Pt Nanoparticles Loaded on $W_{18}O_{49}$ Nanocables–rGO Nanocomposite as a Highly Active and Durable Catalyst for Methanol Electro-Oxidation

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ABSTRACT: Highly active and durable electrocatalysts are vital for commercialization of direct methanol fuel cells. In this work, a three-dimensional nanocomposite consisting of platinum nanoparticles, $W_{18}O_{49}$ nanocables, and reduced graphene oxide composite (Pt/$W_{18}O_{49}$ NCs–rGO) has been prepared as an electrocatalyst for methanol oxidation reaction (MOR). The catalyst is prepared through a two-step method. The $W_{18}O_{49}$ nanocables and the reduced graphene oxide composite are prepared by a solvothermal process. Then, Pt nanoparticles are loaded on the $W_{18}O_{49}$ nanocables and the reduced graphene oxide composite by a hydrogen reduction at ambient condition. The obtained catalyst has a special three-dimensional architecture consisting of two-dimensional nanosheets, assembled one-dimensional nanocables, and the loaded nanoparticles on their surface. The Pt/$W_{18}O_{49}$ NCs–rGO catalyst shows 1.56 time mass activities than the Pt/C, with the current density of the forward anodic peak reaching 1624 mA/mgPt at 0.854 V versus reversible hydrogen electrode potential in 0.1 M HClO4 and 0.5 M CH3OH mixed electrolyte. It also shows a strong antipoisoning property toward CO. For the durability testing, the current density of Pt/W18O49 NCs shows 1.56 time mass activities than the Pt/C, with the current density of the forward anodic peak reaching 1624 mA/mgPt at 0.854 V versus reversible hydrogen electrode potential in 0.1 M HClO4 and 0.5 M CH3OH mixed electrolyte. It also shows a strong antipoisoning property toward CO. For the durability testing, the current density of Pt/W18O49 NCs–rGO catalyst shows a 37% decay, whereas the current of Pt/C catalyst shows a 41% degradation from 600 to 3600 s at 0.7 V. The high activity toward MOR, good antipoisoning for intermediate products, and excellent stability are ascribed to strong metal–support interaction effects between the Pt nanoparticles and the $W_{18}O_{49}$ NCs.

1. INTRODUCTION

Platinum-based catalysts were used in both electrodes of direct methanol fuel cells (DMFCs). Preparing platinum nanoscale catalysts with special morphologies, such as platinum nanoparticles,6–10 platinum nanowork,11 and other designed Pt nanostructures,12–14 enable to improve the activity of platinum. But, it will lose active sites during working, which results from poisoning of intermediate species during anode reaction process in DMFCs.15–17 To overcome this problem, various metal elements, such as Pd, Ni, and others were used for incorporation into platinum to prepare alloy catalysts.15–17 It not only reduces the amount of platinum but also improves the ability of CO tolerance via a bifunctional mechanism.18–20 Unfortunately, many alloy catalysts are not stable at the inclement circumstance in DMFCs. Great efforts have been made to enhance the stability; some compositions are easy to dissolve from the reaction interface of the alloy catalyst.21–25 Transition-metal oxides as a support composite with noble-metal catalysts have attracted much attention due to their high activity, stability, special microstructure and morphology, and other properties.6–28 In previous works, our group found that platinum and transition-metal oxide composites, such as Pt/MoO329 and Pt/W18O49,31 can improve both anti-CO-poisoning ability and stability in harsh circumstance. It was ascribed to the contribution of a strong metal–support interaction (SMSI). A reversible reaction between $WO_3$ and tungsten bronze compound ($H_2WO_3$) is an important medium...
in the methanol electro-oxidation reaction process. It is helpful for the small molecules adsorption on the Pt/W18O49 catalyst surface. Meanwhile, the oxygen defect of W18O49 is beneficial for oxygen transport from catalyst to reaction interface. But, the low conductivity between the reaction interfaces limits the rate of electrocatalytic reaction. Although we can find some transition-metal oxides with a better conductivity, such as Mo4O11, Ti4O7, and W18O49, sometime, it is still not good enough for the electrocatalytic reactions in DMFCs. The conductivity of the catalysts still needs to be improved.

