Structure-controlled tungsten carbide nanoplates for enhanced hydrogen evolution reaction

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Abstract

Developing a low-cost and durable non-noble metal electrocatalyst for hydrogen evolution reaction (HER) is critical in efficient hydrogen production. Herein, tungsten carbide nanoparticles (WC NPs) with typical mesoporous structure were prepared by a controlled hydrothermal reaction followed by a gas-solid carburization process. The crystal phases, microstructure and chemical components of the nanoplates were characterized, and their electrochemical properties were measured. The results show that the as-prepared WC NPs expose active sites upmost, and exhibit enhanced conductivity and superior HER performance in acid solution in terms of a small $\eta_{10}$ (overpotential to obtain a current density of 10 mA cm$^{-2}$) of 120 mV, a Tafel slope of 58 mV dec$^{-1}$ and outstanding long-term cycling stability. These indicate that the HER properties of WC NPs are dramatically enhanced compared to that of all phase pure WC materials reported in recent years. This enhancement can be attributed to their unique structural and electronic properties, which can be exploited to improve the electrochemical properties of traditional non-noble metal material.

1. Introduction

Hydrogen, as a clean and efficient alternative energy source to conventional fossil fuels, has been received considerable attention to meet the growing energy demand and warming all over the world. Hence, to achieve efficient routes for hydrogen production is becoming increasingly important. Hydrogen production via electrochemically water splitting is sustainable and eco-friendly compared to the other technologies, such as coal gasification, steam reforming of natural gas, and partial oxidation of heavy oil [1–3]. Electrochemical water splitting offers a strategy to realize clean and sustainable energy through the efficient conversion of water to H$_2$ via electric energy, and there is an increasing demand to achieve active and efficient electrocatalysts for hydrogen evolution reaction (HER). Pt-based metals are regarded as benchmark catalysts for HER due to their low overpotential and fast kinetics. However, their high cost and limited natural reserves are main obstacles toward wide practical application [4, 5]. Therefore, it’s necessary to develop alternatively inexpensive and earth-abundant electrocatalysts in terms of both superior activity and durability.

Recently, a number of non-precious catalysts including alloys [6], transition metal chalcogenides [7], selenides [8], phosphides [9], nitrides [10] and carbides [11] have been emerging as attractive electrocatalysts to replace the Pt-based metals towards HER. Among these catalysts, transition metal carbides have attracted much attention owing to their several advantageous physical and chemical properties, such as high electrical conductivity, relatively good anticorrosion performance, and favorable stability, etc. [1, 12], which make them ideal materials in electrocatalysis. Notably, W-based carbides are known for their Pt-like catalytic behavior such as in hydrogenolysis [13]. Their remarkable catalytic activities are confirmed to be attributed to their electron configuration around Fermi level [14]. These properties enable tungsten carbide (WC) to be a promising candidate in electrocatalytic application as a non-noble metal electrocatalyst for HER in acidic media. Nevertheless, it has remained a great challenge to scalable synthesize tungsten carbides with relatively low
hydrogen binding energy and carbon-coke, which restricts hydrogen desorption process during electrocatalysis [15–17], and to improve their electrocatalytic activity for HER without the assistance of noble metals catalyst. Therefore, it is valuable and critical to explore WC based materials with better performance. In general, HER activity of WC can be further improved by increasing its exposed surface area, active sites, and manipulating the reactants transportation across the interface between electrolyte and electrode [18]. It is evident that mesoporous structure with high specific surface area and large catalytic active site are propitious to rapid and efficient reaction [19]. However, the investigations related to the mesoporous structure of tungsten carbides with their HER ability are few. Therefore, it is quite reasonable and valuable to design WC based electrocatalysts with a large number of active sites to enhance their catalytic activity.

Herein, mesoporous WC nanoplates fabricated by combining a hydrothermal reaction with a subsequent gas-solid carburization process were reported. Their enhanced HER electrocatalytic activity with a low onset overpotential of 63 mV, $\eta_{10}$ of 120 mV, and Tafel slope of 58 mV dec$^{-1}$ in acid solution, and their prominent long-time stability with unobservable degradation of the catalytic ability were presented concerning phase pure WC. This enhancement can be attributed to their unique structural and electronic properties, which can be exploited to improve the electrochemical properties of traditionally non-noble metal material.

