Ultrasmall Tungsten Carbide Catalysts Stabilized in Graphitic Layers for High-performance Oxygen Reduction Reaction

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KEYWORDS: tungsten carbide nanoparticles; graphitic layers; electron microscopy; electrocatalysts; oxygen reduction reaction

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Abstract

Tungsten carbide (WC) has been proven Pt-like features in many catalytic reactions, and presents promising potentials to substitute noble metal-based electrocatalysts. However, the catalytic performances cannot be improved to the industrial standard due to the low density of catalytically active sites that are relevant to the size and stability of catalysts. Herein, we synthesized WC catalysts with a mean diameter of 1.9 ± 0.9 nm, comprising a high density of single W atoms, sub-nanometer and nanometer WC clusters, which are completely encapsulated in high-defective graphitic layers (WC@C). Such high-defective graphitic layers not only improve the overall conductivity for accelerating the penetration and exchange of ions and electrons during the electrocatalytic process of oxygen reduction, but also suppress the chemical/thermal coarsening of WC catalysts, thus providing excellent electrocatalytic performances in four-electron transfer process for oxygen reduction reaction.

1. Introduction

The oxygen reduction reaction (ORR) is the most important reaction in energy converting systems such as polymer electrolyte fuel cells (PEFC).[1] However, the energy converting efficiency and power density are seriously limited by oxygen reduction rate that is closely related to cathode catalysts utilized, for example, on a Pt electrode the exchange current density of hydrogen oxidation is several orders higher than that of ORR.[2] Therefore, development of high-performance cathode catalysts has been attracting considerable attention.[3-5] Currently, noble metal-based catalysts have exhibited the best overall performance;[6-10] nevertheless, with the cost, scarcity and tolerance, researchers have realized the importance on the exploration of

substitutes. Among all the candidates, carbides of groups IV through VI have been proven Pt-like catalytic features.[11-13]For examples, they have been applied in catalyzing decomposition of methanol,[14]dehydrogenation of butane,[15]as well as hydrogenation and dechlorination of Freon[16]. However, in the electrochemical catalysis reactions, carbides themselves cannot present desirable activity for oxygen reduction in alkaline atmospheres;[17] therefore they were only used as promoters for the synergistic catalytic effect together with noble-based catalysts.[18, 19]

Although it has been well recognized that the smaller catalyst exhibits the higher catalytic activity, but the coarsening of catalysts during the reaction process, which results in undesirable chemical and structural stability, cannot be effectively resolved yet.[20-25]On the other hand, the traditional techniques for synthesizing carbide catalysts involving high-temperature annealing processes are also lack of effectiveness in controlling the size down to ~3 nm.[26-33]All these issues thus limit their practical industrial applications.

In this work, we prepared WC catalysts with the currently-reported smallest size of 1.9 ± 0.9 nm with kilogram-scale production of 1.2~2.4 kg/day using a modified arc-discharging method in a flowing methane atmosphere.[34]The product is constituted of a high density of single W atoms, sub-nanometre and nanometre WC clusters, all of which are completely encapsulated in graphitic layers, thus providing exceptionally catalytic stability and activity in electrochemical reactions.

2. Methods

2.1. Sample synthesis

The sample was prepared by a modified arc-discharge method.[34] A high-purity tungsten rod forms the anode, attached to a water-cooled copper stage for rapid sample cooling, whereas the upper carbon rod serves as the cathode. The chamber is first evacuated to reach $\sim 10^{-2}$ Pa and, subsequently, methane (CH_4) is introduced as a gaseous carbon source to reach 0.1×10^5 Pa. Evaporating the tungsten rod by arc-discharge at $\sim 30\text{V}$ and $\sim 90\text{A}$ results in a simultaneous decomposition of methane. The current and voltage are controlled by adjusting the distance between the tungsten rod and the carbon rod for continuous stable operation. During this evaporation process, we have noticed that the carbon rod has negligible loss compared with the carbon decomposed from the methane. The arc-evaporated tungsten and decomposed carbon form black smoke and simultaneously deposit on the cool walls of the chamber. The as-fabricated product is collected after about $\sim 6\text{h}$.

