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Pt-Ni-P nanocages with surface porosity as efficient bifunctional electrocatalysts for oxygen reduction and methanol oxidation[†]

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The structure- and composition-controlled synthesis of Pt-based nanocatalysts is highly important for improving their catalytic performance while reducing the overall use of precious Pt. Here, an effective strategy is developed to combine surface porosity, hollow cavities and metal-nonmetal incorporation engineering on Pt, resulting in ternary Pt-Ni-P mesoporous nanocages (Pt-Ni-P MNCs). Owing to the mesoporous surface, hollow structure and synergistic electronic effects derived from Pt, Ni, and P elements, the as-prepared Pt-Ni-P MNCs exhibit excellent electrocatalytic activity and long-term stability for both the oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR), enabling them to be promising ORR-MOR bifunctional electrocatalysts for direct methanol fuel cells.

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1. Introduction

Direct methanol fuel cells (DMFCs) represent a class of promising clean power sources and are especially important in powering portable electronic devices.^{1–3} The sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode and the methanol oxidation reaction (MOR) at the anode is the key obstacle for the commercialization of DMFCs.^{4,5} To date, Pt and Pt-based nanomaterials have been recognized as the most efficient electrocatalysts for both the ORR and MOR in DMFCs.^{6–12} However, a number of problems including high cost, limited utilization and their poisoning by strongly adsorbed species (*e.g.*, carbon monoxide) have greatly limited their large-scale practical application. Therefore, large efforts are currently being made to significantly increase the Pt utilization efficiency of DMFCs and reduce the extent of catalyst poisoning of Pt while maintaining suitable performance.

Efforts to boost the catalytic performance of Pt and increase the Pt utilization efficiency have been concentrated on the delicate structural design of Pt and Pt-based nanocatalysts.¹³⁻¹⁸ In this regard, hollow nanostructures with welldefined porous surfaces have special advantages over their counterparts with solid interiors and compact exteriors as they allow for effective use of both the outer and inner surfaces of the materials when used as catalysts.¹⁹⁻²¹ Another

alternative effective strategy is alloying or incorporating Pt with other transition metals to form bi-metallic or multimetallic Pt-based nanostructures.22-30 The foreign metal atoms could modify the electronic properties of Pt by charge transfer processes and lowers the adsorption energy of related reaction species onto the Pt surface due to the ligand or the electronic effect. Beyond this, one recent research trend in this field is the introduction of phosphorus (P), an inexpensive metalloid element consisting of abundant valence electrons, into Pt and Pt-based nanostructures. By using various strategies and P sources, a broad variety of P-containing Pt-based nanocatalysts have been developed which demonstrated superior electrocatalytic performance and CO tolerances.³¹⁻³⁵ Despite these advances, the synthesis of ternary Pt-non-precious-metal-P hollow nanostructures with a welldefined mesoporous surface is still challenging yet significant.

Herein, we demonstrate the synthesis of Pt–Ni–P mesoporous nanocages (Pt–Ni–P MNCs) by means of a facile strategy. The current strategy involves the template-assisted deposition of Pt mesoporous nanocages (Pt MNCs) and the subsequent Ni, P-co-incorporation into the pre-made Pt MNCs. The asfabricated ternary Pt–Ni–P nanoarchitectures integrate the structural advantages of hollow nanocages and mesoporous surfaces and the compositional properties of metal–nonmetal multicomponents, allowing for rational engineering of the density and reactivity of the active sites for electrocatalysis applications. As expected, the as-prepared Pt–Ni–P MNCs exhibit superior electrocatalytic activities towards both the ORR and MOR compared with binary Pt–Ni MNCs and commercial Pt/C, making them promising ORR–MOR bifunctional electrocatalysts for DMFCs.

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2. Experimental

2.1 Materials and chemicals

All chemicals and solvents were used as received without further purification. Nickel chloride hexahydrate (NiCl₂·6H₂O), sodium hypophosphite (NaH₂PO₂), sodium borohydride (NaBH₄), ammonium hydroxide solution (NH₃·H₂O), hydrofluoric acid (HF), tetraethyl orthosilicate (TEOS), ethanol (CH₃-CH₂OH), methanol (CH₃OH), perchloric acid (HClO₄) and Lascorbic acid (AA) were purchased from Aladdin Industrial Corporation (Shanghai, China). Potassium tetrachloroplatinate (K₂PtCl₄), 3-aminopropyltrimethoxysilane (APTMS) and Pluronic F127 were provided by Sigma-Aldrich. Commercial Pt/C catalysts (20 wt%) were ordered from Alfa Aesar.

