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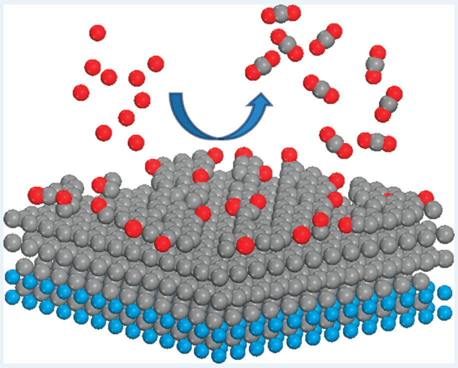
Activation of Tungsten Carbide Catalysts by Use of an Oxygen Plasma Pretreatment

Xiaofang Yang,[†,‡] Yannick C. Kimmel,[‡] Jie Fu,[†] Bruce E. Koel,[†,*] and Jingguang G. Chen[‡,*]

[†]Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States
[‡]Catalysis Center for Energy Innovation, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716, United States

ABSTRACT: Tungsten carbide (WC) has been considered a promising replacement for precious metal-based catalysts and electrocatalysts; however, synthesis of high-quality WC that is free of surface carbon remains a major challenge. Surface carbon adversely influences the catalytic activity of WC and hinders direct interaction between metal adlayer modifiers and the WC substrate. In this letter, we report the beneficial effects of pretreatments of WC foil by atomic oxygen generated in an oxygen plasma source. We found that the graphitic carbon at the WC surface could be removed controllably by the atomic oxygen without causing oxidation of WC, and this improved performances for electrocatalytic methanol oxidation and hydrogen evolution.



KEYWORDS: *tungsten carbide, oxygen plasma treatment, methanol oxidation reaction (MOR), hydrogen evolution reaction (HER)*

Successful applications of proton exchange membrane (PEM) fuel cells and PEM-based electrolyzers are largely dependent on development of advanced electrocatalysts that are not only highly active but also economical and durable. Currently, the most active electrocatalysts for PEM fuel cells and electrolyzers are based on platinum-group metals.[1] The high cost and low abundance of these precious metals prevent them from large-scale use in a PEM fuel cell economy.[2] In the search for inexpensive electrocatalysts to replace precious metals, tungsten monocarbide (WC) has been widely studied as a potential candidate due to the similarity of its electronic structure and catalytic properties to those of platinum.[3−5] Recently, much progress in using WC, either as an electrocatalyst or as a substrate to support low coverages of precious metals, has been made to demonstrate its promising catalytic properties in a variety of electrochemical reactions, such as the oxygen reduction reaction,[6,7] methanol oxidation reaction (MOR),[8,9] and hydrogen evolution reaction (HER).[10]

Phase-pure WC foils and particles are typically synthesized from W or WO_3 at temperatures >1200 K in a flow of hydrocarbon (e.g., methane or acetylene) and H_2,[6,11,12] but this often forms graphitic carbon on the WC surfaces. This additional surface carbon was found to negatively affect the catalytic activity of WC in the HER and MOR.[13,14] Another study found that although the high surface area of WC particles could be stabilized by surface carbon, the catalytic activity for methanol oxidation was reduced.[15] Thus, it is important to understand the activity of WC in the absence of surface carbon. In addition, a platinum monolayer supported on WC has demonstrated comparable performance to that of pure platinum in HER and MOR,[6,9,10,16,17] but the presence of excess carbon on WC before depositing Pt may weaken the role of the WC substrate in modifying the electronic properties of the surface Pt monolayer.[13] Therefore, there is a need to find methods to eliminate extraneous surface carbon from WC materials to better understand these important materials and design better catalysts. In this study, atomic oxygen from an O_2 plasma source was utilized to remove graphitic carbon present on WC surfaces. Two probe reactions, MOR and HER, were selected to evaluate the effect of this plasma treatment to WC foils on both the electrocatalytic activity of WC foils and a Pt monolayer on WC foils. We found that extraneous carbon on WC surfaces could be removed at room temperature without causing substantial oxidation of the WC foil by optimizing the conditions of the plasma exposure. This treatment resulted in significant improvement of the catalytic activity of WC.

