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A facile soft-template synthesis of ordered mesoporous carbon/tungsten carbide composites with high surface area for methanol electrooxidation

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ABSTRACT

Ordered 2D hexagonal mesoporous carbon/tungsten carbide (OMC/WC) composite nanomaterials have been successfully synthesized for the first time by the soft-template method with ammonium metagungstate as tungsten precursor and poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) tri-block copolymer (PEO–PPO–PEO) (F127) as a soft-template. With loaded Pt, the Pt@OMC/WC demonstrates better performance than the commercial PtRu@C for methanol electrooxidation in terms of specific mass activity by a factor of 2.4 (per mg Pt) and 3.2 (per mg metal). Its high activity could be attributed not only to the synergetic effect of WC, but also to its highly ordered nanostructure and large surface area for high utilization efficiency of Pt and desirable mass transportation in a porous electrode. This work is expected to provide a feasible approach for the preparation of ordered mesoporous self-supported metal carbides.

1. Introduction

Up to now, PtRu supported on carbon is still the well-recognized catalyst with the most desirable activity towards methanol electrooxidation reaction (MOR) [1–4]. However, in order to achieve the accepted direct methanol fuel cell (DMFC) performance, high loading catalysts are needed. With both Pt and Ru as the noble catalysts, it is unavoidable to provide DMFCs with the disadvantage of high cost. Recently, tungsten carbides (WC) have been found to possess beneficial effect on the activity of Pt catalysts to MOR and their tolerance to CO poisoning of Pt catalysts [5,6]. Various tungsten carbides with different shape and structures have been prepared by different methods and applied in catalysis and electrocatalysis [7–11]. On the other hand, these WC materials have low surface area (several – 113 $m^2 g^{-1}$) and non-uniform mesostructures. The former makes them unsuitable for support materials and the latter seriously devalues the mesoporous performance in the chemical reactions. As known, ordered mesoporous materials possess good electrochemical properties because of their unique ordered mesostructure [12–14]. Recently, Wu et al. [11] have successfully synthesized ordered mesostructure tungsten carbide and carbon composites by a temperature-programmed carburization approach with mesoporous silica as the hard template. However, the hard template method is obviously elaborate, high-cost, and thus industrially unfeasible. Therefore, the soft template method with supramolecular self-assembly arises a great interest in the synthesis of the nanocomposites of ordered mesoporous carbon and WC with open frameworks.

Herein we report for the first time the synthesis of ordered mesoporous carbon and tungsten carbide composites (OMC/WC) with high surface area through the soft template method. In this process, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) tri-block copolymer (PEO–PPO–PEO) (F127) has been adopted as a soft-template, ammonium metatungstate salt (AMT) as the tungsten precursor, and phenol/formaldehyde resol as the carbon source. And then, the as-prepared OMC/WC was combined with platinum as the electrocatalyst for MOR, exhibiting superior performance to a commercial PtRu@C catalyst (Tanaka) with a higher metal loading (30.2 wt.% Pt–23.5 wt.% Ru).

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2. Experimental details

2.1. OMC/WC preparation

For the preparation of OMC/WC samples, 0.61 g of phenol was melted in a flask and mixed with 0.13 mL of 5.0 mol L^{-1} NaOH aqueous solution under stirring (where the phenol/formaldehyde/NaOH/F127 ratio was taken from Ref. [15]). Then 1.05 g of 37 wt.% formaldehyde aqueous solution was added. Subsequently, the clear mixture reacted under stirring at 70 °C for 1 h, and then cooled down to room temperature. After that, the pH value of the solution was adjusted to about 7.0 by the drop-wise addition of 5.0 mol L^{-1} HCl aqueous solution. The final product was dissolved in ethanol to obtain a resol solution.