2. Experimental

2.1. Preparation of WO$_3$·H$_2$O NPs

Uniform WO$_3$·H$_2$O NPs precursor was synthesized according to modified reported method [20]. 5.28 g of Na$_2$WO$_4$·2H$_2$O was dissolved in 40 mL of deionized water, and 2 mol L$^{-1}$ HCl was dropwise added into the Na$_2$WO$_4$·2H$_2$O solution until its pH had reached 0.5. Then 0.67 g of H$_2$C$_2$O$_4$·2H$_2$O was added into the mixed solution, which formed a yellow-green solution. The obtained solution was transferred into a hydrothermal reactor and kept at 100°C for 12 h. After the reactor cooled naturally to room temperature, WO$_3$·H$_2$O NPs were obtained by centrifugation.

2.2. Preparation of WC NPs

0.5 g of WO$_3$·H$_2$O NPs precursor was put into a quartz boat and the boat was set in the middle of a tubal stove. Prior to the elevation of temperature, a N$_2$ carrier gas was applied to the stove for 30 min to remove air in it. Then the N$_2$ was replaced by a mixed carrier gas of CH$_4$ and H$_2$ with a volume ratio of 2:3 (CH$_4$ to H$_2$). Subsequently, the stove was heated from room temperature to a definite temperature (550°C, 650°C, 750°C, and 850°C) with a ramp rate of 5°C min$^{-1}$, and maintained at this temperature for 5 h. When the tubal stove was cooled to room temperature under the protection of pure N$_2$ gas, the powders in the boat were collected, symbolized as WC550, WC650, WC750, and WC850 corresponding to their reaction temperatures, and used as the samples for further explorations. For comparison, WC (CH$_4$:H$_2$ = 3:2) was synthesized under the same procedures expect replace the gas volume ratio of 2:3 (CH$_4$ to H$_2$) to 3:2.

2.3. Characterizations

The crystal phases, morphologies and microstructures of WO$_3$·H$_2$O NPs and WC NPs were characterized by x-ray diffraction (XRD, CuK$_\alpha$, $\lambda = 0.154056$ nm, PANalytical Netherlands), scanning electron microscope (SEM, S-4700 II Hitachi, Japan) and high-resolution field emission transmission electron microscope (HRTEM, Tecnai G2 F30 S-Twin, Philips- FEI, Netherlands), respectively.

2.4. Electrochemical measurements

All electrocatalytic experiments were conducted on CHI660e (Chenhua Ltd., Shanghai China) with a three-electrode system containing 0.5 M H$_2$SO$_4$ at room temperature (25°C). A graphite rod and an Ag/AgCl electrode were used as the counter and reference electrode, respectively. All the potentials listed in this paper were calibrated to RHE, $E_{RHE} = E_{Ag/AgCl} + 0.0591pH + 0.1987$, and the polarization curves demonstrated were corrected for IR losses. Typically, 4 mg of the as-prepared catalyst was added in 300 $\mu$L of mixed solution (270 $\mu$L of isopropanol and 30 $\mu$L of Nafton (5 wt%)). The mixed solution was ultrasonic for 20 min to get a homogeneous catalyst ink. Later, 4 $\mu$L of the ink was fetched and dropped onto the surface of a glassy carbon electrode (GCE, catalyst loading $\sim$0.53 mg cm$^{-2}$) and dried in air. Linear sweep voltammetry (LSV) was performed in 0.5 M H$_2$SO$_4$ at a rate of 5 mV s$^{-1}$. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 10 MHz to 10 mHz at a constant 0.15 V. The electrochemical stability of the catalyst was conducted by cycling the potential between $–0.15$ to 2.5 V at a scan rate of 100 mV s$^{-1}$ for 5000 cycle. I-t test was measured at a potential of $–0.15$ V for 15 h. The double-layer capacitances (Cdl) were estimated based on cyclic voltammograms (CV) at various sweep rates from 5 to 100 mV s$^{-1}$. 
3. Result and discussion

