Controllable synthesis of two-dimensional tungsten nitride nanosheets as electrocatalysts for oxygen reduction reaction

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ABSTRACT A facile synthetic strategy was developed for *in-situ* preparation of two-dimensional (2D) highly crystalline tungsten nitride (WN) nanosheets with controllable morphology as oxygen reduction reaction (ORR) catalysts. The dependence of the crystal structure and morphology of WN on K_2SO_4 content, pH, and pyrolysis temperature was thoroughly examined. The electrocatalytic performance of WN toward ORR in an alkaline electrolyte indicated that K^+ plays an important role in the control of size and shape in the hydrothermal and nitridation process, thereby promoting the formation of plate-like WO_3 and 2D WN nanosheets. The WN nanosheets, with largely exposed edge sites, provide abundant catalytic active sites and allow fast charge transfer. Furthermore, they exhibit high stability for ORR and methanol tolerance.

Keywords: tungsten nitride, nanosheets, electrocatalysts, oxygen reduction reaction

INTRODUCTION

Direct methanol fuel cells (DMFCs) have been widely explored because of their high energy density, high efficiency, and quick start-up time at a low operating temperature [1–3]. Oxygen reduction reaction (ORR) catalysts for the cathodic reaction of DMFCs have been extensively investigated to replace platinum-containing groups, with the aim of enhancing the catalytic activity of ORR while reducing the cost [4,5]. A number of alternative ORR catalysts including non-precious metal (NPM), metal composites, and metal-free composites have been recently considered as potential substitutes for platinum-containing groups catalysts. As a consequence of recent advances in the field of NPM catalysts, several

transition metal-based electrocatalysts, such as transition metal carbides [6,7], transition metal dichalcogenides [8,9], transition metal phosphides [10], transition metal oxides [11–13], and transition metal nitrides (TMNs) [14–16], have been developed for the purpose of illuminating the catalytic mechanism and achieving excellent electrocatalytic performance.

Among these catalysts, TMNs have been comprehensively examined because of their potential applications in fuel cells, which result from their high electrical and thermal conductivity, excellent electronic properties, and chemical resistance to corrosion in aqueous media. However, their large-scale production and practical applications have been hindered by difficulties associated with facet control that arises from inferior anisotropy and rigorous high-temperature synthesis routes during nitridation [17]. In an attempt to solve these problems, nitride nanostructures with uniform dispersion, specific facet exposure, and unique architectures have been prepared, including tungsten nitride nanocrystals [18], single crystalline-like molybdenum nitride nanobelts [19], VN hollow spheres [20], layered $Co_3Mo_2O_xN_{6-x}$ [21], and alloyed Co–Mo nitride [22]. In many cases, nitrides not only serve as support for loading noble metals with synergistic effects but also act as ORR catalysts.

Two-dimensional (2D) nanostructures find application in the fabrication of high-performance supercapacitors, lithium-ion batteries, and biosensors because they can provide large specific surface area, short transport distance, and good conducting pathways in electrochemical reactions [23–26]. However, to date, few studies have been conducted on 2D TMN crystals for ORR in fuel cells. These structures present a nanoscale dimension in

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the *c*-axis and growth from an exposed edge and show the potential for ORR catalysts because their unique electronic structure and morphology allow the modulation of electron transport and the enhancement of 2D host capabilities [27,28]. Among 2D structures of the active materials, highly dispersed nitrides nanosheets not only possess a high nitrogen content, and large aspect ratios but also exhibit an excellent electrical conductivity. For example, a new form of hybrid NiC–Ni₃N nanosheets was served as a robust catalyst for the hydrogen evolution reaction because it is chemically stable and metallically conductive [29]. Therefore, we believe that 2D TMN applications in fuel cells should be further investigated and developed.

In this study, 2D tungsten nitride nanosheets (denoted as WN NSs) were designed and fabricated through simple hydrothermal synthesis followed by nitridation. Hydrothermal synthesis was performed to obtain WO₃ nanostructures, which were subsequently subjected to calcination in an NH₃ atmosphere to ensure that an oxygen atom in WO₃ was completely substituted by a nitrogen atom. This method proved to be low cost, template- and organic solvent-free, and environment-friendly. The underlying relationship between crystal structure characteristics and preparation conditions was also elucidated. Both ORR performance and stability were analyzed by linear sweep voltammetry (LSV) and chronopotentiometry.