2.2 Preparation of SiO₂ spheres

Typically, 200 mL of ethanol was added to a solution containing 15.2 mL of H_2O and 6.4 mL of $NH_3 \cdot H_2O$. After stirring vigorously for 1 h at room temperature, 12 mL of TEOS was injected into the above solution. After 3 h, the sample was collected by centrifugation at 10 000 rpm for 5 min, followed by washing with ethanol and water. The product was finally dried at 50 °C in a vacuum oven for 10 h.

2.3 Preparation of Pt MNCs

The obtained SiO₂ spheres were initially modified with an amino group. 50 mg of SiO₂ particles were dissolved in a mixture containing 10 mL of isopropanol and 200 µL of APTMS. Then the mixed solution was heated to reflux at 80 °C for 12 h. The functionalized SiO₂ spheres were collected by centrifugation at 6000 rpm for 3 min, followed by washing with ethanol and water, and dried at 40 °C in a vacuum oven for 10 h. In a typical synthesis of Pt MNCs, the functionalized SiO₂ spheres (2 mg) and Pluronic F127 (20 mg) were dispersed in 2 mL of K₂PtCl₄ solution (20.0 mM). After Pluronic F127 was completely dissolved, 2 mL of AA solution (0.1 M) was added to the above solution. Then the mixed solution was sonicated for 1 h at 35 °C. The as-formed SiO₂@Pt product was collected by centrifugation at 6000 rpm for 10 min and washed for 3 cycles with water. The SiO2@Pt was then redispersed in 10 wt% HF (20 mL) for 12 h to erode the SiO₂ templates. The final Pt MNCs were collected by centrifugation at 3000 rpm for 10 min and washed with water 5 times. Finally, the Pt MNCs were re-dispersed in H₂O (5 mL) for further use.

2.4 Preparation of Pt-Ni-P MNCs

0.5 mL of NiCl₂·6H₂O (20.0 mM) and 4.5 mL of NaH₂PO₂ (20.0 mM) solutions were added to the as-prepared Pt MNC dispersion under stirring, then, a freshly prepared NaBH₄ solution (2 mL, 0.2 M) solution was quickly added. After stirring for 10 min at room temperature, the slurry was washed with water and collected by centrifugation at 3000 rpm for 5 min. The final product was dried at 50 °C in a vacuum oven for 10 h before the electrochemical tests.

2.5 Characterization

The surface morphology and structure of the catalysts were characterized using a scanning electron microscope (SEM) (ZEISS SUPRA 55) with an accelerating voltage of 15 kV. The hollow structure of the catalysts was investigated using a transmission electron microscope (TEM) (JEOL JEM-2100F) operated at 200 kV equipped with an energy dispersive X-ray spectrometer (EDX) analyzer. The wide-angle X-ray diffraction (XRD) analysis was performed on an X-ray diffractometer (PANalytical X'Pert PRO) with Cu K α radiation ($\lambda = 0.1542$ nm) at 40 kV and 30 mA. The X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB MK II spectrometer (VG Scientific, UK) with Al Ka X-ray radiation for excitation. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were carried out by using an Elan DRC-e instrument. Nitrogensorption isotherms were collected using a model Autosorb IQ3 instrument (Quantachrome, USA). The surface areas of the samples were calculated by the Brunauer-Emmett-Teller (BET) method. The pore-size distribution was derived from the desorption branch using the Barrett-Joyner-Halenda (BJH) method.

2.6 Electrochemical measurements

Electrochemical measurements were performed in a conventional three-electrode cell consisting of a working electrode, an Ag/AgCl (saturated KCl) reference electrode and a Pt wire counter electrode using an electrochemical workstation (CHI 760E). All potentials, if not specified, were recorded relative to the reversible hydrogen electrode (RHE) in this work.