Meanwhile, ammonium metatungstate (AMT) was dissolved in ethanol/H_2O ($V_{\text{ethanol}}/V_{H_2O} = 4/1$) mixture solvent under stirring and then was mixed with 1.0 g of Pluronic F127 (EO_{106}–PO_{70}–EO_{106}) and 2.0 mL of H_2O. The feeding weight ratio between AMT and F127 was 0.1. Next, the above resol solution was added into the present mixture under stirring to obtain a homogeneous mixture. After that, it was transferred to a dish and evaporated at room temperature for 18 h, followed by heating at 100 °C for 24 h. The as-prepared product was carbonized at 900 °C for 3 h in N_2 flow. The heating rate was 2 °C min^{-1} below 600 °C and then was increased to 5 °C min^{-1} above 600 °C. The final product was defined as OMC/WC. The above detailed preparation process for OMC/WC is schematically described in Fig. 1. For comparison, the conventional ordered mesoporous carbon (OMC) was also prepared. Its preparation procedure was exactly the same as that of the OMC/WC, except that the addition of AMT was bypassed.

2.2. Catalysts preparation

The Pt@OMC and Pt@OMC/WC catalysts with a Pt loading of 20 wt.% were easily and fast prepared by a pulse-microwave assisted polyol method [16]. Chloroplatinic acid, the starting precursor of Pt, was well mixed with ethylene glycol (EG) in an ultrasonic bath, and then OMC or OMC/WC was added into the mixture. After the pH value of system was adjusted to more than 10 by the addition of 1.0 mol L^{-1} NaOH/EG, the well-dispersed slurry was obtained with stirring and ultrasonication for 30 min. Thereafter, the slurry was microwave-heated in the pulse form of 10-s ON/10-s OFF for several times. The resulting black solid sample was filtered, washed, and dried at 80 °C for 10 h in a vacuum oven. The commercial 30.2 wt.%Pt–23.5 wt.%Ru@C (Tanaka) was also employed as a reference electrocatalyst for MOR (denoted as PtRu@C).

2.3. Physicochemical characterization

The structural analysis of the samples was carried out by X-ray diffraction (XRD) on a D/Max-IIIA X-ray diffractometer (Rigaku Co., Japan) equipped with a Cu Kα source. Low-angle XRD patterns were recorded on a D-MAX 2200 VPC diffractometer using Cu Kα radiation (40 kV, 30 mA). The unit cell parameter (a) was calculated using Eq. (1):

$$a = \frac{2d_{10}}{\sqrt{3}} \tag{1}$$

where d_{10} represents the d-spacing value of the 10 diffraction. TEM images were obtained by a JEM-2010HR microscope. N_2 adsorption–desorption measurements were carried out using a Micromeritics ASAP 2010 analyzer at 77 K. The thickness of carbon wall (T_{CW}) was calculated according to Eq. (2):

$$T_{\text{CW}} = a - D_{\text{C}} \tag{2}$$

where D_{C} stands for the diameter of channel which was obtained from Barrett–Johner–Halendar (BJH) pore size distribution. The BET surface area (S_{BET}), the mesopore volume (V_{mes}), and the micropore volume (V_{mic}) were determined by Brunauer–Emmett–Teller (BET) theory, BJH method, and t-plot theory, respectively.

2.4. Electrochemical characterization

Electrochemical measurements were conducted on CHI 750 instrument in a standard three-electrode cell in a constant temperature water bath. A saturated calomel electrode (SCE) and a platinum foil were used as the reference electrode and the counter electrode, respectively. A glass carbon (GC) disk electrode was used as the substrate for the electrocatalyst thin film in the electrochemical measurements. The thin film catalyst layer as the working electrode was prepared as follows: a mixture containing 5.0 mg electrocatalyst, 1.8 mL ethanol and 0.2 mL Nafion solution (5 wt.%)