EXPERIMENTAL SECTION

All reagents were of analytical purity and used as received. A schematic of the 2D WN NS synthesis is shown in Fig. 1. For the synthesis of WO₃ with different morphologies, 3.5 mmol Na₂WO₄·2H₂O and 1.75 mmol K₂SO₄ were dissolved in 40 mL of deionized (DI) water with magnetic stirring to prepare a transparent solution. Then, 3 mol L⁻¹ HCl solution was added into the suspension to adjust the pH value until the formation of yellow precipitates was observed. The mixture was transferred to a 100 mL Teflon-lined autoclave and held at 180°C for 12 h. The yellow precipitates were then collected from the solution by filtration, washed with DI water and ethanol several times, and dried in a vacuum oven at 80°C overnight to obtain WO₃-K11 (W/K=1:1).

For comparison, WO₃ nanostructures with W/K molar ratios of 4:1, 2:1, and 1:2, denoted as WO₃-K41, WO₃-K21, and WO₃-K12, respectively, were also prepared under the same conditions. The WO₃ sample without K₂SO₄ was marked as WO₃-K0. Finally, the resulting WO₃ samples were annealed at 700°C for 3 h under an

Figure 1 Schematic illustration of the preparation process of WN NSs.

NH₃/Ar flow of 100 sccm to produce the WN nanostructures.

X-ray diffraction (XRD) patterns were obtained using a powder diffractometer (DX-2700, Dandong, China) with a Cu K α radiation source. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos AxisULTRA X-ray photoelectron spectrometer equipped with a 165 mm hemispherical electron energy analyzer. The morphological characteristics of the electrocatalysts were determined using a scanning electron microscope (SEM, JSM-5900LV, JEOL Co.) and a transmission electron microscope (TEM, Carl Zeiss SMT, Libra 200FE).

Rotating disk electrode (RDE) measurements were performed using a glassy carbon (GC) electrode with a typical three-electrode system. A graphite plate and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. For the preparation of the working electrodes, 5 mg of catalyst was ultrasonically suspended in a mixture of 1 mL of ethanol and 50 μ L of Nafion[®] solution (5 wt%, Du Pont) for 30 min to obtain a homogeneous ink. Then, 20 μ L of the catalyst ink was dropped onto a GC electrode with a diameter of 5 mm and dried under an infrared lamp. RDE measurements were performed on a Pine electrochemical system at rotating rates varying from 400 rpm to 2,025 rpm (revolutions per minute) with a scan rate of 10 mV s⁻¹. The number of transferred electrons (*n*) can be calculated according to the Koutecky–Levich (K–L) equation [30]: $J^{-1} = J_k^{-1} + J_L^{-1} = J_k^{-1} + B^{-1} \omega^{0.5}$ and $B = 0.2nFD(O_2)^{2/3} \nu^{-1/6} C(O_2)$.

RESULTS AND DISCUSSION

Fig. 2a shows the XRD pattern of the WO₃ samples prepared with different W/K molar ratios. For WO₃-K0 and WO₃-K12, the characteristic diffraction peaks corresponding to the monoclinic system of WO₃ (JCPDS card no. 43-1035) are found at 23.2°, 24.4°, 26.5°, 34.1°, 41.9°, 49.8°, and 55.8°, respectively ascribed to the (002), (200), (120), (202), (222), (041), and (142) diffraction planes. In contrast, only the sharp peak of (002) can be detected in the patterns of WO₃-K41, WO₃-K21, and WO₃-K11 with different K₂SO₄ contents, with relatively

Figure 2 (a) XRD patterns of WO_3 and (b) XPS spectra of W 4f in WO_3 synthesized with the different W/K molar ratios.

weak intensity. These patterns match well with those of the hexagonal WO_3 samples (JCPDS card No. 85-2459). This difference implies that the addition of K_2SO_4 causes WO_3 to orient along the (002) direction. In WO_3 -K0 product (Fig. S1a), the WO_3 nanostructures without the assistance of K_2SO_4 are mainly agglomerated. Fig. S1b displays that WO_3 hydrothermally synthesized in the presence of a moderate amount of K_2SO_4 exhibits an assembly of nanoplates with a regular arrangement. K_2SO_4 , which acts as an inductive agent, strongly influences the final morphology of WO_3 . Consistent with previous findings, our results indicate that the hexagonal WO_3 phase is composed of layers stacked to form open one-dimensional tunnels [31]. Fig. 2b illustrates the XPS spectra in the W and K regions of WO_3 . The binding energies (BEs) of WO_3 -K0 at 35.8 and 37.9 eV can be assigned to W 4f_{7/2} and W 4f_{5/2}, respectively, which are similar to the reported values of 35.6 and 37.7 eV [32]. However, the BE of W on WO_3 is positively shifted to a high BE as the amount of K^+ significantly increases, thereby demonstrating that electron transfer occurs on the WO_3 surface during the hydrothermal process. On the basis of the XPS results, it seems reasonable to conclude that K^+ is incorporated into the WO_3 lattice.