WC surfaces were primarily synthesized on a clean W foil (1 cm^2) by carburization at 1273 K in a mixture of 21 vol % methane/hydrogen (total flow rate of 155 cm^3 /min) in a quartz tube furnace. Details of the synthesis of the WC foils are described in a previous paper.[12] The freshly synthesized WC foil usually consists of a 100-nm WC film on the W substrate.[18] In addition, to avoid contamination and oxidation from exposure to air and to examine the growth of the WC film under relatively clean conditions, synthesis was also performed at 1273 K at a pressure of 3 Torr methane in a small high-

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pressure antechamber/load lock attached directly to an ultrahigh vacuum (UHV) chamber used for surface analysis. Specifically, after carburization in the antechamber, the produced WC foils were transferred into the UHV surface analysis chamber equipped with low-energy ion scattering (LEIS), auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). XPS spectra in the C1s and W4f regions were recorded to determine the chemical states of carbon and tungsten and to probe the carbon concentration of the WC foils. Binding energies (BE) are reported referenced to a clean W foil with the W4f$_{7/2}$ peak at 31.4 eV. The surface W coverage was also measured by LEIS. A LEIS spectrum of clean W foil was used as a reference for calculating the number of exposed W sites on the WC foil.

Figure 1A presents typical XPS spectra from a WC foil freshly synthesized in the antechamber. Two distinct C1s peaks confirm the presence of two types of carbon species at the surface: graphitic and carbidic carbon. The W4f$_{7/2}$ peak of WC appears at 31.7 eV BE, which is shifted by 0.3 eV from that of a clean W foil (31.4 eV BE). The number of exposed W sites (calculated as surface coverage (%)) was determined using LEIS by taking the ratio of the W peak intensity of a WC foil to that of a clean W foil. In Figure 1B, a plot is shown of the relationship between the W composition (%) at the surface determined by LEIS and the XPS C1s graphitic/carbidic carbon peak ratio at various stages in the synthesis procedure. A large amount of carbon was always present at the surface from the synthesis of the WC foil, and the graphitic carbon present could completely eliminate the availability of W sites at the surface.

It is necessary to eliminate this excess surface carbon, since it is well-known that such deposition of carbon at WC surfaces can lead to the reduction or deactivation of the catalytic activity. One way to remove surface carbon is through thermal oxidation at high temperature. However, this method often leads to undesirable oxidation of tungsten carbide. An alternative method is to expose the WC surface at low temperatures to an O_2 plasma, as reported here. Plasma processing is widely utilized in semiconductor device manufacturing for surface cleaning and surface modification, but it has rarely been applied for the modification of heterogeneous catalysts. The high reactivity of oxygen ions and atoms in the plasma allows oxidation of surface carbon at relatively low temperature. Furthermore, selection of atomic oxygen from the plasma by filtering out oxygen ions minimizes sputtering effects and should cause less damage to the WC substrate and, thus, reduces deep-layer oxidation.

The antechamber attached to the surface analysis chamber was equipped with a differentially pumped plasma source (tectra Gen2) that was used to process the WC foil samples, which were synthesized in the quartz tube furnace. This plasma source can be operated in atom source mode (with the ion trap switched on) or ion/atom hybrid mode (with the ion trap switched off). For these measurements, the ion trap was switched on to filter out oxygen ions during plasma treatment using 2.0×10^{-5} Torr O_2 pressure. XPS spectra were recorded at 30 s intervals of O_2 plasma exposure to examine changes in the surface carbon. A total exposure of 5 min was used to activate the WC foils for electrochemical measurements.

A comparison of the XPS C1s peaks before and after exposing the WC foil to the O_2 plasma is given in Figure 2A. In spectrum a, three types of carbon were observed in peaks at 282.7, 284.7, and 285.8 eV BE and are assigned as carbidic, graphitic, and "C−OH" carbon, respectively. The XPS C1s peaks of WC treated by 5 min of O_2 plasma are shown in spectrum b. O_2 plasma treatment caused an increase in the carbidic carbon peak and a decrease in the graphitic carbon peak. Other C1s peaks at 286.8 and 288.3 eV BE can be assigned to various oxidized carbon species at the surface. Inspection of the XPS W4f spectra displayed in Figure 2B shows O_2 plasma treatment resulted in a significant increase in the W4f intensity, consistent with the removal of surface carbon. This treatment caused only slight oxidation of the WC foil. Therefore, atomic oxygen exposure on WC samples at room temperature is an effective method to controllably remove noncarbidic surface carbon.