In this work, platinum nanoparticles and W18O49 nanocables loaded on reduced graphene oxide nanosheet composite (Pt/W18O49 NCs−rGO) as a new three-dimensional (3D) nanostructured catalyst for methanol oxidation reaction was designed and prepared successfully via a self-assembly method. The methanol oxidation reaction (MOR) and CO stripping tests were used to compare the electrocatalytic activities of the as-synthesized catalyst and commercial Pt/C catalyst. The Pt/W18O49 NCs−rGO shows better activity, durability, and anti-CO-poisoning ability than the commercial Pt/C catalyst, which can be attributed to the highly dispersed platinum nanoparticles and the SMSI between Pt, W18O49, and rGO. Various characterizations provide evidence of the mechanism of enhanced catalytic properties. The present work not only provides a promise catalyst for methanol electrocatalytic oxidation but also presents an approach for designing various multifunctional materials.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Nanostructure Pt/W18O49 NCs−rGO Catalyst. Graphene sheet as a conductive material was designed to enhance the conductivity of the catalyst. The oxygenous group on the surface of graphene (especially graphene oxide GO) would provide an attachment active site during the growing W−O Magnéli phase. According to the previous reports, the ethanol solvothermal condition of producing the W18O49 nanocables (W18O49 NCs) and solvothermal condition for reduced graphene oxide are very similar. W18O49 nanocables (W18O49 NCs), a substoichiometric tungsten oxide, can in situ grow and reduce graphene oxide nanosheet to produce W18O49 NCs−rGO in an ethanol−water mixture solvothermal system. Finally, platinum nanoparticles were loaded onto the tungsten oxide to prepare a structural and functional optimization catalyst for methanol oxidation reaction.

Figure S1 (Supporting Information) shows the X-ray powder diffraction (XRD) patterns of W18O49 NCs−rGO and Pt/W18O49 NCs−rGO samples. It indicates that the as-prepared product is a pure monoclinic phase W18O19 (JCPDs No. 05-0392). The (010) peak shows the highest intensity, suggesting a preferred crystal growth of the W18O49 NCs along [010]. No diffraction peaks of graphene was observed. After Pt loading, broad platinum (111), (200), and (220) peaks (JCPDS No. 04-0802) are observed. Morphology and microstructure of the sample were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Figure 1a shows that the as-synthesized catalyst and commercial Pt/C catalyst. The Pt/W18O49 NCs−rGO shows better activity, durability, and anti-CO-poisoning ability than the commercial Pt/C catalyst, which can be attributed to the highly dispersed platinum nanoparticles and the SMSI between Pt, W18O49, and rGO. Various characterizations provide evidence of the mechanism of enhanced catalytic properties. The present work not only provides a promise catalyst for methanol electrocatalytic oxidation but also presents an approach for designing various multifunctional materials.

Figure 1. TEM image (a) and SAED (b) of Pt/W18O49 NCs−rGO. (c) HRTEM image of Pt/W18O49 NCs−rGO. (d) HRTEM image of single W18O49 NC with a Fourier transformed (FT) pattern inset from the marked yellow region. (e) In situ observation of a Pt nanoparticle in Pt/W18O49 NCs−rGO composite under the irradiation of electron beam in HRTEM. (f) The particle size-distribution statistics of Pt particles in (a).
rGO composite. The surface of the Pt nanoparticle is composed of alternating the \{100\}, \{111\} facets and kinks at the corners, which normally are the active sites for catalytic reactions. Figure 1f shows the particle size distribution Statistics of Pt nanoparticles, with a mean size of 2.71 ± 0.39 nm. It was reported that platinum nanoparticles with 2–4 nm size exhibit the highest activity for electrocatalysis.36–38 The Pt loading in Pt/W18O49 NCs–rGO is 18.75 wt % analyzed by induced coupled plasma-atomic emission spectroscopy (ICP-AES).

A Pt nanoparticle on the W18O49 NCs was observed continuously during the electron beam irradiation under an acceleration voltage of 200 kV, as shown in Figure 2. As time went by, the edge atom pointed by the arrow moved with the energy gained from irradiation. The movement of the edge atom exhibits a low activation energy of the bond breaking. It implies a high activity of the catalyst.

It is noted that there are defects in W18O49 NCs as pointed by the two arrows (Figure S4a). From the enlarged part of the defect region (Figure S4b), the shear plane marked by arrows is the main crystal structure of the Magnéli phase. Figure S4c presents another part of the same crystal, showing relatively perfect crystal planes of (010) and (103). Figure S4d shows the computer-simulated atom sites, further indicating that the W18O49 NCs grow along the 010 direction.