As for ORR measurements, the working electrode was a glassy-carbon rotating disk electrode (RDE) (3 mm in diameter) modified by the catalyst. 2 mg of the Pt-Ni-P MNCs was dispersed in 1 mL of deionized water and sonicated for 20 min to produce an ink. Then, the glassy-carbon RDE was coated with the catalyst ink to achieve a Pt loading of 28.2 μ g cm⁻² and allowed to air dry. Following catalyst addition, 5 µL of Nafion (0.5 wt%) was coated on the catalyst-modified glassy-carbon RDE surface to ensure catalyst adhesion. The glassy-carbon RDE modified by other samples was prepared with similar procedures and the Pt loading on the electrode was kept the same for different catalysts. The ORR evaluation was performed by using a RRDE-3A rotation system (ALS Co. Ltd, Japan). Linear sweep voltammetry (LSV) measurements were carried out in an oxygen saturated 0.1 M HClO₄ solution at a scan rate of 5 mV s⁻¹ and rotation rate of 1600 rpm. Chronoamperometric (CA) investigation for the ORR was conducted in an oxygen saturated 0.1 M HClO₄ solution at 0.9 V (vs. RHE) with a rotation rate of 1600 rpm. The kinetic currents were calculated using the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d}$$

where j, j_k and j_d represent the measured, kinetic and diffusionlimited current densities, respectively. The electron transfer number (n) and the peroxide yield (H₂O₂%) could be calculated as follows:

$$n = \frac{4I_{\rm D}}{(I_{\rm D} + I_{\rm R}/N)}$$

$$H_2O_2\% = {200I_R\over (I_DN + I_R)}$$

where I_D and I_R are the disk current and ring current, respectively; and N = 0.4286 is the current collection efficiency of the Pt ring.

As for MOR measurements, the working electrode was a glassy carbon electrode (GCE) modified with the catalyst. The preparation process of the working electrodes was the same as that of the ORR measurements. Cyclic voltammograms (CV) were recorded in a solution of 0.5 M N₂-saturated H₂SO₄ solution containing 1 M CH₃OH at a scan rate of 50 mV s⁻¹. CA measurements were carried out in a 0.5 M H₂SO₄ solution containing 1 M CH₃OH at a potential of 0.8 V (ν s. RHE). For CO stripping measurements, high-purity CO was pre-adsorbed on the working electrode by bubbling it in a 0.5 M H₂SO₄ solution for 30 min while holding the electrode potential at 0.24 V (ν s. RHE). After the solution was purged with N₂ for 20 min to remove the remaining CO, the CO stripping curve was obtained by CV at a scan rate of 50 mV s⁻¹.

3. Results and discussion

As illustrated in Fig. 1, the Pt-Ni-P MNCs were fabricated by a three-step strategy. The first step involves the synthesis of SiO₂@Pt core-shell mesoporous nanospheres. SiO₂ spheres (~180 nm in diameter), which were obtained by the Stöber method,³⁶ were used as the hard-templates for the deposition of Pt nanostructures (Fig. S1[†]). The presence of F127 as the structure-directing agent for the growth of Pt contributes to the formation of a well-defined mesoporous surface on the asdeposited Pt nanostructures.37,38 After the removal of the SiO₂ templates by HF solution treatment in the second step, Pt MNCs with uniform morphology can be produced (Fig. S2[†]). In the third step, the pre-constructed Pt MNCs served as the precursors for Ni, P-co-incorporation by using NiCl₂, NaH₂PO₂ and NaBH₄ as the Ni source, P source and reduction agent, respectively. The Ni, P-co-incorporation step could be achieved at room temperature without the need for high reaction temperature and dangerous phosphorus sources.

The detailed morphology and structure features of the assynthesized Pt–Ni–P MNCs are characterized by SEM and TEM. The low magnification SEM image (Fig. 2a) reveals that well-dispersed Pt–Ni–P MNCs with sphere-like morphology are generated in a high yield. The average diameter of the as-formed



Fig. 1 Schematic illustration of the formation process of Pt-Ni-P MNCs.