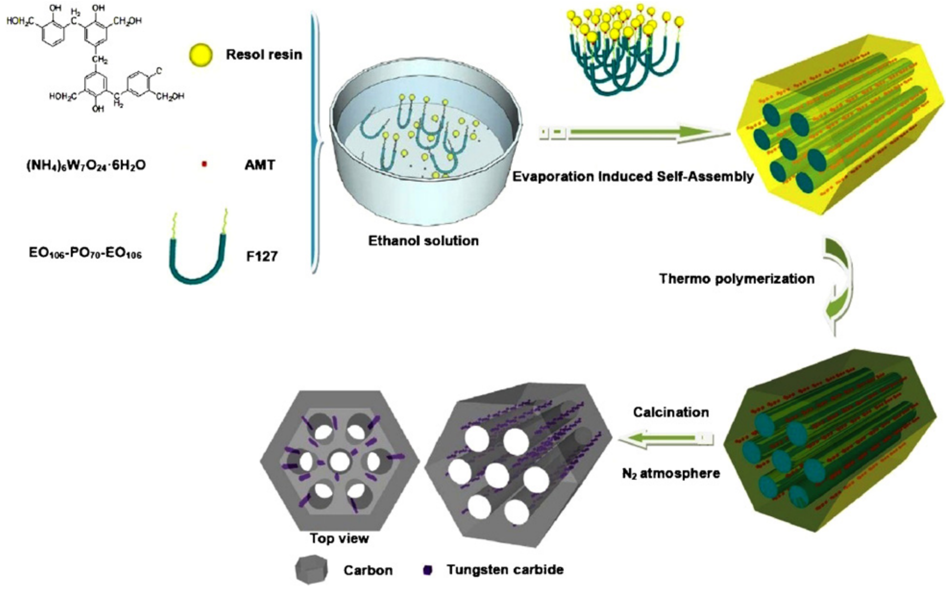


Fig. 1. Synthetic process of ordered 2D hexagonal mesoporous carbon/tungsten carbide with F127 as a soft-template, ammonium metatungstate salt (AMT) as the tungsten precursor, and phenol/formaldehyde resol as the carbon source, respectively, by a soft template method.

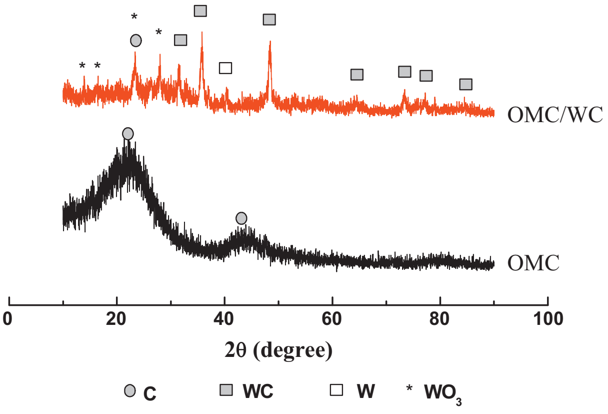


Fig. 2. Wide-angle XRD patterns of OMC and OMC/WC.

was dispersed in a ultrasonic bar for 15 min to obtain a well-dispersed ink. The catalyst ink was then quantitatively transferred onto the surface of the GC electrode using a micropipette, and dried to obtain a catalyst thin film. An aqueous solution containing 0.5 mol L^{-1} H_2SO_4 + 1.0 mol L^{-1} CH_3OH was used as the electrolyte, which was deareated with high-pure nitrogen. It should be noted that all the potential is referred to the SCE without specification.

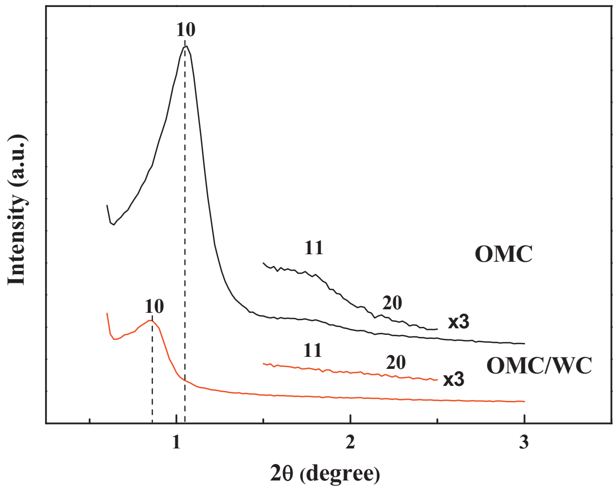


Fig. 3. Low-angle XRD patterns of OMC and OMC/WC.