Raman spectroscopy and thermogravimetry (TG) analysis were introduced for further characterization on the W18O49 NCs–rGO. Raman spectra of GO, W18O49 NCs, and W18O49 NCs–rGO are compared in Figure S5. The peaks located at 247 and 813 cm−1 for W18O49 NCs and W18O49 NCs–rGO are due to the stretching mode of the O–W–O and W–O bonds. For the spectrum of graphene oxide, two broad peaks at about 1334 and 1596 cm−1 can be assigned to the D and G peaks of graphene nanosheets. The D band is stronger than the G band in the spectrum of graphene oxide, which can be ascribed to a disordered structure of the surface oxygenous groups.39,40 But the intensity ratio of I_D/I_G does not show an obvious change after the reduction. It could be ascribed to the disordered structure of rGO, which is induced by interactions between W18O49 NCs and graphene. The O–W–O bond, which connects W18O49 NCs and graphene, provided a probable bridge for the electron transport to the delocalized δ bond of graphene.41,42 The weight loss of W18O49 NCs–rGO or Pt/W18O49 NCs–rGO sample under heat treatment in air can be an evidence of the carbon existing in the composite. From Figure S6, a mass loss is observed before 200 °C for both samples, which may be due to dehydration. Another mass loss at 561 °C for W18O49 NCs–rGO may be due to the carbon oxidation reaction. The latter mass loss is actually a combination process of graphene oxidation and the oxidation of W18O49 to WO3. The gained mass is much less than the lost one, so it shows a serious mass loss. For Pt/W18O49 NCs–rGO, carbon is lost at a lower temperature, 458 °C, because of the loading of Pt nanoparticles on W18O49 NCs–rGO. The loading of Pt nanoparticles plays a key role in the catalysis of carbon oxidation reaction. The activation energy of the carbon oxidation reaction was reduced, which means there is an interaction between Pt catalyst and the W18O49 NCs–rGO support.

To characterize the change in oxidation states during synthesis, X-ray photoelectron spectroscopy (XPS) analyses were carried out for the samples of W18O49 NCs, W18O49 NCs–rGO, and Pt/W18O49 NCs–rGO. Figure S7a shows the deconvolution results of W4f peaks of W18O49 NCs, W18O49 NCs–rGO, and Pt/W18O49 NCs–rGO. The specific deconvolution results are listed in Table S1. In pure W18O49 NCs, the W6+ and W5+ are correlated to the binding energy at 36.7 and 37.8 eV of the W 4f5/2 peak, the relative content of W6+ was 0.83 at the surface. When W18O49 NCs were combined with rGO to form W18O49 NCs–rGO, the W 4f5/2 peaks related to W6+ and W5+ were moved to 37.2 and 38.3 eV, respectively. The relative content of W6+ increases to 0.89 on the surface. During the solvothermal process, GO was reduced to rGO, and the oxygen became a bridge to connect the W18O49 NCs and rGO. Excess W6+ ions remained in the material. After Pt loading, the relative content of W6+ was back to 0.72 on the surface, the W 4f5/2 peaks related to W5+ and W6+ shifted to 37.8 and 38.2 eV, respectively. The dissolving hydrogen reduces W6+ to W5+. These shifts indicate that the interactions exist among the Pt nanoparticles, W18O49 NCs, and rGO. The coexistence of W6+ and W5+ in Pt/W18O49 NCs–rGO is beneficial for the hydrogen spillover and oxygen buffering effects, which can contribute to the improved tolerance toward intermediate species and enhanced electrocatalytic activity.