For nitridation products, the SEM image (Fig. 3a) of WN-K0 (obtained from WO_3 -K0) displays a severely agglomerated powder. As can be extracted from Fig. 3b–d, WN-K41, WN-K21, and WN-K11 are well homogeneously distributed, exhibiting uniformly dispersed microstructures. On the other hand, for the sample with the highest amount of potassium salt (WN-K12; Fig. 3e), the bulk morphology is observed. These results indicate that the K^+ ions influences not only the formation of WO_3 nanostructures but also the preferential growth of WN NSs along a certain lattice plane. WN-K11 exhibits the smallest nanostructure size among the specimens in-

Figure 3 SEM images of (a) WN-K0, (b) WN-K41, (c) WN-K21, (d) WN-K11, (e) WN-K12, and (f) TEM image and SAED pattern (inset) of the WN-K11.

vestigated and high dispersion; consequently, a larger active surface area may be available in WN-K11 for the electrochemistry reaction. In addition, the TEM image of an individual WN-K11 sample is shown in Fig. 3f.

The electron diffraction pattern of a selected area (inset) indicates a polycrystalline structure and a well-defined crystalline lattice with a lattice spacing of 0.255 nm corresponding to the (100) plane of hexagonal WN. The phase identity of WN-K11 (Fig. 4) was further confirmed by the XRD pattern corresponding to (100), (101), (110), and (200), which is also consistent with the hexagonal WN (JCPDS card No. 25-1256).

A formation mechanism of WO_3 is illustrated in Fig. 5. Accordingly, in the initial reaction stage (I), colloidal H_2WO_4 is rapidly formed after the dropwise addition of

Figure 4 XRD pattern of WN-K11.

Figure 5 Formation process of the WO_3 nanoplate and WN NSs. Inset (a) Schematic of the hexagonal WO_3 viewed to the (002) crystal plane and (b) side-view of the WN NSs.

HCl into the solution containing Na_2WO_4 and K_2SO_4 . Nucleation occurs, and a WO_3 crystal is obtained at the beginning of the hydrothermal reaction [33]. In the second stage (II), the formation of hexagonal WO_3 (Fig. 5a) can be attributed to the presence of K^+ ions, which stabilize the hexagonal structure by their adsorption onto the hexagonal channels preventing the thermodynamic conversion of WO_3 into a monoclinic phase [34,35]. In the third stage involving nitridation (III) at 700°C for 3 h, the hexagonal phase of the as-prepared WN maintains while a lattice contraction occurs. Fig. 5b shows that the surfaces of WN contain apical W atoms, which hold the nitrogen atoms in the center of the structure and connect them to the basal plane of the hexagonal lattice. This finding confirms that K^+ also stabilizes the hexagonal structure of WN, thereby constituting an ideal regulatory component for the formation of hexagonal WN NSs.

To gain more insight into the formation of the WN nanostructure, the nitridation experiment with the 1:1 W/K molar ratio was conducted at different pH values. The SEM images of the as-grown samples are shown in Fig. S2. A mixture of nanosheets and smaller particles is obtained at pH 0.5 (Fig. S2a), whereas no such particles can be detected in the samples prepared at pH 1, 1.5, and 2. Moreover, the thickness of the sheets was found to increase from pH 1 (Fig. 3d) to pH 2 (Fig. S2c), possibly because the formation of H_2WO_4 is a fast reaction and numerous H^+ quickly react with WO_4^{2-} . High H^+ concentrations may inhibit the growth of grains on WO_3 , leading to the generation of WN particles at low pH.