3. Results and discussion

The wide angle XRD patterns of OMC and OMC/WC are shown in Fig. 2. In the case of OMC/WC, the respective diffraction peaks at 31.4°, 35.6°, and 48.4° correspond to (0 0 1), (1 0 0) and (1 0 1) facets of WC, while those at 2θ of 23° and 46° correspond to the diffraction facet of carbon. There also exist the corresponding diffraction peaks of WO_3 as marked with star in Fig. 2. This could be due to the part oxidation of WC during the XRD measurements. Obviously, WC could be successfully obtained in the present synthesis conditions. The formation of WC maybe undergo the transition from W to W_2C, and finally converting to WC as the main phase with a long reaction time (3 h) [5]. The low-angle XRD patterns of OMC and OMC/WC are displayed in Fig. 3. Obviously, in the case of OMC, it exhibits an intense diffraction peak (1 0) and two resolved peaks (1 1) and (2 0), indicating the formation of a highly ordered 2D hexagonal (*p*6*m*) mesostructure [17]. Parallel arranged channels can be observed in the TEM image of OMC (Fig. 4a). When adding AMT as the tungsten precursor with an AMT/F127 mass ratio of 10%, the resulting OMC/WC has a slightly lower order degree, judging from the disappearance of the diffraction peak (1 1) and peak (2 0) in Fig. 3. However, the peak (1 0) is still intense, and the TEM image in Fig. 4b also shows that the ordered structure is maintained. This clearly indicates that the addition of AMT does not hamper the self-assembly of the tri-block copolymer F127 and the phenol–formaldehyde resol to form an ordered 2D hexagonal mesostructure, which gives us the feasibility to make ordered OMC/WC composites. Moreover, the 2θ value of the diffraction peak (1 0) decreases from 1.04° of OMC to 0.86° of OMC/WC (see Fig. 3) and correspondingly the unit cell parameter (a) increases from 9.6 to 11.8 nm (see Table 1), implying the existence of the structural extension due to the introduction of AMT.

The pore structure of OMC and OMC/WC samples is further investigated by N_2 adsorption–desorption isotherms (Fig. 5). Both samples exhibit typical type IV isotherms with a distinct hysteretic loop, clearly indicating the mesoporous nature of the as-prepared samples. Moreover, it can be clearly seen from the inset in Fig. 5 that both OMC and OMC/WC have a unimodal, narrow pore size distribution with a maximum around 4.3 and 7.2 nm. The extended pore size by introducing AMT provides OMC/WC as the electrocatalyst supports with higher metal utilization coefficient and consequently higher electrocatalytic activity [18]. Moreover, this gives us a new direction for enlarging the pore size for ordered mesoporous materials. The surface area and mesopore volume of OMC and OMC/WC are 676 m^2 g^{-1} and 0.43 cm^3 g^{-1}, 538 m^2 g^{-1}