The catalytic activity of Pt is normally determined by zero-valence Pt0 and its oxides (PtO and/or PtO2). The XPS spectra of Pt 4f in Pt/W18O49 NCs–rGO and Pt/C were deconvoluted to reveal the oxidation species (Figure S7b). The binding energy at 71.3, 72.2, and 75.3 eV for the Pt 4f7/2 peak, together with three corresponding subpeaks at 74.6, 75.5, and 78.6 eV for Pt 4f5/2 peak in Pt/W18O49 NCs–rGO corresponded to Pt0, PtO, and PtO2, respectively.43,44 The peaks positions of Pt in Pt/W18O49 NCs–rGO are lower than those of the Pt/C. For example, the peak position of zero-valence Pt0 in the Pt/W18O49 NCs–rGO is left-shifted about 0.2 eV compared to that of Pt0 of the Pt/C due to a strong metal–support interaction effect.43,45,46 The actual Pt species loading was obtained by integrating the peak emission line (Table S2). The percent ratio of Pt with the higher valence states in the Pt/W18O49 NCs–rGO (57.76%) is equivalent to those in the Pt/C (57.34%). Normally, the high valence states of Pt show high catalytic activity toward oxidation.
2.2. Electrocatalytic Performance of Pt/W18O49 NCs−rGO for the MOR and Anti-CO-Poisoning Test. The small size of Pt nanoparticles and possible interaction of between Pt catalyst and the W18O49 NCs−rGO support in W18O49 NCs−rGO are favorable to enhance its catalytic performance. It is normally believed that the high catalytic current and the high stability at a given applied potential were two important factors for a good catalyst in methanol electro-oxidation. Pt/W18O49 NCs−rGO with 18.75 wt % Pt loading was used for electrochemical measurements. The cyclic voltammogram (CV) curves of the MOR for the Pt/C and Pt/W18O49 NCs−rGO are shown in Figure 3a. The forward anodic peak of the Pt/W18O49 NCs−rGO is observed at 0.854 V, which is 0.018 V lower than that of the commercial Pt/C at 0.872 V. The current density of forward anodic peak for Pt/W18O49 NCs−rGO is 1624 mA/mgPt, which is 1.56 times that of the Pt/C (1040 mA/mgPt). The backward anodic peak of the Pt/W18O49 NCs−rGO is at 0.725 V, which is 0.033 V higher than that of the commercial Pt/C (0.692 V). The current density is close to that of the backward anodic peak. Thus, Pt/W18O49 NCs−rGO gives a higher mass activity. The nanostructured Pt/W18O49 NCs−rGO catalyst shows a higher catalytic performance because the W18O49 NCs act as a oxygen reservoir, which may provide more Oads species on the Pt surface.31

In previous works, it has been reported that the anodic peak in the reverse scan is related to the removal of the intermediate species absorbed on the catalyst surface, e.g., CO and HCOO−.31,45,47−51 These species occupy the active site of Pt, leading to decreasing catalytic activity and energy transformation efficiency. Consequently, the ratio of the forward anodic peak current density (If) to the backward anodic peak current density (Ib) can be also used to indicate the tolerance of the catalyst toward intermediate products species. Usually, a catalyst with a high ratio of \( \frac{I_f}{I_b} \) shows a good tolerance toward intermediate products. It can be clearly found that the ratios of \( \frac{I_f}{I_b} \) for Pt/W18O49 NCs−rGO and Pt/C are 1.16 and 0.75, respectively, as shown in Figure 3b. The \( \frac{I_f}{I_b} \) ratio of Pt/W18O49 NCs−rGO is 1.55 times than that of the Pt/C catalyst.

To further examine the anti-methanol poisoning property, CO stripping voltammetry was tested as a function of CO poisoning time in 0.1 M HClO4 solution. A CO oxidation peak is found at 0.822 V. Pt/W18O49 NCs−rGO exhibits a higher catalytic activity than the Pt/C catalyst due to the following reasons. W18O49 NCs provides a large amount of active sites for CH3OH absorption, and the tunable ratio of W6+ to W5+ in W18O49 NCs causes the formation of the tungsten bronze (\( \text{HWO}_x \)) with a good proton conductivity. Hydrogen spillover effect would promote the dehydrogenation of CH3OH. Second, the number and efficiency of the active sites are increased due to the synergistic effect because W18O49 NCs act as a oxygen reservoir, which may provide more Oads species on the Pt surface.31