2.2. Characterization

The microstructures of W-in-C and WC-in-C complexes were analyzed using a Hitachi S-4700 transmission/scanning electron microscope operated at a voltage of 30 kV. STEM imaging and EELS were performed using an aberration-corrected STEM (Nion-UltraSTEM100) operating at a low accelerating voltage of 60 kV. The achievable spatial resolution using this fifth-order aberration corrected microscope at 60 kV is $\sim 1.2\text{\AA}$. ADF images were obtained using 58–200 mrad detector half-angle. EEL spectra were collected using a Gatan Enfina spectrometer with a collection half-angle of 48 mrad. The energy resolution of the EELS spectrum measured from the zero-loss full width at half-maximum was 0.3 eV. A Siemens D-500 X-ray diffractometer with $\text{CuK}\alpha$ ($\lambda=0.154\text{ nm}$) radiation at a voltage of 30 kV and a current of 30mA was used to study the phase structure of the products at a scan step of 0.2° .

2.3. Theoretical simulation.

The calculations have been performed using the Vienna ab initio simulation pack.[35] The projected augmented wave method and the Perdew–Wang generalized gradient approximation were used to describe electron–ion interactions. A thermal broadening of 0.1 eV was applied to improve the convergence of the self-consistent procedure and non-spin polarization was employed for all calculations, except the O₂ adsorption simulation with plane-wave cut-off energy of 50 Ry. For bulk WC, a 20×20×20 Monkhorst–Pack grid was used for the integration of the elemental unit cell over the Brillouin zones. The WC clusters with different sizes were located in the 25Å× 25Å×25Å simulation box, and the stable configurations were obtained through full relaxation according to the Hellmann–Feynman forces.

3. Results and discussion

Herein we report an arc-discharge approach to synthesize the WC clusters with a mean diameter of 1.92±0.95 nm, which is the smallest WC size in currently reported literatures. The ultra-small WC clusters are encapsulated completely in graphitic layers, thus presenting highly-performance structural stability. Moreover, by an atomic-scale microscopy characterization, we observed a high density of single W atoms and abundant sub-nanometre crystalline and amorphous WC clusters in the product. These microstructural features endow WC@C composite compelling advantages as a highly-efficient catalyst, and meanwhile provide direct evidence on the correlation between the macroscopic electrochemical behaviors and the atomic-scale origin of the catalytic sites. In particular, our approach can reach a productivity of 50-100 g per hour, and thus has significant potentials in the development of WC catalysts for industrial needs.

The microstructures of WC@C composite were characterized by using a fifth-order aberration-corrected scanning transmission electron microscope (STEM, Nion-UltraSTEM100), coupled with an electron energy-loss spectrometer (EELS, Gatan Enfina spectrometer). The low

accelerating voltage of 60 kV avoids the electron beam induced damage to the ultra-small WC clusters and crystallization of some amorphous WC clusters and single W atoms, thus providing the reliable microstructural information.[36]**Fig. 1A** shows a representative bright-field (BF) image of WC@C composite, in which one cannot observe any heterogeneous phase due to the ultra-small size of WC clusters. However, these WC clusters can be clearly distinguished in the corresponding annular dark-field (ADF) image, shown in **Fig. 1B**, because the mass-thickness contrast differences, i.e., higher-density and/or heavier elements generate brighter contrast.[37, 38]With ADF imaging, the mean WC cluster diameter was estimated to be 1.92 ± 0.9 nm (**Fig. 1C**) by a statistic analysis of more than 500 WC clusters (except for dispersive single W atoms). ADF image shown in **Fig. 1D** presents the zoomed-in microstructures of one representative tungsten carbide nanoparticle, evidencing that the quantitative ratio of ADF intensity between the tungsten carbide particle and the graphite matrix is ~ 2.62 and the particle diameter of ~ 2 nm.