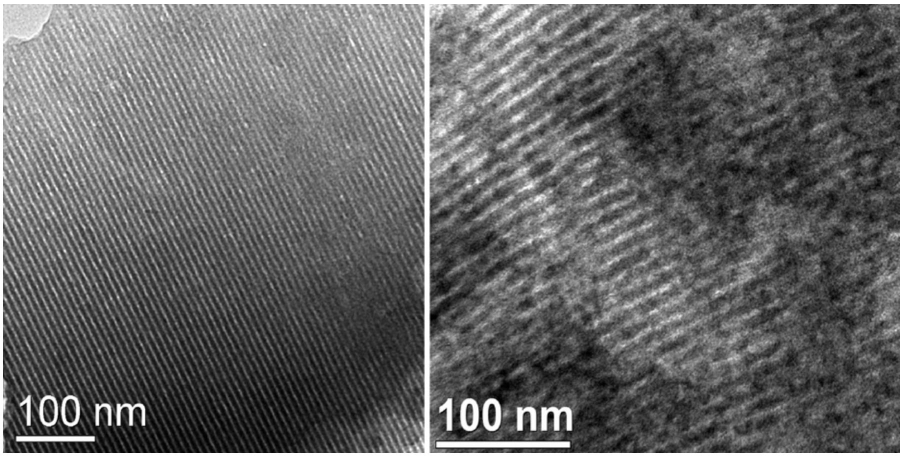


Fig. 4. TEM images of OMC (a) and OMC/WC (b).

Table 1
Pore structure parameters of OMC and OMC/WC.

Sample	S_{BET} ($m^2\,g^{-1}$)	S_{ext} ($m^2\,g^{-1}$)	S_{mic} ($m^2\,g^{-1}$)	V_t ($cm^3\,g^{-1}$)	V_{mes} ($cm^3\,g^{-1}$)	V_{mic} ($cm^3\,g^{-1}$)	D_C[a] (nm)	a[c] (nm)	T_{CW}[b] (nm)
OMC	676	304	372	0.43	0.31	0.17	4.3	9.6	5.3
OMC/WC	538	268	270	0.59	0.53	0.125	7.2	11.8	4.6

[a] D_C is calculated from BJH pore size distribution (desorption isotherms).
[b] $T_{CW} = a - D_C$.
[c] $a = 2d_{10}/\sqrt{3}$.

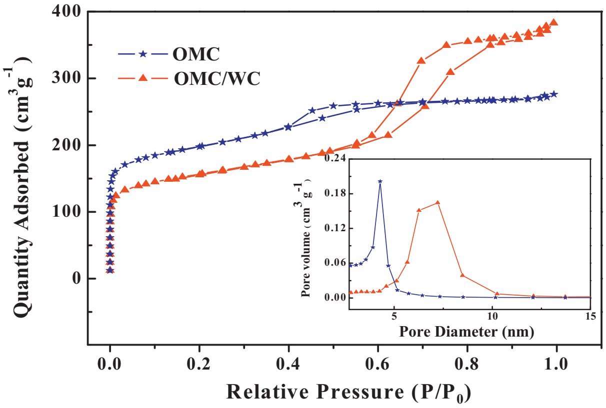


Fig. 5. N_2 adsorption–desorption isotherms of OMC and OMC/WC samples (inset: BJH pore size distributions).