Fig. 2 (a and b) SEM and (c and d) TEM images of Pt–Ni–P MNCs. The inset in (c) shows the SAED pattern. (e) HRTEM image of the edge part of a single Pt–Ni–P MNC. (f) The Fourier-filtered lattice fringe image of the marked area in (e). The inset in (f) displays the corresponding FFT pattern.

Pt-Ni-P MNCs is around 200 nm (Fig. S3[†]). A magnified SEM image clearly reveals the mesoporous surface of the Pt-Ni-P MNCs (Fig. 2b). Nitrogen adsorption-desorption isotherms further reveal the mesoporous features of the Pt-Ni-P MNCs (Fig. S4a[†]). The hollow structure of these Pt-Ni-P MNCs is clearly confirmed by TEM observation (Fig. 2c), and an enlarged TEM image further confirms that the thickness of the shell is around 20 nm (Fig. 2d). The surfaces of the Pt-Ni-P MNCs consist of abundant tiny interconnected nanoparticles with a diameter of around 3 nm, which could serve as catalytically active sites during electrocatalysis. The polycrystallinity feature of the as-prepared Pt-Ni-P MNCs is confirmed by the selected area electron diffraction (SAED) pattern (inset of Fig. 2c). Fig. 2e shows a high-resolution TEM (HRTEM) image of the edge part of a single Pt-Ni-P MNC. The lattice fringes with a spacing of 0.23 nm correspond to the (111) planes of the Pt-based facecentered cubic (fcc) structure, as also revealed by the corresponding fast Fourier transform (FFT) pattern (Fig. 2f).

EDX analysis validates the presence of Pt, Ni and P elements in the Pt–Ni–P MNCs (Fig. S5†). Quantitative analysis results from the EDX spectrum show the composition of Pt–Ni–P MNCs to be 61.39 at% Pt, 11.87 at% Ni, and 26.74 at% P, which is almost in accordance with the ICP-MS data (62.73 at% Pt, 10.56 at% Ni, and 26.71 at% P). Fig. 3a shows the high-angle annular dark field-scanning TEM (HAADF-STEM) image of a single



Fig. 3 (a) HAADF-STEM image and (b–d) elemental mapping images of a single Pt-Ni-P MNC.

Pt–Ni–P MNC, which also demonstrates that the inner cavities and well-defined surface porous structure. The elemental mapping images reveal the Pt, Ni and P elements are homogeneously distributed throughout the whole Pt–Ni–P MNC (Fig. 3b–d). These results indicate the Ni and P elements have been successfully incorporated into the Pt structure, forming ternary Pt–Ni–P nanostructures.

The crystallinity and phase purity of the Pt–Ni–P MNCs are confirmed by wide-angle XRD analysis. The Pt–Ni MNC counterparts without the P component were also synthesized for comparison (Fig. S6†). As shown in Fig. 4a, all diffraction peaks observed for the samples can be assigned to the corresponding (111), (200), (220), (311) and (222) planes of the fcc Pt-based



Fig. 4 (a) XRD patterns of the Pt–Ni–P MNCs and Pt–Ni MNCs. The inset image shows the slow scan XRD profile at $2\theta = 35-45^{\circ}$. XPS spectra of the Pt 4f (b), Ni 2p (c) and P 2p (d) for the Pt–Ni–P MNCs and Pt–Ni MNCs.

crystal structure. No other impurity diffraction peaks were observed from the XRD pattern of Pt–Ni–P MNCs, indicating the formation of a ternary alloyed structure. When compared with standard diffraction patterns of pure Pt (JCPDS no. 65-2868), the diffraction peaks of Pt–Ni MNCs clearly shift to a higher 2θ angle due to the partial substitution of larger Pt atoms by smaller-sized Ni atoms. It can also be seen that the diffraction peaks of Pt–Ni–P MNCs exhibit a slightly negative shift relative to Pt–Ni MNCs, suggesting the expansion of the lattice due to the introduction of P atoms.³⁹