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V (vs reversible hydrogen electrode (RHE)) for the commercial Pt/C after purging with pure CO for 0.1–5 s, and the equilibrium CO coverage reaches within 0.1 s (Figure 4a). For Pt/W_{18}O_{49} NCs–rGO, the CO oxidation peak is observed at about 0.743 V (vs RHE) after purging with pure CO for 1–30 s, and even after 30 s, the CO coverage does not reach an equilibrium (Figure 4b). Pt/W_{18}O_{49} NCs–rGO exhibits a stronger CO tolerance ability compared with the Pt/C. It is attributed to the SMI between Pt and composite support. As a poisoning molecular, CO is easily adsorbed and covered at the active Pt sites and blocks the catalytic reaction. The interactions between Pt and the W_{18}O_{49} NCs can promote a spillover of the oxygen along their interface, leading to enrichment of the O\(_{ads}\) species on the Pt surface, thus promoting oxidation of intermediates (such as Pt–CO\(_{ads}\), Pt–CH\(_2\)O\(_{ads}\), Pt–CH\(_3\)O\(_{ads}\), and Pt–CHO\(_{ads}\)) to H\(_2\)O and CO\(_2\). This regeneration makes Pt sites free for further oxidation of methanol. It could be interpreted that the CO coverage was not easy to reach the equilibrium for the Pt/W\(_{18}\)O\(_{49}\) NCs–rGO system. Another reason might be that due to the high specific area of rGO, some poisonous species might be adsorbed on the surface of rGO to reduce the possibility of blocking the active sites on the surface of Pt. So, the catalyst Pt/W\(_{18}\)O\(_{49}\) NCs–rGO shows a high CO tolerance and a high anti-intermediate products poisoning properties. Normally, the electrochemically active surface area can be estimated by measuring the charge associated with H\(_{upd}\) adsorption (Q\(_{H_{upd}}\)). A comparison of the catalytic performance of Pt/W\(_{18}\)O\(_{49}\) NCs–rGO and other related catalysts reported in literatures is listed in Table S3. It can be seen that the Pt/W\(_{18}\)O\(_{49}\) NCs–rGO composite catalyst exhibits a higher mass activity, 1624 mA/mgPt.

Chronoamperometry test was usually used to investigate the durability of the catalyst. The test was estimated by CA sweeps at 0.7 V (vs RHE) for 3600 s in an Argon-purged 0.1 M HClO\(_4\) and 0.5 M CH\(_3\)OH solution at room temperature. It indicates that Pt/W\(_{18}\)O\(_{49}\) NCs–rGO has a higher catalytic current density for MOR than the Pt/C in the chronoamperometry test, as shown in Figure 5. A comparison of the transient current densities of the Pt/W\(_{18}\)O\(_{49}\) NCs–rGO and Pt/C catalysts is listed in Table S4. The mass current density of Pt/W\(_{18}\)O\(_{49}\) NCs–rGO catalyst is almost twice that of the Pt/C. Meanwhile, there was a 41% decrease in the current density of the Pt/C catalyst from 600 to 3600 s during the chronoamperometry test, whereas only 37% decrease in the Pt/W\(_{18}\)O\(_{49}\) NCs–rGO is observed in the same test.