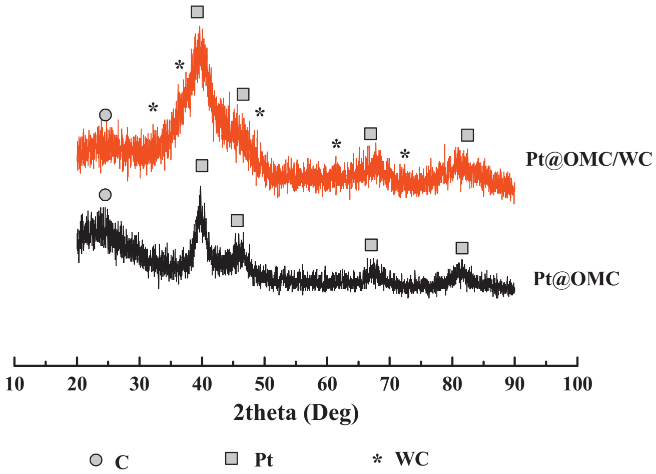


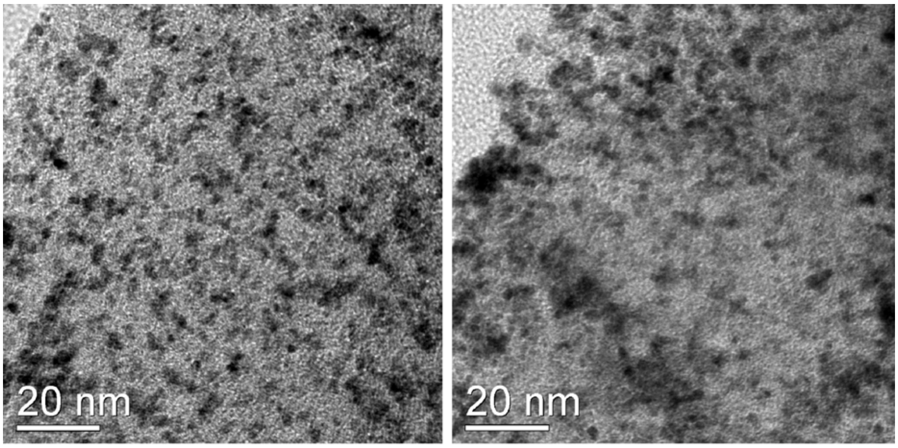
Fig. 6. XRD of the as-prepared Pt@OMC and Pt@OMC/WC.

and 0.59 $cm^3\,g^{-1}$, respectively (Table 1). The BET surface area of OMC/WC is much higher than those by the other methods [5,6], which makes them suitable as the support materials for highly dispersing metal particles.

Fig. 6 shows the XRD results of the as-prepared Pt@OMC and Pt@OMC/WC. Except for the characteristic peaks of WC in the case of Pt/OMC/WC, both samples exhibit the typical characteristics of a crystalline Pt face centered cubic (fcc) structure. According to Scherrer's formula, the calculated average Pt particle size using the fitted (2 2 0) plane are 3.5 nm for Pt@OMC and 3.5 nm for Pt@OMC/WC. Moreover, it can be seen from the TEM results (Fig. 7) that the Pt nanoparticles are uniformly dispersed on the pore surface of both OMC and OMC/WC.

The CV results for MOR depicted in Fig. 8 clearly indicate that Pt@OMC gives the lowest activity, which could be due to that Pt alone, is prone to be poisoned by the CO-like immediate products from MOR. Moreover, the pore size of OMC might be so small (4.3 nm) that many loaded Pt particles are unavailable [18]. One can also see that Pt@OMC/WC even outperforms the commercial PtRu@C. This could be ascribed not only to the synergetic effect of WC [5,6], but also to its highly ordered mesostructure and large surface area for high utilization efficiency of Pt and desirable mass transportation in a porous electrode [18].

Considering that increasing Pt utilization can reduce Pt usage, and consequently decrease the catalyst cost, the specific mass activity is further compared. In the case that Pt alone is considered, the specific mass activity of Pt@OMC/WC is 854 mA per mg of Pt, which is about 2.4 times as large as that of PtRu@C (Fig. 8b). Moreover, Ru is also a noble metal. The Ru-free catalyst is also attracting for noble-metal-economic catalyst development. In the case that the total noble metal is considered, the specific mass activity of Pt@OMC/WC magnifies 3.2 times by comparing Pt@OMC/WC and PtRu@C (Fig. 8c). The present mass activity is quite higher than the reported results [6]. More precisely, the reported specific mass activity was 560 mA per mg of Pt @0.75 V (*vs.* Ag/AgCl), while our



(A) Pt@OMC (B) Pt@OMC/WC

Fig. 7. TEM images of the as-prepared Pt@OMC (a) and Pt@OMC/WC (b).