To investigate the effect of nitridation temperature on the formation of the WN nanostructure, we calcinated WO_3 at 600 and 800°C (the as-prepared WN nanostructures were denoted as WN-600 and WN-800, respectively) while maintaining the other experimental parameters constant. The corresponding XRD results (Fig. S3) confirm the phase purity and crystal structure of WN. For WN-700 and WN-800, all the diffraction peaks can be well indexed to a hexagonal WN crystalline phase (JCPDS card no. 25-1256). Furthermore, the strong and sharp diffraction peaks from WN-700 indicate its good crystallinity and strong preferential growth direction along the (100) plane. Conversely, WN-600 presents the typical (111), (200), (311), and (222) diffraction peaks consistent with cubic WN (JCPDS card No. 65-2898). As can be seen in Fig. S4, WN-600 consists of abundant nanoparticles as a result of inadequate nitridation caused by low temperature. The SEM image of WN-700 and WN-800 shows similar dispersible nanosheets, indicating that nitridation at 700 and 800°C transforms the nanoplates into 2D WN NSs, which is in accordance with the XRD result. We also evaluated the effect of nitridation time on the morphological characteristics of WN, conducting the nitridation process at 700°C for 1 and 4 h. Fig. S5 illustrates that no obvious changes are observed in the structure of WN obtained after 1 h calcination (denoted as WN-1h) compared with that of WO_3 , most likely because the short calcination time affords an insufficient nitridation reaction, with concomitant slight particle aggregation in the dominant layered product. When the process is extended for 3 or 4 h, WN with a high purity and a smooth surface is formed. The XRD pattern in Fig. S6 shows that all the diffraction peaks for the as-prepared samples can be indexed to the WN phase. However, the intensity of the (100) peak corresponding to the WN structure prepared after 3 h nitridation is larger than that for the other samples, suggesting that nanocrystal growth

Figure 6 Linear sweeping voltammetry of (a) the WN prepared with different W/K molar ratio, (b) WN prepared with various pH value during hydrothermal process, (c) WN prepared by different nitridation temperature, and (d) the WN with optimized synthetic condition at different rotation rates. The inset shows corresponding Koutecky–Levich plots at 0.30, 0.35, 0.40, 0.45 and 0.50 V (vs. RHE), respectively, in 0.1 mol L⁻¹ KOH saturated with O₂, scan rate: 10 mV s⁻¹, rotating rate: 1,600 rpm.

occurs preferentially along the (100) plane with a high degree of crystallinity. Therefore, 3 h can be considered as the optimum nitridation time for the formation of WN NSs.

We tackled the evaluation of their activity and kinetic properties for ORR catalysis by performing RDE measurements. Fig. 6a shows that WN-K11 exhibits a more positive onset potential (E_{onset}) and a higher current density than the WN samples prepared with other W/K ratios. Consistent with the SEM results, the positive potential shift and the improved performance of WN-K11 can be attributed to the enhancement of electron transfer from the 2D-layered structure to the adsorbed oxygen. Fig. 6b illustrates the LSV curves of WN obtained at different pH values during the hydrothermal process. Among the catalysts, that obtained at pH 1 (WN-pH1) exhibits the highest ORR activity, onset potential, and current density. As shown in Fig. 6c, the catalyst performance reaches a maximum when the nitridation temperature is 700°C, and a minimum at 600°C, indicating that 700°C is the optimum temperature for the formation of the exposed active sites. With the appropriate temperature, a desirable structure with rich active catalytic sites on the surface has been confirmed to facilitate electron transport during the catalytic process

[36]. The possible reason can be explained by XPS results, as shown in Fig. S7. The peaks at 32.7 and 34.8 eV represent the BEs of W 4f in a pure WN NSs, which is consistent with a previous report [18]. Specially, the extended N 1s peak of WN-700 also suggests that numerous N atoms participate in the nitridation that affords electroconductivity of the nitride products. Therefore, optimal WN NSs are obtained with a W/K ratio of 1, at pH 1, and on performing the nitridation at 700°C for 3 h. Table S1 demonstrates the comparisons of E_{onset} and half-wave potential ($E_{1/2}$) among the various non-precious catalysts, where our prepared WN NSs displays an enhancement on E_{onset} than that in some other reports.