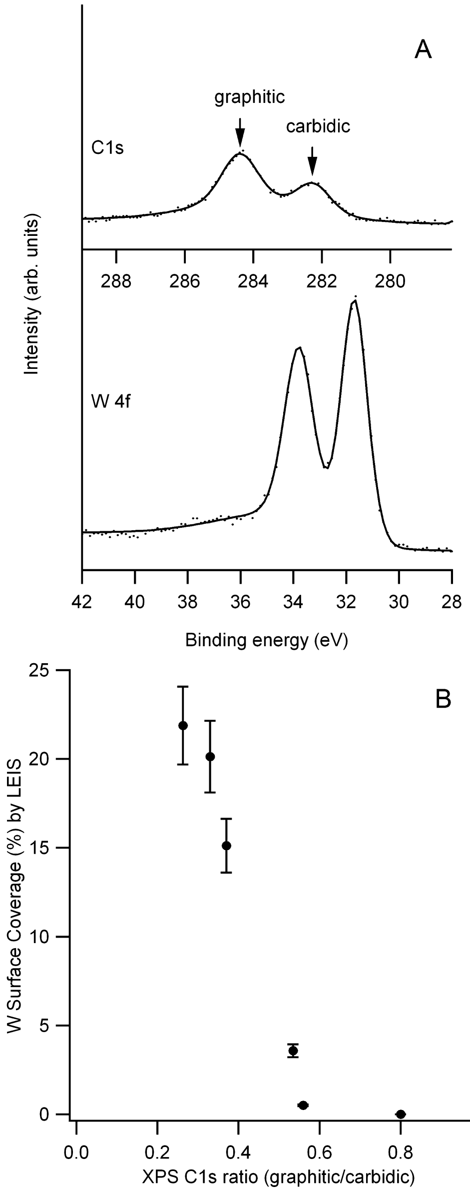

Figure 1. A. XPS spectra of C(1s) and W(4f) regions of a WC foil freshly synthesized on a W substrate in the antechamber. Graphitic and carbidic carbon is present at the surface. Formation of WC is marked by the appearance of the W4f$_{7/2}$ peak at 31.7 eV BE. B. Plot of the surface W coverage determined by LEIS versus the XPS C1s ratio of graphitic/carbidic carbon.

Following O_2 plasma treatment and surface analysis by XPS, the WC foil sample was transferred into an electrochemical cell, and the MOR and HER were studied to evaluate the effect of

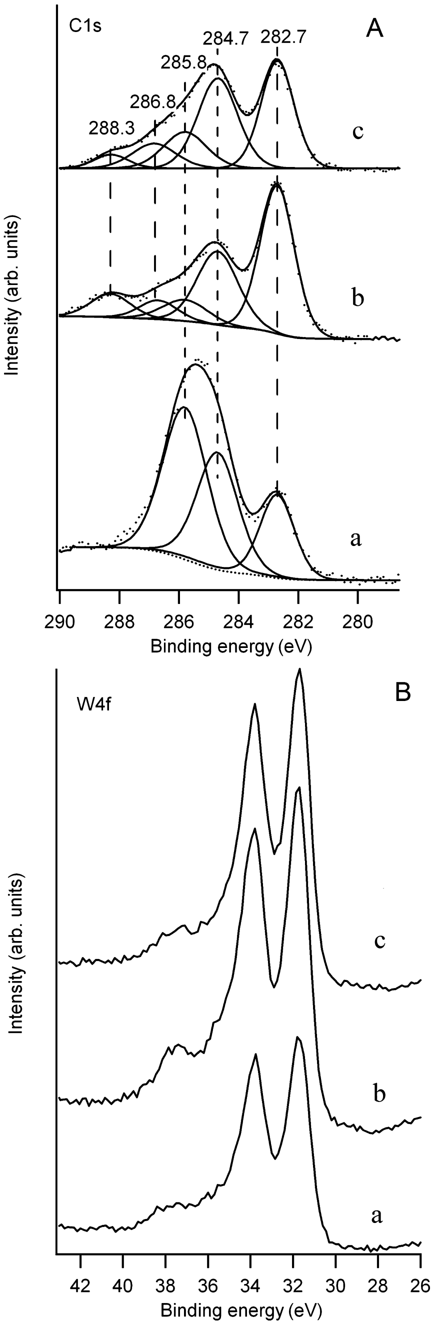

Figure 2. A. XPS spectra of the C1s region for WC foil samples (a) before O_2 plasma treatment, (b) after O_2 plasma treatment, and (c) after MOR. O_2 plasma treatment is able to remove the graphitic carbon. After MOR, some carbon was redeposited onto the surface. B. XPS spectra of the W4f region for WC foil samples. No apparent oxidation of the WC foil was caused by O_2 plasma treatment or MOR.