XRD patterns of WO$_3$·H$_2$O precursor (figure 1(a)) and WC samples (figure 1(b)), curve b1-b4 represents XRD patterns of WC550, WC650, WC750, and WC850, respectively are presented in figure 1. From figure 1(a), one can see five diffraction peaks with 2θ at 16.54, 25.64, 34.14, 34.96, and 52.65°, respectively, which could be accordingly assigned to (020), (111), (200), (002), and (222) planes of orthorhombic WO$_3$·H$_2$O (PDF: 84–0886), respectively. In addition, two sharp peaks, corresponding to (020) and (111) planes, with much higher intensities than those of other planes, indicate that the crystallinity of WO$_3$·H$_2$O precursor hydrothermally treated is very well. XRD patterns of WC550 exhibit 10 main peaks with 2θ at 34.53, 37.97, 39.40, 40.28, 52.35, 58.36, 61.72, 73.12, 74.71, and 75.87°, respectively, as shown in figure 1(b1). Among these peaks, the ones with 2θ at 40.28, 58.36, and 73.12° could be indexed to cubic W (PDF: 89–3659); those with 2θ at 34.53, 37.97, 39.40, 52.35, 61.72, 74.71, and 75.87° could be assigned to hexagonal W$_2$C (PDF: 89–2371). These ascriptions indicate that the crystal phase of WC550 is composed of W and W$_2$C almost. Further, when the WO$_3$·H$_2$O precursor was reduced and carbonized at 650 °C, the crystal phase of W disappeared, and 4 peaks with 2θ at 31.46, 35.59, 48.36, and 73.21° which could be assigned to (001), (100), (101), and (111) planes of hexagonal WC (PDF: 89–2727), respectively, could be seen in figure 1(b2). These imply that the crystal phases of WC650 are composed of WC and W$_2$C, and the main phase of WC650 is W$_2$C (W$_2$C:WC ≈ 2.70). When the reduced and carbonized temperature of the precursor was over than 750 °C, XRD patterns of WC750 (figure 1(b3)) is almost the same as that of WC650, however, the ratio between W$_2$C and WC has decreased to 1.33, indicating that higher temperature benefits the formation of partial W$_2$C in WC. Moreover, it’s should be noted that no obvious peak could be assigned to the crystal planes of W$_2$C or W in WC850, indicating that the crystal phase of WC850 was WC only. These results illustrate that as the reduced and carbonized temperature increasing, the dispersion of C atoms in WC lattice was increased. This facilitates the gas-solid reaction and carbonization in the process of sample preparation, and results in the formation of pure phase WC. Based on the above results, one conclusion can be drawn that the synthesis of WC follows WO$_3$·H$_2$O $\rightarrow$ W $\rightarrow$ W$_2$C $\rightarrow$ WC sequence. This indicates that the control of crystal phase of tungsten carbide might be easily achieved by adjusting its preparing temperature.