The surface composition and electronic structure of the Pt-Ni-P MNCs and Pt-Ni MNCs are further investigated by XPS. The XPS survey spectrum further confirms the presence of Pt, Ni and P elements on the surface of Pt-Ni-P MNCs (Fig. S7[†]). In the Pt 4f XPS spectrum of Pt-Ni-P MNCs (Fig. 4b), two peaks centered at 74.5 eV and 71.3 eV could be assigned to $Pt^0 4f_{5/2}$ and Pt⁰ 4f_{7/2}, respectively. A small percentage of Pt exists as Pt^{II} in Pt-Ni-P MNCs. Meanwhile, a slight negative shift (0.31 eV) of the Pt 4f binding energy for the Pt-Ni-P MNCs compared with the Pt-Ni MNCs is also observed. As seen from the Ni 2p spectrum, the majority of the surface Ni was in the form of Ni^{II}. Positive shifts are observed for the binding energy of Ni 2p in Pt-Ni-P MNCs relative to the Pt-Ni MNCs (Fig. 4c). In the P 2p spectrum, the two peaks of P 2p at 131.4 and 133.3 eV can be ascribed to elemental P^0 and oxidized P species, respectively (Fig. 4d). The binding energy position of the P^0 peak exhibits a positive shift compared with that of pure P (130.4 eV).40,41 The presence of oxidized species (Pt^{II}, Ni^{II}, and P^I) arises from the superficial oxidation of the Pt-Ni-P MNCs when exposed to air, as also reported in other previous studies.^{31-34,42} The results reveal that there is a strong interaction between the Pt, Ni and P atoms, which should also be due to the formation of the Pt-Ni-P alloy. Based on the above characterization and analysis results, it can be concluded that ternary Pt-Ni-P nanostructures with a well-defined mesoporous surface and hollow cavities were successfully synthesized. Such a unique nanoarchitecture could integrate the structural advantages of hollow nanocages and the mesoporous structure and the compositional properties of metal-nonmetal multicomponents, allowing for rational engineering of the density and reactivity of the catalytically active sites.

We first evaluate the electrocatalytic performance of our asmade Pt-Ni-P MNCs towards the ORR in acidic media, benchmarked against the Pt-Ni MNCs and commercial Pt/C catalyst. The BET surface areas of these three catalysts are measured to be 21.47 $\text{m}^2 \text{g}^{-1}$ for the Pt–Ni–P MNCs, 20.44 $\text{m}^2 \text{g}^{-1}$ for the Pt– Ni MNCs, and 85.36 m² g⁻¹ for the Pt/C (Fig. S4^{\dagger}). The electrochemically active surface areas (ECSAs) of the electrocatalysts can be calculated from the charges associated with the areas of both the desorption and adsorption hydrogen region after double-layer correction in CV curves recorded in N2-purged 0.5 M H₂SO₄ solution with a scan rate of 50 mV s⁻¹ (Fig. S8[†]). Accordingly, the ECSAs are calculated to be 44.3 m² g_{Pt}^{-1} 35.3 m² g_{Pt}^{-1} and 57.6 m² g_{Pt}^{-1} for Pt–Ni–P MNCs, Pt–Ni MNCs and Pt/C, respectively. We further performed electrochemical double-layer capacitance (C_{dl}) measurements. The corresponding C_{dl} values of the catalyst-modified electrodes can be

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calculated using the slope extracted from the linear relationship of the current density with the increasing scan rates. The $C_{\rm dl}$ values are evaluated to be 0.27 mF cm⁻², 0.24 mF cm⁻², and 0.32 mF cm⁻² for Pt–Ni–P MNCs, Pt–Ni MNCs and Pt/C, respectively (Fig. S9†).