Fig. 2A and **B** shows the powder X-ray diffraction pattern and Raman spectroscopy of WC@C powders, verifying the components of W_2C , WC and graphite components. The total fraction of the W component determined by energy-dispersive X-ray (EDX) spectroscopy was measured to be 19.2 wt.%. It should be noted that the fitted Raman spectroscopy shown in **Fig. 2B** presents four typical peaks (I, II, III and IV) at 1224.4 cm^{-1} , 1324.8 cm^{-1} , 1452.7 cm^{-1} , and 1583.4 cm^{-1} . The ones at 1324.8 cm^{-1} and 1583.4 cm^{-1} were thought to be from D band and G band ascribed to graphitic phases, while the ones at 1224.4 cm^{-1} and 1452.7 cm^{-1} can be attributed to the coexistence of sp^2 and sp^3 bonds, resulting from the high density of defects associated with serious lattice disorder at atomic scale.[39, 40]It evidently implies that the

combined operation of arc-discharge evaporation and rapid-cooling non-equilibrium processes results in the diversity of product.

Fig. 3A and **B** show BF and ADF images of a region consisting of several WC clusters and a high density of single-atom W dispersion, respectively. The carbon matrix is composed of amorphous phase and severely distorted graphitic layers, which result in pronounced microstructure defects such as ripple, wrinkle and porosity. In the ORR catalytic process, it has been unambiguously proven that O₂ molecules are more prone to penetrate and react at defective sites.[38, 41-47]Therefore, although the WC clusters and single-atom W-C complex are caged, we reasonably convince that such a highly-defective feature of graphitic layers also provide and even enhance the synthetic catalytic role.[48]Furthermore, the magnified regions and the Fast Fourier Transform(FFT) patterns in **Fig. 3A**, marked as **A1**, **A2**, **A3** and **A4**, provide more detailed insights into the WC clusters, revealing atomic-scale structures, such as lattice distortion(**A2**), amorphous phase(**A3**) and even a high density of dispersed single-atom W(**A4**). It is well known that, the redistribution of *d*-band electrons of the metal atoms of carbides, ascribed to lattice expansions arising from the interstitial carbon atoms, is the origin of the Pt-like catalytic characteristics.[11-13]The observed microstructures unambiguously indicate that the lattice expansion of W atoms in the WC@C composite might be further enhanced due to these severe defects, particularly for the dispersed single-atom W-C complex. The WC@C synthesized herein provides multi-combined advantages as a synthetic catalyst.

In order to confirm the electrochemical catalytic properties of WC@C composite, the ORR properties were evaluated systematically in N₂- and O₂-saturated 0.1M KOH electrolytes by using an Ag/AgCl three-electrode electrochemical cell. The WC@C composite was deposited on a rotated-disk glassy carbon (GC) electrode (5.6 mm in diameter) and the mass density was

controlled at $60 \mu\text{gcm}^{-2}$. **Fig. 4A** shows the cyclic voltammetry (CV) curves of the catalysts recorded in both electrolytes at room temperature and at a scan rate of 100 mVs^{-1} . It can be seen that, a well-defined cathodic O_2 reduction current peak appears at $-0.1 \text{ V} \sim -0.4$ in the O_2 -saturated 0.1 M KOH electrolyte, but it is absent in N_2 -saturated 0.1 M KOH electrolyte, proving the ORR catalytic activity of WC@C composite.