Most traditional methods (such as those using solid carbon precursors) are unable to yield WC at a relatively low temperature for nanoparticles are often sintered at higher temperature, and carbon diffusion across solid-solid interface and enter into tungsten lattice normally proceeds too slow for WC phase to be completely engineered. In this work, gaseous methane was used as carbon precursor and hydrogen as reductant may present a unique solution to this problem. Under this gaseous environment, the chemical activity of gaseous carbon precursors is relatively higher to that of solid carbon. They would accelerate carbon diffusion across gas-solid interface much faster, opening up the possibility to obtain the pure tungsten carbide phase even at low temperature, such as 650 °C. Guided by this design principle, a two-step approach to prepared mesoporous pure tungsten carbide nanoplates (figure 2(a)) was proposed. The optimal conditions to afford porous nanoplate structure and phase-pure catalyst were found at 650 °C for 5 h (WC650). WC650 prepared under optimized conditions exhibits the best HER performance. Therefore, it was utilized in further investigation to understand the relationship between its property and structure. The SEM images of the precursor, WO$_3$·H$_2$O, are shown in figures 2(b) and (c), from which, the morphology of the precursor is regular square plate with smooth surface and regular edge. The thickness of the nanoplates is between 60–90 nm, and the width of the plates is in the range of 500–800 nm. SEM images of WC650 are shown in figures 2(d) and (e), from which, the morphology of the sample is also regular square plate with rough surface. The thickness of the plates is between 60–90 nm, and the
The width of the nanoplates is in the range of 500 to 800 nm. These parameters are almost the same with that of its precursor, WO$_3$·H$_2$O, which indicates that the macro-characteristic of the sample prepared at 650 °C did not change obviously. However, there is a critical difference in terms of their mesostructure, i.e., the nanoplate of the precursor does not display any special characteristic, while for the sample, it is constituted of nanoparticle and mesopore, as shown in figure 2(e), with the crystallite size of the nanoparticle changing from 20 to 30 nm and the aperture of the mesopore varying from 5 to 40 nm. The reason for the critical difference might be explained by the following mechanism. When heated, WO$_3$·H$_2$O precursor would decompose into WO$_3$ (s) and H$_2$O (g), and the H$_2$O (g) would continuously produce during the reduction-carbonization process due to the reduced of WO$_3$ (s) by a mixed flow (H$_2$ and CH$_4$), which could then react with the WO$_3$ intermediate at high temperature, according to the formula: H$_2$O (g) + WO$_3$ (s) → WO$_2$(OH)$_2$ (g) [21–23]. As a result, some WO$_3$ and H$_2$O would continuously be transformed to gaseous WO$_2$(OH)$_2$, which would be removed away by the mixture flow of H$_2$ and CH$_4$, and result in the mesostructure formation of the samples. Besides, three oxygen atoms of the WO$_3$·H$_2$O precursor were replaced by one carbon atoms during the in situ reduction-carbonization process, which inevitably lead to the creation of cavity.

Figures 2(f) and (g) are TEM images of the WO$_3$·H$_2$O precursor. From figure 2(f) and its inserted image, the morphology of the precursor is square plate with smooth surface and edge whose width varies from 500 to 800 nm. These results are consistent with that of SEM images. In addition, from figure 2(g), lattice fringes in two directions could be clearly seen, and in one direction, an interplanar spacing of 0.3786 nm, might correspond to the (120) plane of WO$_3$·H$_2$O, which is consistent with that of the XRD test. The morphology of the sample prepared at 650 °C is also regular square plate, as shown in figure 2(h) and 2(i). However, the nanoplates are with rough surface which is constituted of nanoparticles and mesopores. This is consistent with SEM images. The microstructure of the nanoplate is shown in figure 2(i), in which lattice fringes in several directions are exhibited. The lattice fringe with an interplanar spacing of 0.2478 nm could be attributed to the (100) plane of WC, and an interplanar spacing of 0.2281 nm could be attributed to the (121) plane of W$_2$C, assuring the existence of both WC phase and W$_2$C phase in the nanoplates. The pattern of selected area electron diffraction (SAED) of the nanoplate is concentric circles with uneven brightness, as shown in the inserted image of figure 2(i), indicating the nanoplate is polycrystalline.

The surface electronic structure and elemental valence of WC650 were investigated by x-ray photoelectron spectroscopy (XPS). The wide range XPS spectrum of the WC650 is shown in figure 3(a), revealing the surface
The chemical elements of WC650 are composed of O, C and W. All binding energies have been calibrated with reference to C 1s (284.6 eV). The XPS spectra of W 4f of WC650 sample are shown in figure 3(b). The W 4f spectrum of WC650 could be deconvoluted into three doublets. Two peaks observed at 32.6 and 34.7 eV can be correspond to W4+, and other two peaks at 32.0 and 34.1 eV can be assigned to W2+. The peaks with binding energies at 36.0 and 38.1 eV can be indexed to W6+, and attributed to the inevitable surface oxidation of WC650 exposed to air [24]. The specific area and aperture of WO3·H2O precursor and WC650 were measured by nitrogen adsorption/desorption measurements and the results are shown in figure 3(c). The adsorption and desorption curves of both samples are typical IV model. In addition, the estimated results based on Brunauer–Emmett–Teller (BET) data show that the specific area and average aperture of WO3·H2O are 8.12 m² g⁻¹ and 15.69 nm, respectively, while that of WC650 are 22.00 m² g⁻¹ and 11.63 nm, respectively, indicating the nanoplates of WC650 are mesoporous, which is consistent with that of their SEM and TEM images.