O_2 plasma treatment on WC electrocatalytic activity. In addition, a Pt ML was deposited on WC foils with and without plasma treatment, and HER activities from these two samples were compared to examine the role of the plasma treatment in modifying the catalytic performance of the Pt ML/WC samples. To enable clean transfer of the sample from the UHV analysis chamber to the electrochemical cell used for CV measurements, the antechamber was first filled to atmospheric pressure using high-purity N_2, and then a droplet of pure water (HPLC grade, Fisher) was added to the WC surface. The sample was then immediately transferred into the electrochemical cell and immersed in a 0.1 M $HClO_4$ solution. Electrochemical measurements were performed in a standard three-electrode electrochemical cell using a Pt wire counter electrode and a reversible hydrogen reference electrode (RHE). Other details of the electrochemical analysis are described in our previous papers.[19,20]

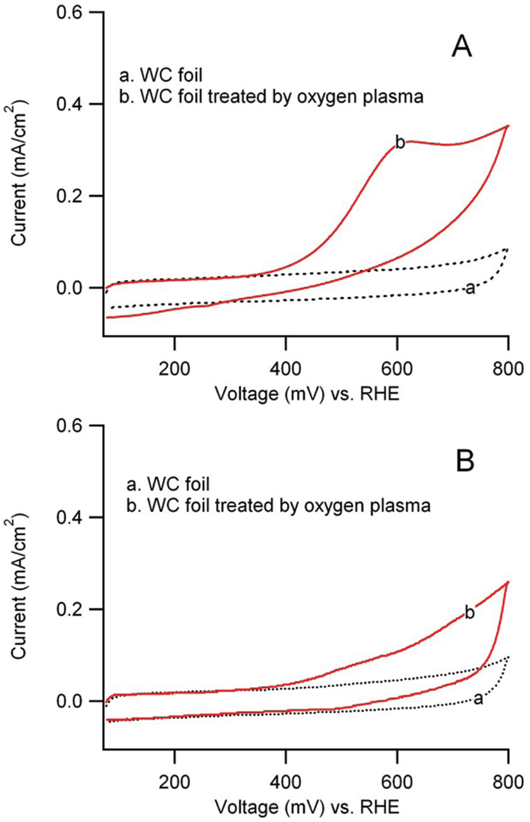

Figure 3. (A) First scan and (B) 40th scan for CV curves of MOR for WC foils (a) before and (b) after O_2 plasma treatment. The untreated WC foil sample does not exhibit activity for methanol oxidation. After 40 cycles, the methanol oxidation reactivity of the O_2 plasma-treated WC decreases. Conditions for MOR: 0.1 M $HClO_4$ with 0.2 M CH_3OH, and scan rate of 50 mV/s.

Cyclic voltammetry (CV) curves of methanol oxidation in acid media are plotted in Figure 3A. Before O_2 plasma treatment, CVs of WC foil (curve a) displayed only capacitance features, indicating no activity for methanol oxidation in the potential range of 0.075−0.8 V versus RHE. After O_2 plasma treatment, a large peak appeared in the CV with an onset potential and peak potential of 400 and 600 mV, respectively, during the positive scan. All these features were not observed in the CV of WC after plasma treatment in the absence of methanol in the solution (not shown), showing that the MOR activity was significantly improved by plasma treatment. It is worth noting that the MOR onset potential of 400 mV on the treated WC foil (curve b) is more negative than that of Pt.[21] This strongly suggests that WC is potentially more active than Pt for the MOR.

After 40 cycles of CV scans, a reduction in the methanol oxidation current was observed, as shown in Figure 3B. At least two possible mechanisms are responsible for this slow deactivation: one is the oxidation of WC, causing damage to the surface, and the other is a carbon poisoning effect due to the decomposition of methanol. To distinguish between these