The morphology of the catalysts also has a great influence on the activity of the reaction. Nanoparticles tend to agglomerate spontaneously by Ostwald ripening. And, it is a thermodynamically favorable process. To gain insight into the degradation mechanism of the Pt/C and Pt/W\(_{18}\)O\(_{49}\) NCs–rGO composite activity, Pt/W\(_{18}\)O\(_{49}\) NCs–rGO and Pt/C samples were prepared and observed by TEM before and after chronoamperometry test, respectively. As shown in the TEM image (Figure S8a,c), the Pt NPs are uniformly dispersed on the substrates in both samples initially. Mean sizes of Pt NPs are 3.25 ± 0.32 and 2.18 ± 0.29 nm in Pt/W\(_{18}\)O\(_{49}\) NCs–rGO and Pt/C, respectively. After the test, it is observed that some platinum nanoparticles dropped from carbon support due to the electrochemical corrosion (Figure S8b). Meanwhile, some Pt NPs become agglomerated particles with a mean size of 7.25 ± 0.89 nm. The agglomeration of Pt due to Ostwald ripening reduces the specific area of Pt NPs. It leads to a decrease in the current density and the activity loss of the Pt/C catalyst. No significant difference was observed for the Pt/W\(_{18}\)O\(_{49}\) NCs–rGO catalyst before and after the test. Although some larger nanoparticles with a diameter around 6–9 nm were observed after the test, the size of most Pt NPs in Pt/W\(_{18}\)O\(_{49}\) NCs–rGO after the test is 3.30 ± 1.20 nm. So, it maintains a high current density during the chronoamperometry test and exhibits a high stability. The high catalytic activity and excellent stability of the Pt/W\(_{18}\)O\(_{49}\) NCs–rGO are ascribed to the following two possible reasons. First, there are strong SMI effects between platinum and W\(_{18}\)O\(_{49}\) NCs. If no hydrogen gas is introduced into the suspension system consisting of W\(_{18}\)O\(_{49}\) NCs–rGO and K\(_2\)PtCl\(_4\) during synthesis, we can still observe the Pt nanoparticles marked by blue circles deposited on the surface of W\(_{18}\)O\(_{49}\) NCs, the (010) plane was marked 0.378 nm, as shown in Figure S9. Pt NPs are difficult to oxidize due to the redox property of W\(_{18}\)O\(_{49}\) NCs. Second, Pt NPs are well dispersed and separated by the nanocables in Pt/W\(_{18}\)O\(_{49}\) NCs–rGO. This increases the barrier of the collision of the Pt NPs and reduces the possibility of the collision of the materials and agglomeration. Ostwald ripening is a thermodynamically spontaneous process, the barrier is favorable for preventing them from agglomeration. Moreover, the 3D nanostructure is also very stable because there is still strong connection between W\(_{18}\)O\(_{49}\) NCs and graphene via the O–W=O bond. This bonding makes the W\(_{18}\)O\(_{49}\) NCs connect with the graphene nanosheet, which is favorable for electronic transport. The unique oxygen defect structure and different valence states of W in W\(_{18}\)O\(_{49}\) NCs become active sites for Pt NPs deposition and removing the adsorbed poisonous intermediate products by oxygen reservoir function of W\(_{18}\)O\(_{49}\). Figure S10 shows the electrochemical impedance spectroscopy (EIS) spectra of commercial Pt/C and Pt/W\(_{18}\)O\(_{49}\) NCs–rGO. It can be seen that the Pt/W\(_{18}\)O\(_{49}\) NCs–rGO shows a smaller charge transfer resistance compared to that of the commercial Pt/C catalyst. This combination of Pt NPs, W\(_{18}\)O\(_{49}\) NCs, and graphene provides more reactive centers for MOR and enhances the antipoisoning property toward intermediate products. The unique structure of the composite consisting of two-dimensional nanosheet and one-dimensional nanocable is favorable for enhancing the stability of the materials. The well-dispersed morphology is attributed to the interaction between tungsten oxide and graphene oxide.
This work may provide a new approach to prepare 3D nanostructured composite catalysts.

3. CONCLUSIONS

In summary, we prepared a 3D nanostructured composite Pt/W18O49 NCs-rGO as an efficient and durable catalyst for methanol oxidation reaction. Graphene oxide nanosheet was reduced to graphene through a solvothermal process. As a conductive support material, W18O49 NCs were produced and assembled on the surface of rGO via oxygen atom bridges. Both W18O49 NCs and rGO nanosheets have good electronic conductivity. The Pt NPs were loaded on the W18O49 NCs-rGO composite support via hydrogen reduction. W18O49 NCs are the active centers for the reduction reaction. Pt NPs with a size of about 3 nm were homogeneously distributed on the surface of W18O49 NCs. The nanocomposite catalyst also exhibits a long-term durability. This research opens a new avenue to prepare 3D conductive support material, W18O49 NCs were produced and reduced to graphene through a solvothermal process. As a conductive support material, W18O49 NCs were produced and assembled on the surface of rGO via oxygen atom bridges. Both W18O49 NCs and rGO nanosheets have good electronic conductivity. The Pt NPs were loaded on the W18O49 NCs-rGO composite support via hydrogen reduction. W18O49 NCs are the active centers for the reduction reaction. Pt NPs with a size of about 3 nm were homogeneously distributed on the surface of W18O49 NCs. The SERS between platinum and W18O49 NCs-rGO provides good reactivity for electro-catalysis. The forward anodic peak current density of the Pt/W18O49 NCs-rGO nanocomposite catalyst reaches 1624 mA/mg at 0.854 V (vs RHE) in 0.1 M HClO4 and 0.5 M CH3OH mixed electrolyte. It is almost 1.56 times that of the commercial Pt/C catalyst. Moreover, Pt/W18O49 NCs-rGO shows excellent CO tolerance and anti-intermediate poisoning properties. This is attributed to spillover and oxygen buffering effects of composite support of W18O49 NCs-rGO. The nanocomposite catalyst also exhibits a long-term durability. This research opens a new avenue to prepare promising catalysts to advance their applications in direct methanol fuel cells and offers a rational strategy to design heterogeneous catalysts.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Raw Materials. K2PtCl6 and WCl6 were purchased from Aladdin Industrial Corporation. Commercial Pt/C was bought from Alfa Aesar. Graphene oxide was purchased from Graphene Supermarket. Ethanol and other chemicals were bought from Tianjin Fuchen Chemical Reagents Factory.