To shed light on the effect of the as-prepared samples (WC550, WC650, WC750 and WC850) on electrocatalytic performance, the catalytic properties of the as-prepared samples toward HER were evaluated by LSV with iR-correction in 0.5 M H2SO4. Meanwhile, the HER polarization curves of WO3·H2O and Pt/C (10 wt%) were also measured under the same test conditions for comparison. As shown in figure 4(a), Pt/C
exhibited a nearly zero HER onset overpotential in acid solution and delivered a current density of 10 mA cm$^{-2}$ at an overpotential of 10 mV versus RHE. Whereas, WO$_3$·H$_2$O precursor exhibits negligible HER activity. WC$_{650}$ catalyst yields the best performance with a lowest $\eta_{10}$ of 120 mV versus RHE in contrast to WC$_{550}$ (192 mV), WC$_{750}$ (254 mV), WC$_{850}$ (360 mV). WC$_{550}$ catalyst exhibits inferior HER performance, which might be due to the insufficient conversion of W$_2$C from W at lower temperature. Previous reports have demonstrated that the W$_2$C phase exhibits better HER activity than WC because of a closer to zero hydrogen adsorption free energy and a higher electronic density of states (DOS) at the Fermi level [25]. When the temperature is over 750 °C, the ratio between W$_2$C and WC of the sample was decreased to 1.33, also induced the decrease of HER activity. To further understand the kinetic mechanism of the as-prepared catalysts, the corresponding Tafel plots of Pt/C and WC NPs are shown in figure 4(b). The Tafel slope of WC$_{650}$ is estimated to be 58 mV dec$^{-1}$ in 0.5 M

Figure 4. (a) LSV curves and (b) Tafel plots of WO$_3$·H$_2$O, Pt/C, WC$_{550}$, WC$_{650}$, and WC$_{850}$ in 0.5 M H$_2$SO$_4$. (c) CV curves of WC$_{650}$ with different scan speeds in 0.5 M H$_2$SO$_4$. Inset: the variation of the current density $\Delta J$ at 0.21 V (versus RHE) against the scan speed (5–100 mV s$^{-1}$) for WC$_{650}$. (d) Estimated Cdl of WC$_{350}$, WC$_{650}$, WC$_{750}$, and WC$_{850}$ in 0.5 M H$_2$SO$_4$. (e) EIS curves of WO$_3$·H$_2$O, WC$_{350}$, WC$_{650}$, WC$_{750}$, and WC$_{850}$ at 0.15 V versus RHE in 0.5 M H$_2$SO$_4$. (f) Polarization curves of WC$_{650}$ before and after 5000 CV cycles in 0.5 M H$_2$SO$_4$. Inset: Time-dependent current density curves of WC$_{650}$ at a constant overpotential of −150 mV for 15 h in 0.5 M H$_2$SO$_4$.
H₂SO₄, which is lower than that of WC550 (68 mV dec⁻¹), WC750 (76 mV dec⁻¹), WC850 (98 mV dec⁻¹). The exchange current density 𝑗₀ (obtained by the extrapolation method on the basic of Tafel plot) of the WC550, WC650, WC750, and WC850 were estimated to be 1.64 × 10⁻², 8.38 × 10⁻², 5.97 × 10⁻³, 3.44 × 10⁻³ mA cm⁻² respectively. The above results imply that the HER process of WC650 is more efficient than that of the other samples, which indicating that it exhibits faster HER reaction kinetics that follow a Volmer-Heyrovsky mechanism.