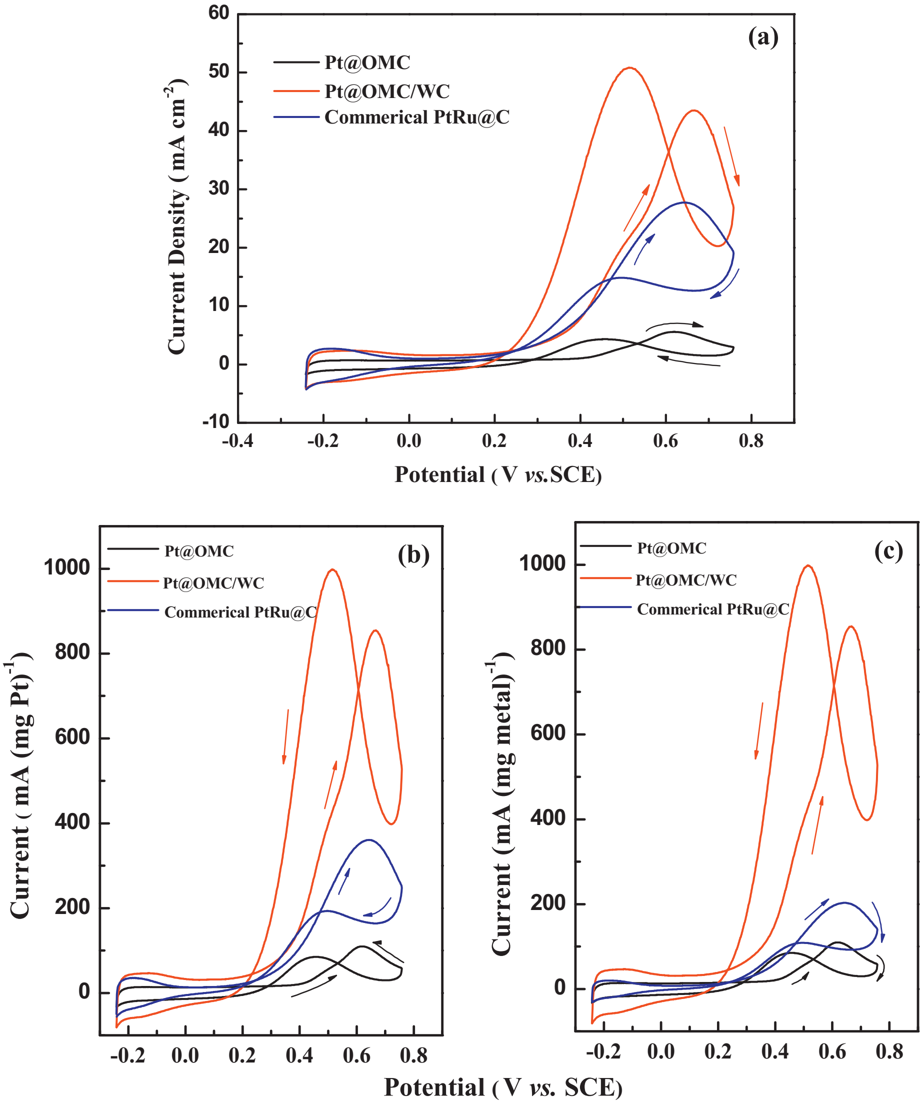


Fig. 8. Cyclic voltammograms of methanol electrooxidation on Pt@OMC, Pt@OMC/WC, and the commercial PtRu@C in 0.5 mol L^{-1} H_2SO_4 + 1.0 mol L^{-1} CH_3OH solution. Scan rate: 50 mV s^{-1}. Temperature: 30 °C.

corresponding data is 784 mA per mg of Pt. This is an exciting improvement since just adopting OMC/WC as the support material could cause a considerable reduction in the unit metal loading to achieve the same performance as the commercial PtRu@C. This is quite important to reduce the noble metal usage and consequently decrease the cost of the catalysts and fuel cells.

4. Summary

In summary, ordered 2D hexagonal mesoporous tungsten carbide (OMC/WC) composite nanomaterials have been successfully synthesized for the first time by the soft-template method. The ordered mesoporous OMC/WC composites have high surface areas and large pore volumes and narrow pore size distributions. Pt@OMC/WC demonstrates superior specific mass activity of MOR activity to the commercial PtRu@C by a factor of 2.4 (per mg Pt) and 3.2 (per mg metal). The higher specific mass activity is of interest and importance for noble-metal-economic catalysts identification and consequently for fuel cell development. Furthermore, the present work is expected to render a universal and feasible approach for the preparation of ordered mesoporous self-supported metal carbides.

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