has the largest ECSA value (79.2 m² g⁻¹) among these catalysts, indicating the synergetic effects of N, P dual doping and alloying with Co can further improve the electrochemical catalyst for Pt based catalyst. As shown in Figure 4b, the ECSA value of PtCox is the largest among these samples, similar to H₂SO₄ electrolyte.

Figure 4c exhibits the representative set of CV curves of Pt@MC, Pt@NMC, PtCo@PMC, and PtCo@NPMC in in a solution containing 0.5 M H₂SO₄ and 0.5 M CH₃OH at a scan rate of 50 mV s⁻¹ at room temperature. The CV curves show two typical oxidation peaks, which are owing to the oxidation of methanol and the continuous oxidation of intermediate species (such as CO) adsorbed on the surface of catalyst in the forward sweep, respectively. In general, the forward peak current (I_f) to the backward peak current density (I_b), (I_f/I_b) can be used to evaluate the poison tolerance to CO. [20] The higher the I_f/I_b ratio is, the better the CO tolerance. Notably, PtCo@NPMC shows the highest value of I_f/I_b (1.82) among these catalysts, indicating enhanced poison tolerance to CO adsorbed for PtCox@NPMC. Furthermore, the forward peak current of PtCo@aNMC/gCN electrode is ~1458 mA/mg Pt, which is about 1.7, 5.8 and 11.5 times as much as those for PtCo@bNMC/gCN, PtCo@MC, Pt@NMC/gCN. Moreover, the onset potential of PtCo@NMC/gCN electrode is ~ 0.361 V, which is considerably lower than other catalysts, indicating superior electrochemical activity.

The long-term stability of these catalysts for methanol oxidation was examined by chronoamperometry at a fixed potential of 0.6 V for 1 h, shown in Figure 4d. It is clear that the potentiostatic current decreases quickly at the initial stage and then decreases slowly for these electrodes. PtCo@NMC shows the highest current density among these catalysts through the whole test stage, indicating the excellent long-term stability.

The electrochemical performance in alkaline electrolyte was also studied. Figure 4e shows the representative set of CV curves of Pt@MC, PtCo@MC, Pt@NMC, and PtCo@NMC in a solution containing 1 M KOH at a scan rate of 50 mV s^{-1} . Figure 4e exhibits the representative set of CV curves of Pt@MC, PtCo@MC, Pt@NMC, and PtCo@NMC in a solution containing 1 M KOH and 0.5 M CH_3OH at a scan rate of 50 mV s^{-1} at room temperature. The CV curves also show two typical oxidation peaks, while the second oxidation peaks are obviously weaker than those in acidic electrolyte. As shown in figure 4f, PtCo@NMC shows the highest current density and the best stability among these electrodes, indicating superior electrochemical activity.

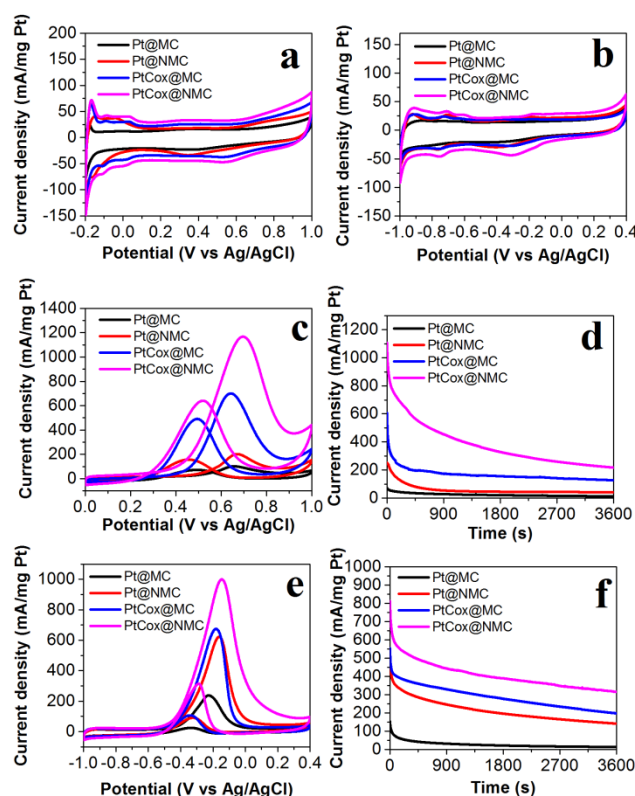


FIGURE 4 CV curves in 0.5 M H_2SO_4 solution (a) and in 1 M KOH solution (b) purged with N_2 at 50 mV s^{-1} ; CV curves (c) and chronoamperometric curves (d) in 0.5 M H_2SO_4 and 1M methanol solution; CV curves (e) and Chronoamperometric curves (f) in 0.5 M KOH and 1M methanol solution for Pt@MC, Pt@NMC, PtCox@MC and PtCox@NMC

In all, there are multiple merits for as-prepared PtCo@NPMC composites. One hand, the unique support composed of N and P dual-doped mesoporous carbon help to utilize the advantages both mesopore and co-doping due to the presence of more anchor sites.[21-24] On the other hand, alloying with Co is able to further enhance the electrochemical activity due to the modified electronic structures. For example, materials with a large surface area and high conductivity show the substantial advantages due to the convenient mass and charge transport and high electrode/electrolyte contact area. In addition the sheets-like structure favors the uniform distribution of PtCo nanoparticles. The functional groups help to achieve better adhesion with Pt nanoparticles, furthermore, the doping may be responsible for improved tolerance to CO observed in PtCo@NPMC.

4 Conclusion

In summary, we have demonstrated the successful preparation of PtCox nanoparticles catalysts on dual N, P co-doped mesoporous carbon via a wet-chemistry assisted method. The dual support composed of N,P co doped mesoporous carbon take the advantages porous structure as well as doping, providing

large accessible area, porous structures for fast mass and electron transportation, good electronic conductivity, more active sites and high nitrogen content, while the alloying with Co further enhance the catalytic activity. The as-prepared supports exhibit obvious advantages over single undoped mesoporous carbon. The PtCox@NPMC shows substantial electrochemical enhancement in poison tolerance and high catalytic current density as anode DFMC in alkaline as well as in acidic electrolytes. Through the combination of alloying with Co and use of dual-doped support the catalyst activity toward MOR has been greatly enhanced, therefore, the as-designed PtCox@NPC has great potential as an efficient electrocatalyst toward MOR field. Furthermore, this strategy of combination of dual doped support and alloying can be extended to prepare a series of other catalysts with superior electrochemical catalysts.

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