To uncover the electrochemical kinetic feature of WC@C composite during the ORR electrochemical process, polarization curves were carried out at a scan rate of 5 mVs^{-1} and at different rotation rates ranging from 200 to 1400 rpm, as shown in **Fig. 4B**. The mass-transfer-limited current density was evidently enhanced as increasing the rotation rate, associated with an onset potential at -0.23 V . **Fig. 4C** shows the calculated Koutecky-Levich (*K-L*) plots (J^{-1} vs. $\omega^{-1/2}$) based on the Koutecky-Levich (*K-L*) equations [Eq. (1-3)], in which the expected linearity and parallelism at all the potential simply first-order reaction kinetics. According to the *K-L* plots, the limited diffusion currents (J_K) and the electron transfer number (n) can be obtained:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_o(D_o)^{2/3}\nu^{-1/6} \quad (2)$$

$$J_K = nFkC_o \quad (3)$$

Where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of rotated-disk electrode, n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant ($F=96485 \text{ C}\cdot\text{mol}^{-1}$), C_o is the bulk concentration of O_2 , ($C_o = 1.2 \times 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$), ν is the kinematic viscosity of the electrolyte ($\nu=0.01 \text{ cm}^2\cdot\text{s}^{-1}$), D_o is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$). The n and J_k were calculated to be $3.8 \sim 4.2$ and $6.2 \sim 23.3 \text{ mAcm}^{-2}$ at the potential range of $-0.4 \text{ V} \sim -0.8$

V, respectively, as shown in **Fig. 4D**. It is proven the four-electron transfer process of oxygen reduction for WC@C catalyst.

The durability of the WC@C catalyst was evaluated by the normalized chronoamperometric curve recorded at -0.40 V and a rotation rate of 1400 rpm in an O₂-saturated 0.1 M KOH electrolyte. As shown in **Fig. 5A**, the residual current density after 30000s measurement can effectively remain at ~80 %, presenting more superior durability than that of graphene, mesoporous carbon and commercially Pt-C.[41-44] Furthermore, the anti-interfering experiments were carried out in the chronoamperometric measurement in the O₂-saturated 0.1M KOH electrolyte, as shown in the inset of **Fig. 5A**. One cannot observe noticeable current change by the additions of 10 ml methanol or ethanol in a 500 ml electrolyte cell. Such high selectivity of the WC@C catalyst towards the ORR can effectively avoid crossover effects in polymer electrolyte fuel cells. In particular, the current density (6.2~23.3 mAcm⁻² at -0.4 ~ -0.8 V) and stability of J_k (**Fig. 5B and C**) are comparable to that of other currently reported catalysts, such as commercially Pt-C (5.1 mAcm⁻²),[41]graphene (3.3~5.3 mAcm⁻² for S-doped and 2.5~7.8 mAcm⁻² for N-doped), [41] and born/nitrogen-doped CNTs (5.4~9.5 mAcm⁻²).[43, 44]

As we known, the origin of the catalytic characteristics of carbides of groups IV through VI can be ascribed to the increased density of states (DOS) near the Fermi surface.[12] Here we calculated the electronic properties of WC clusters with different sizes and single W atoms and the iso-surfaces of the charge densities in a small energy window near the Fermi surface are shown in **Fig.6A**. It suggest that the d-electrons located both at external corners and edges of low-coordinated W atoms in the carbide particles, as well as the electrons on the single W atoms incorporated into the graphitic layers, result in an increased DOS near the Fermi surface. **Fig.6B and C** show the DOS of d-electrons of W and present much higher values for ultra-small clusters

and single W atoms compared with bulk WC.