Fig. 5a shows the ORR polarization curves of the electrocatalysts. The Pt-Ni-P MNCs exhibit more positive onset potential (E_{onset} , 0.99 V) and half-wave potential ($E_{1/2}$, 0.94 V) compared to the Pt-Ni MNCs ($E_{\text{onset}} = 0.97, E_{1/2} = 0.91$ V) and commercial Pt/C catalyst ($E_{\text{onset}} = 0.92$ V, $E_{1/2} = 0.85$ V), suggesting the easier reduction of oxygen on the surface of Pt-Ni-P MNCs. The Tafel slope of the Pt-Ni-P MNCs (62.4 mV dec^{-1}) is lower than those of the Pt-Ni MNCs (76.3 mV dec⁻¹) and Pt/C (63.5 mV dec⁻¹), indicating that Pt-Ni-P MNCs are more prone to catalyzing oxygen reduction (Fig. 5b). The kinetic currents of the catalysts are derived from the ORR polarization curves using the Koutecky-Levich equation. Fig. 5c and d compare the kinetic currents of these catalysts at 0.9 V, normalized to the ECSA (specific mass) and the Pt loading mass (mass activity), respectively. The Pt-Ni-P MNCs show a specific activity of 2.35 mA cm $^{-2}$, which is 3.5 and 9.0-times higher than that of the Pt-Ni MNCs (0.67 mA cm⁻²) and commercial Pt/C $(0.26 \text{ mA cm}^{-2})$ catalysts, respectively. The mass activity of the obtained Pt–Ni–P MNCs (1.21 mA μg_{Pt}^{-1}) exhibited 2.1 and 7.6fold enhancement as compared to that of the Pt-Ni MNCs (0.58 mA μg_{Pt}^{-1}) and commercial Pt/C (0.16 mA μg_{Pt}^{-1}), respectively. In order to study the influence of composition on the catalytic performance, we further compared various Pt-Ni-P catalysts with different Ni contents and demonstrated the superior ORR activity of our typical Pt-Ni-P MNCs (Fig. S10[†]).

The polarization curves of the Pt–Ni–P MNCs at different rotation rates are recorded to further examine the ORR kinetics. Fig. S11a and b† show the rotation-rate-dependent current– potential curves of the Pt–Ni–P MNCs and the corresponding K–L plots at different potentials, respectively. Based on the K–L plots, the electron transfer number is calculated to be around 4,



Fig. 5 (a) ORR polarization curves of the catalysts in an O₂-saturated 0.1 M HClO₄ solution with a scan rate of 5 mV s⁻¹ and a rotation rate of 1600 rpm. (b) The corresponding Tafel plots. (c) Specific activities and (d) mass activities of the electrocatalysts at 0.9 V.

indicating an efficient four-electron reaction route is the main reaction on Pt–Ni–P MNCs for the ORR process. Rotating ringdisk electrode (RRDE) investigations reveal that the yield of H_2O_2 for Pt–Ni–P MNCs is lower relative to that of the Pt/C, implying that the production of H_2O_2 is hindered in the process of the ORR catalyzed by Pt–Ni–P MNCs (Fig. S11c†). The electron transfer number obtained from RRDE experiments is determined to be around 4 (Fig. S11d†), which further testifies the four-electron reaction pathway for the ORR.

The durability test of the Pt-Ni-P MNCs and commercial Pt/ C catalysts toward the ORR is investigated through an accelerated durability test (Fig. S12a and b^{\dagger}). The degradation of $E_{1/2}$ of the Pt-Ni-P MNs (15 mV) is much lower than that of the Pt/C (43 mV) after 10 000 cycles. In addition, the mass activity of the Pt-Ni-P MNCs drops by only 22.3% after 10 000 cycles, while the commercial Pt/C catalyst decreases by 41.5% (Fig. S12c[†]). Chronoamperometric investigations are further carried out to compare the stability of the Pt-Ni-P MNCs and Pt/C. After testing for 5 h, the Pt-Ni-P MNCs retain 77.98% of their initial current density, which is higher than that of the Pt/C (48.76%) (Fig. S12d†). XPS was further conducted on Pt-Ni-P MNCs after the ORR durability test (Fig. S13[†]). In the Pt 4f spectrum, both the metallic state of Pt and a small amount of oxidized Pt species can be detected (Fig. S13a[†]). In the Ni 2p spectrum, the surface Ni component is present in the form of Ni^{II} owing to the exposure to air (Fig. S13b[†]). The decrease in Ni content compared with that before the ORR test could be ascribed to the chemical etching of Ni from the outer surface of Pt-Ni-P MNCs during testing.42,43 Differing from those of the samples before the ORR (Fig. 4d), the P 2p peaks disappear after a long-term durability test (Fig. S13c[†]), indicating that the P species at the surface have been etched or dissolved into the electrolyte, as reported in previous studies.42,44,45 EDX analysis confirms that Pt, Ni and P elements are still present in the Pt-Ni-P MNCs after the durability test (Fig. S14[†]), while the Ni content (8.54 at%) and P content (19.21 at%) are slightly lower than those before the ORR test (11.87 at% Ni and 26.74 at% P) due to the partial dissolution of P and Ni at the surface.