4.2. Synthesis of W18O49 Nanocables (W18O49 NCs). W18O49 NCs were synthesized by WCl6 alcoholysis reaction as reported by Yang et al.33

4.3. Synthesis of W18O49 Nanocable-Reduced Graphene Oxide Composite (W18O49 NCs-rGO). Graphene oxide was used as a raw material. It was added directly during the alcoholysis process. Typically, 20 mg graphene oxide and 40 mg WCl6 were suspended and dissolved in 60 mL ethanol via sonication. Then, the obtained dark yellow suspension was transferred into a Teflon-lined autoclave and solvothermally treated at 180 °C for 24 h. The black solid product was obtained by centrifugation and washed by deionized water and alcohol. The obtained product was denoted as W18O49 NCs-rGO, which was dried at 60 °C under vacuum atmosphere for 12 h.

4.4. Synthesis of Pt/W18O49 NCs-rGO Catalyst. Pt nanoparticles were loaded on the W18O49 NCs-rGO support via a hydrogen-assisted reducing method. Typically, 40 mg W18O49 NCs-rGO powder was dispersed in 50 mL ethanol via ultrasonication. Then, 2.5 mL K2PtCl6 water solution (1 g/100 mL) was added to the suspension dropwise. It was magnetically stirred for 30 min and continuously stirred with a 300 mL/min hydrogen gas flow into the suspension for another 4 h. The obtained black product was washed with deionized water and alcohol, dried at 60 °C under vacuum atmosphere overnight, and denoted as Pt/W18O49 NCs-rGO. The amount of Pt loading in Pt/W18O49 NCs-rGO could be adjusted by changing the addition volume of the K2PtCl6 solution.

4.5. Materials Characterization. The crystalline phases of the W18O49 NCs-rGO support and the Pt/W18O49 NCs-rGO nanocomposite were characterized by X-ray powder diffraction (XRD) (D8 Advance, Bruker, Germany). Raman spectra were measured with a micro-Raman spectrometer (HR 800, Jobin Yvon, France) at 457.9 nm wavelength. X-ray photoelectron spectroscopy (XPS) was performed with an Al Ka radiation (Kratos AXIS Ultra DLD, Britain). The thermal analysis was measured by thermogravimeter (TG/differential thermal analysis (DTA), 6300, SEIKO, Tokyo, Japan). Scanning electron microscopy (SEM) was performed on a scanning electron microscope (Hitachi S-4300, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a microscope (JEOL JEM2100F, Japan) operated at 200 keV. The compositions of the catalysts were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher).

4.6. Electrochemical Measurements. Glassy carbon electrodes were polished with alumina powder, ultrasonically washed, and blow dried before being dropped into the catalyst ink. The electrode preparation and electrochemical measurements are similar to that reported in the literature previously.31 The same procedures were used to prepare Pt/C electrode (Hispec3000, Johnson Matthey).

MOR tests were performed in a 0.1 M HClO4 and 0.5 M CH3OH solution at a scan rate of 100 mV/s. Chronoanalyzer measurements were carried out in a 0.1 M HClO4 and 0.5 M CH3OH solution after a 50 cycle CV activity in Ar-purged 0.1 M HClO4 solution at a scan rate of 100 mV/s. For details, please refer to the literatures.31 For CO stripping voltammetry, the procedures are similar to those reported in the literature previously.31 For comparison, the potentials measured were calculated to the values (vs RHE) automatically by the testing software. Electrochemical impedance spectroscopy (EIS) measurements were performed on an Autolab electrochemical workstation (PGSTAT302N) in the frequency range from 100 kHz to 100 mHz with a bias voltage of 10 mV at 0.6 V (vs RHE). The solution for the EIS experiment is 0.1 M HClO4 with 0.5 M methanol, which was purged by argon gas.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02942.

Additional XRD, SEM, TEM, TG/DTA images, and XPS analyses (PDF)

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