To reveal the catalytic ability of these single W atoms in ORR, a simplified model consisting of an O₂ molecule adsorbed on the surface of the single W atom-doped graphite layer was characterized using spin-polarized first-principles calculations. We considered all the possible configurations of a single W atom at a single vacancy, bi vacancy, tri vacancy or quad vacancy of carbon atomic layer. In all the configurations that we proposed, the configuration shown in **Fig.6D** is the most probable site for O₂ catalytic reduction. Accordingly, we studied the catalytic activity of an O₂ molecule adsorbed on this most probable configuration of a single W atom–carbon layer. The free O₂ molecule was added close to the W–carbon layer without any artificial assumption, such as the adsorption sites. By optimizing both the structure and energy at 300 K, the O₂ molecule seeks its most favourable absorption site and configuration, and bonds with the W atom after only ~100 ps (20,000 steps) simulation. The bond length of the O₂ molecule was calculated to be 1.22Å and the atomic configuration of O₂ adsorbed on the single W site was calculated, including spin polarization. The diatomic adsorption effectively weakens the O–O bonding. The O–O bond length and stretching frequency are computed to be 0.151nm and 519 cm⁻¹, significantly weaker than that of O₂ at a perfect Pt[48] surface (0.143nm and 690 cm⁻¹),[48] which thus facilitates the O–O dissociation. From the iso-energy surfaces of electron densities differences shown in **Fig.6D**, an obvious charge transfer from the W atom to the two O atoms can be observed, associated with a filling of π^* anti bonding states. This is the origin of the relatively low O–O dissociation energy barrier. These atomic-scale insights confirm that the low-coordinated and single W atoms are the most active catalyst sites.

The chemical and structural stability of catalysts would be unavoidably reduced as decreasing the catalyst size, in particular down to sub-nanometer scale, which has seriously

limited the optimization of catalytic activity. In the present study, ultrasmall WC catalysts are completely encapsulated within graphitic layers, and thus the agglomeration and coarsening of catalysts can be effectively suppressed during reaction processes. Moreover, high-defective graphitic layers, associated with a high density of sub-nanometre porous channels, significantly improve the penetration and exchange for O₂ molecules, ions and electrolyte, as well as the overall conductivity, as illustrated in **Fig. 7**. These combined advantages therefore make WC@C catalysts simultaneously possess high-performance catalytic activity and stability.

4. Conclusions

In conclusion, the encapsulation architecture of WC@C catalysts not only prohibits the chemical/thermal coarsening of WC clusters, but the highly defective graphitic layers can also improve the overall conductivity and penetration capacities. These combined advantages of WC@C composite thus result in a competitive potential as a substitute of noble metal-based catalysts, and open up a new approach for developing non-noble metal-based catalysts. However, more theoretical and experimental works are also needed to fully understand the roles of individual WC, W₂C and graphitic phases, as well as to further optimize the catalytic performances of WC@C composite by modifying the arc-discharge approach in coming works.

Acknowledgments

JJG and HXZ gratefully acknowledge the National Natural Science Foundation of China (51501124) and Basic Research Project in Shanxi Province (2015021071, 2015011037). PFG gratefully acknowledge the support of the national 1000-plan for young scholars. XFZ acknowledges the support of National Natural Science Foundation of China (51471045), the national 1000-plan for young scholars, and the start-up funding supported from the Northeastern

University of China. XFZ and GWQ thank Changjiang Scholars and Innovative Research Team in University (No. IRT0713). This research used facilities provided by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Science, Basic Energy Sciences, U.S. Department of Energy.

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Fig.1 Microstructural characterizations of WC@C catalysts. **A**, Bright-field STEM image of WC@C complex composite. **B**, ADF image of the same region as Fig.1A, exhibiting ultrasmall tungsten carbide particles (bright points) that are unobvious in the BF image. **C**, the size distribution of WC clusters. **D**, One representative tungsten carbide cluster presents the evident contrast difference compared with the graphitic layer matrix, in which the ADF intensity was quantitatively measured as marked by a white square.

Fig. 2 Microstructural characterizations of WC@C catalysts. **A**, X-ray diffraction pattern of WC@C powders, showing that the product is composed of WC_2 , WC, and graphite phases. **B**, Raman spectroscopy of WC@C powders. Noted that the fitted peaks (I, II, III and IV) at 1224.4 cm^{-1} , 1324.8 cm^{-1} , 1452.7 cm^{-1} , and 1583.4 cm^{-1} can be attributed to the signatures of nanocrystalline diamond, D band, and fullerenes, and G band, respectively.