We also assess the catalytic performance our catalysts towards the MOR in 0.5 M H₂SO₄ containing 1.0 M CH₃OH. To evaluate the electrocatalytic activity, the MOR current was normalized to the ECSA (specific activity) and the mass loading of Pt (mass activity), respectively. Fig. 6a shows the specific activities of the catalysts. The forward peak current density on the Pt-Ni-P MNCs is 2.28 mA cm⁻², which is 1.4 and 4.1 times higher than that of the Pt-Ni MNCs (1.62 mA cm⁻²) and commercial Pt/C (0.56 mA cm $^{-2}$), respectively. As for the mass activities (Fig. 6b), the Pt-Ni-P MNCs yield a forward peak current density of 1.22 mA μg_{Pt}^{-1} , about 1.4 and 2.8 times greater than those of the Pt–Ni MNCs (0.87 mA μg_{Pt}^{-1}) and Pt/C $(0.44 \text{ mA} \mu g_{Pt}^{-1})$, respectively. Moreover, our Pt–Ni–P MNCs also exhibit a higher mass activity compared with some previously reported Pt-based catalysts (Table S1[†]). Chronoamperometric curves were recorded to probe the stability of the catalysts (Fig. 6c). The Pt-Ni-P MNCs show a higher specific current density and slower current decay than the Pt-Ni MNCs and commercial Pt/C during the whole test process. The CO



Fig. 6 (a) Specific activities and (b) mass activities of the MOR for the catalysts recorded in a mixture of 0.5 M $\rm H_2SO_4$ and 1 M CH_3OH at a scan rate of 50 mV s⁻¹. (c) Chronoamperometric curves for the MOR at 0.8 V. (d) CO stripping voltammograms.

tolerance of catalysts is confirmed by CO stripping curves. As shown in Fig. 6d, we can see that the onset potential of CO anodic oxidation on the Pt–Ni–P MNCs (0.89 V) is obviously more negative than that on the Pt–Ni MNCs (0.90 V) and commercial Pt/C (0.92 V). The results demonstrate that the Pt–Ni–P MNCs have an enhanced catalytic activity and CO-tolerant performance in the MOR due to the incorporation of P element.

As for the enhancement in electrocatalytic performance towards both the ORR and MOR, the unique electronic and surface structure effects derived from ternary Pt–Ni–P MNCs are believed to make a major contribution (Fig. 7). On the one hand, the mesoporous surface and hollow structure not only increase the catalytically active area accessible to the reactant molecules but also improve electron mobility in the skeletons of the nanocages and provide effective mass transfer in the electrocatalysis reactions. On the other hand, the synergistic electronic effects derived from Pt, Ni, and P elements could modify the electronic properties of the Pt by charge transfer processes and lowers the adsorption energy of related reaction species onto the Pt surface, and thus facilitate ORR and MOR catalysis. In



Fig. 7 Schematic illustration of the advantages of the Pt–Ni–P MNCs as an efficient bifunctional electrocatalyst for the ORR and MOR.

addition, the structural stability of the as-formed mesoporous nanocages could effectively prevent particle aggregation and Ostwald ripening under electrocatalysis operation conditions;, endowing them with superior catalytic stability and durability.

4. Conclusions

In summary, we have developed an effective strategy to achieve surface porosity, hollow cavities and metal–nonmetal incorporation engineering on Pt to boost the electrocatalytic performance. The as-fabricated ternary Pt–Ni–P nanoarchitectures integrate the structural advantages of hollow nanocages and mesoporous surfaces and the compositional properties of metal–nonmetal multicomponents. As a result, structural and electronic effects remarkably enhance the activity and durability in electrocatalysis, making Pt–Ni–P MNCs an efficient ORR– MOR bifunctional electrocatalyst for DMFCs. This study provides an alternative avenue in designing highly efficient Ptbased nanocatalysts by the combination of geometrically and compositionally favorable factors.

Conflicts of interest

There are no conflicts to declare.

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