From the slopes of the K–L plots at various potentials, the electron transfer number (n) of WN NSs was determined to be 2.56 (Fig. 6d), indicating that ORR catalysis predominantly follows a two-electron transfer pathway. However, ORR catalyzed by 2D WN NSs is most likely a mixed process of two- and four-electron transfers because the 2D morphology provides fast electron transport pathways and a large electroactive surface, which diminishes the gap between the as-prepared WN and commercial Pt/C. Fig. S8a shows a ring current (I_{Ring}) as compared to the disk current (I_{Disk}) and the n value calculated using the RRDE measurement data [37]:

Figure 7 (a) Current-time chronoamperometric response of Pt/C and WN NSs at -0.35 V (vs. Ag/AgCl) in O_2 -saturated 0.1 mol L^{-1} KOH solution. (b) Chronoamperometric response of Pt/C and WN NSs at -0.35 V (vs. Ag/AgCl) in O_2 -saturated 0.1 mol L^{-1} KOH solution. The arrow indicates the introduction of 3 mol L^{-1} methanol.

$\% \text{H}_2\text{O}_2 = (2I_R/N)/(I_D + I_R/N)$ and $n = 4I_D/(I_D + I_R/N)$. The current collection efficiency (N) of the Pt ring is determined to be 0.37 using standard redox couple of ferri/ferrocyanide. Furthermore, the amount of H_2O_2 produced by the above process also was confirmed by RRDE measurements (Fig. S8b). The n value is in good agreement with those obtained from the K–L plots that are based on the RDE measurements, confirming that ORR kinetics for the WN NSs sample is mainly through a mixed process of two- and four-electron transfer. The maximal H_2O_2 yield of WN NSs is 12.6%, which is similar to that of previous reports in the potential range of 0.3 – 0.5 V [38].

To evaluate the durability of WN NSs as ORR catalysts, we conducted chronoamperometric measurements in 0.1 mol L^{-1} O_2 -saturated KOH solution for $18,000$ s at -0.35 V (vs. Ag/AgCl). Fig. 7a shows that the WN catalyst exhibits good electrochemical durability, with current losses of 17.5% after $18,000$ s. To provide comparison, Pt/C was tested under the same conditions, affording obvious activity decay with 27% retention. Because methanol tolerance is another crucial parameter for ORR electrocatalysts [39], the chronoamperometric responses of the WN electrode on the addition of 3 mol L^{-1} methanol were evaluated in comparison with those of commercial Pt/C (Fig. 7b). The current density of the Pt/C electrode was found to decrease sharply after the addition of 3 mol L^{-1} methanol to the 0.1 mol L^{-1} O_2 -saturated KOH solution, whereas the current density of the WN electrode remained virtually unaltered. These findings demonstrate that the tolerance of WN electrodes against methanol is stronger than that of commercial Pt/C electrodes.

CONCLUSIONS

WN NSs were synthesized by self-assembly construction based on a hydrothermal strategy combined with ni-

tridation. K_2SO_4 acts as an inductive agent for the formation of lamellar nanoplates in the hydrothermal synthesis, and favors the crystallization of 2D WN NSs during the high-temperature nitridation. The morphology of WO_3 and WN can be controlled by adjusting the preparation conditions, such as pH, nitridation temperature, nitridation time, K^+ content, and catalytic activity. Optimal WN NSs can be synthesized at W/K ratio=1, pH 1, and nitridation conditions of 700°C and 3 h reaction. The 2D morphology of WN NSs leads to a desirable ORR performance. Taken together, these findings strongly suggest that WN NSs are promising Pt-free cathodic electrocatalysts for ORR in alkaline fuel cells.

Received 27 January 2018; accepted 27 March 2018;
published online 17 April 2018

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- Acknowledgements** This work was supported by the National Natural Science Foundation of China (21306119), the Key Research and Development Projects in Sichuan Province (2017GZ0397, 2017CC0017), and the Science and Technology Project of Chengdu (2015-HM01-00531-SF).
- Author contributions** Zhang J and Chen JW designed the experiments. Zhang J, Luo Y, Chen YH, Kiani M and Wei XY helped with the sample characterization. Luo R and Wang G participated in the interpretation of experimental results. Zhang J wrote the paper with support from Chen JW and Wang RL. All authors contributed to the general discussion.
- Conflict of interest** The authors declare that they have no conflict of interest.
- Supplementary information** Supporting data are available in the online version of the paper.

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二维氮化钨纳米片催化剂的可控制备及其氧还原性能研究

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摘要 本文以钨酸钠和硫酸钾等试剂为原料, 采用水热结合氨气氮化的方法原位获得了一种二维的氮化钨(WN)晶体, 并将其作为氧还原(ORR)反应的催化剂. 通过控制和优化制备条件(水热过程中硫酸钾含量、pH值以及氮化条件包括氮化温度和氮化时间), 实现了纳米WN的可控制备.