Fig. 3 Microstructures of WC@C catalysts. **A** and **B**, ADF image and the corresponding STEM image of WC@C complex consisting of several WC clusters, in which four representative regions are identified. Enlarged A1, A2, A3 and A4 images and the FFT patterns of the regions reveal atomic structures of WC clusters encapsulated in the graphitic layers, such as lattice distortion (A2), amorphous state (A3) and even some dispersed single tungsten atoms (A4) those are marked by white circles.

Fig.4 Evaluation of ORR activity performances of WC@C catalysts. **A**, Cyclic voltammograms (CV) curves of ORR on WC@C complex in a N_2 -saturated 0.1M KOH solution, an O_2 -saturated 0.1M KOH solution at a scan rate of 100 mVs. The inset in **Fig.4A** is the Scanning electron microscopy (SEM) image of deposited WC@C catalyst electrode. **B**, Linear sweep voltammetry curves recorded for WC@C complex in an O_2 -saturated 0.1M KOH solution at a scan rate of 5 mVs $^{-1}$ and different rotation rates. **C**, Koutecky-Levich plot of J^{-1} versus $w^{-1/2}$ at different electrode potentials. **D**, The dependence of electron transfer number (n) on potential and the Kinetic-limiting current density (J_k) at -0.4 V.

Fig.5 Evaluation of ORR stability performances of WC@C catalysts. **A**, Chronoamperometric response curve of WC@C complex recorded at -0.5 V in an O₂-saturated 0.1M KOH at a rotation rate of 1400 rpm. The inset in **A**, Chronoamperometric response curve was further performed under the addition of methanol and ethanol, evidencing the electrocatalytic selectivity of WC@C complex. **B** and **C**, Kinetic-limiting current stability and density (J_k) at -0.5 V in comparison with that of the reported studies. The reference numbers (1), (2), (3), (4), (5), (6),(7) and (8) correspond to the present WC@C complex, commercial Pt nanoparticles[40], Au clusters [21], sulfur-doped graphene[40], nitrogen-doped grapheme[40], nitrogen-doped carbon nanotubes[42], nitrogen/boron-doped carbon nanotubes[42], and nitrogen-doped mesoporous carbon [43], respectively. Noted that the J_k value of BN-CNT is calculated at -0.3 V and the others are at -0.5 V.

Fig.6 Theoretical simulation of the catalytic origins. **A**, The electronic properties of WC clusters with different sizes and single W atoms and the iso-surfaces of the charge densities in a small energy window near the Fermi surface. **B** and **C** show the DOS of d-electrons of W and present much higher values for ultra-small clusters and single W atoms compared with bulk WC. **D**, Isosurface of the difference in electron density before and after O_2 adsorption.

Fig.7 Illustration for WC@C catalysts as the catalytic cathode. WC catalysts are completely encapsulated within high-defective graphitic layers, which improve the catalytic stability by suppressing the crystalline growth and agglomeration of WC clusters, and meanwhile enhance the penetration of oxygen molecules , ions and electrolyte during the reaction processes, as well as the formation of three dimensional conductive skeletons.

Graphical abstract

Ultrasmall Tungsten Carbide Catalysts Stabilized in Graphitic Layers for High-performance Oxygen Reduction Reaction

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We synthesized WC catalysts with a mean diameter of 1.9 ± 0.9 nm, comprising a high density of single W atoms, sub-nanometer and nanometer WC clusters, which are completely encapsulated in high-defective graphitic layers (WC@C). Such high-defective graphitic layers not only improve the overall conductivity for accelerating the penetration and exchange of ions and electrons during the electrocatalytic process of oxygen reduction, but also suppress the chemical/thermal coarsening of WC catalysts, thus providing excellent electrocatalytic performances in four-electron transfer process for oxygen reduction reaction.