To deeply investigate the intrinsic activity of the samples, the electrochemical CV curves and impedance spectrum measurements were conducted. A capacitance of electrochemical double-layer mechanism. Other samples, which indicating that it exhibits faster HER reaction kinetics that follow a Volmer-Heyrovsky mechanism.

The large value of Cdl for WC650 can be attributed to its unique mesoporous nanoplate structure, which well retains the high electrocatalytic activity of the WC and W₂C phase. In addition, the interface behavior and electrode kinetics of as-prepared catalysts were measured by electrochemical impedance spectroscopy (EIS) under HER operating conditions, and the corresponding Nyquist plots of the WC NPs with different pyrolysis temperature (WC550, WC650, WC750, and WC850) are shown in figure 4(e). It can be seen that the charge-transfer resistance value (Rct) of WO₃·H₂O is 3 to 4 orders of magnitude higher than that of the sample after reduction and carbonization, and WC650 (3.2 Ω) is smaller than that of WC550 (108.2 Ω) and WC750 (3.8 Ω), indicating a faster charge transfer kinetics for the HER.

As a virtual assessment of the electrocatalyst, a long-term electrochemical stability test of WC650 in 0.5 M H₂SO₄ solution has been performed. After the working electrode was looped for 5000 consecutive CV sweeps between −0.15 V to 0.3 V (versus RHE) at 0.1 V s⁻¹, the polarization curve of the catalyst showed unmeasurable decline of the cathodic current, and the current density was well maintained without any drastic decrease at an overpotential of 150 mV (20 mA cm⁻²) for 15 h (figure 4(f)). Both results demonstrate that WC650 possesses long-term stability in acidic electrolyte, which is probably due to introduction of highly stable WC, the unique nanoplate structure and mesoporous structure. To understand the superior catalytic stability of the WC650 catalyst, TEM images of the catalyst was obtained after chronotentiometry study for 15 h (figure 5). As shown in the TEM images of the catalyst, it has similar morphology to that of WC650 before chronotentiometry study. In particular, the crystal phase of WC and W₂C were well-maintained without any oxidize, as shown in figure 5b.

The electrocatalytic HER performance of the sample prepared with a volume ratio of 3:2 (CH₄ to H₂) was also investigated, as displayed in figures 6(a) and (b). Although the WC (CH₄:H₂ = 3:2) could act as an excellent methanol oxidation reaction electrocatalyst, the HER occurred at a very high overpotential of ~206 mV (figure 6(a)), which is 86 mV higher than that of WC650. The corresponding Tafel slope of 60 mV dec⁻¹ for WC (CH₄:H₂ = 3:2) (figure 6(b)) is also higher than that of WC650, suggesting too much methane in thermal carburization reaction will hinder the electrocatalytic performance of the catalyst. The HER performance of WC-based HER electrocatalysts, such as WC nanocrystals [26], W₂C@WS₂ [27], WC nanoparticles [28], W₂C@WC₁₋ₓ [29], WC spherical [30], W₂CIO [31], and W₂C@CNT [32], reported in recent years in 0.5 M
H$_2$SO$_4$ are listed in figure 6(c). Among them, WC650 exhibits the best HER activity, which further confirms the remarkably electrocatalytic performance of WC650 in acidic media.

4. Conclusions

In summary, the porous WC NPs catalyst for the HER has been prepared via a hydrothermal reaction followed by reduction carbonization, in which the nanoplate and mesoporous structure is beneficial for providing fast electron transport pathways and improving the transportation efficiency of charge carrier for electrocatalytic reaction. Such porous WC NPs catalyst provides the excellent HER performance in acidic solution in terms of low overpotential, low Tafel slope and long-term stability, which outperformed most of the previously reported WC-base catalysts. The superior activity and good long-term stability can be attributed to the favorable electronic structure of WC and the mesoporous nanoplate structure, which offered more active sites and an improved charge/mass transfer process. This work presents a new avenue to explore the rational structural design of tungsten carbide based electrocatalysts with superior HER activity and suggests a feasible way to explore more efficient transition metal carbide electrocatalyst systems.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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