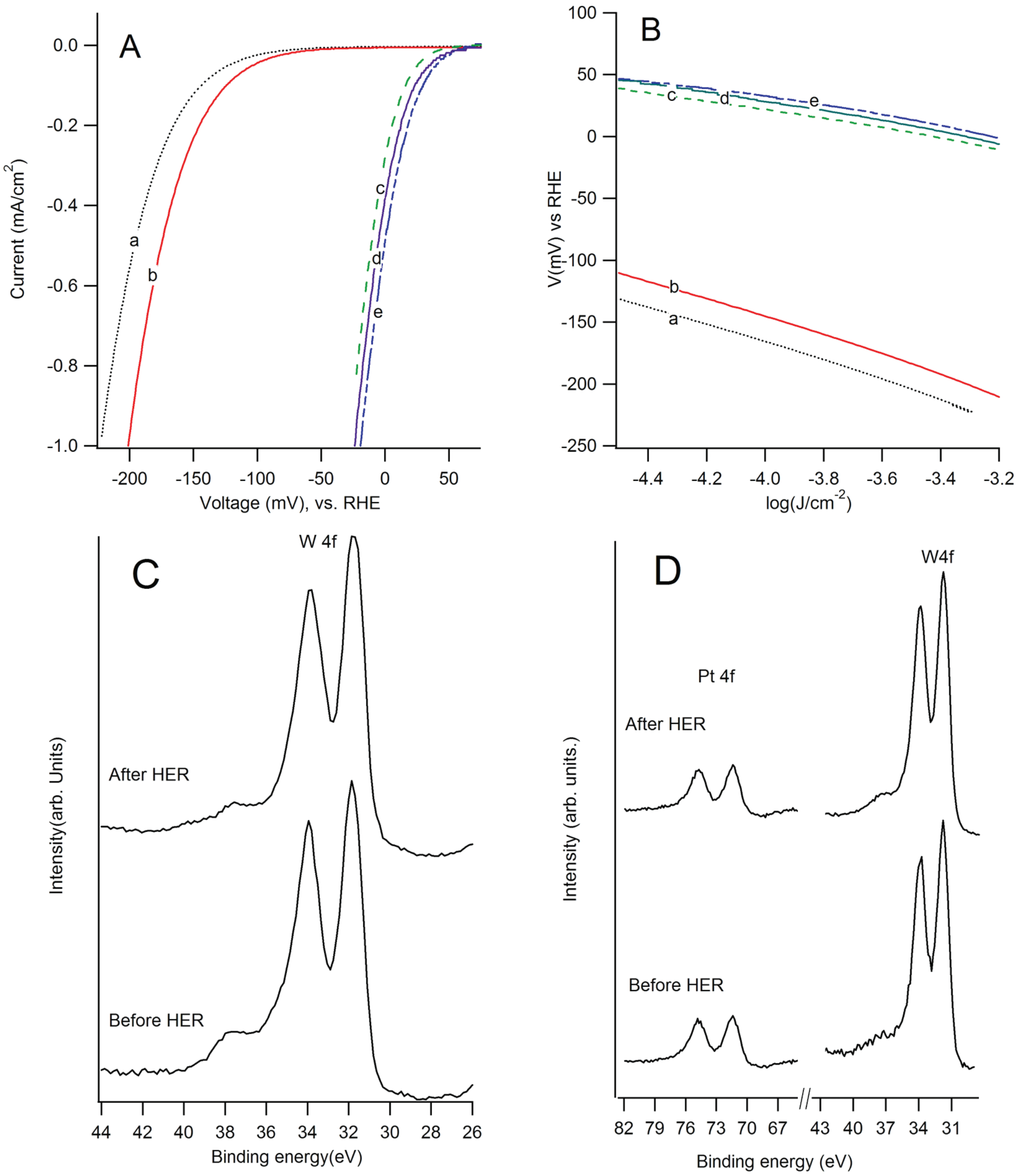

Figure 4. (A) Polarization curves and (B) Tafel plots of HER for (a) WC, (b) O_2 plasma-treated WC, (c) Pt foil, and Pt ML on WC foils (d) before and (e) after O_2 plasma treatment. Conditions for HER: Ar-purged 0.1 M $HClO_4$, and scan rate of 2 mV/s. O_2 plasma treatment of WC improved HER performance. C. XPS spectra of the W(4f) region of O_2 plasma-treated WC before and after HER measurements. D. XPS spectra of Pt4f and W4f regions for Pt ML on O_2 plasma-treated WC before and after HER. No additional oxidation of W was observed due to electrochemical measurements.

two explanations, the WC foil sample was transferred back to the UHV chamber for surface characterization after electrochemical measurements. Curves c in Figure 2A and B show the C1s and W4f peaks, respectively, after electrochemical measurements. No further oxidation in the W4f region was found, which indicates excellent stability of WC foil in this electrochemical environment. A relatively large graphitic carbon peak compared with carbidic carbon is shown in Figure 2A (curve c) after the MOR measurements, indicating that the deactivation of WC during the MOR is due to carbon deposition at the WC surface.

To assess the role of O_2 plasma treatments on the HER activity of WC foils and Pt monolayer (ML)/WC foils, the HER activities were compared before and after O_2 plasma treatments. Here, the Pt ML was deposited by vapor deposition in the UHV chamber on both O_2 plasma-treated and untreated WC foils. Figure 4A and B shows HER polarization curves and Tafel plots from WC and Pt ML/WC samples in a 0.1 M $HClO_4$ solution. Even though WC is not a good electrocatalyst for HER, a noticeable improvement in the HER performance was found after O_2 plasma treatments. Adding one monolayer of Pt on the WC surfaces largely improved the HER performance to the level of bulk Pt foil. The Pt ML on the O_2 plasma-treated WC foil demonstrated higher HER activity than the Pt ML on the untreated WC foil. These results further prove the significance of the removal of surface carbon by an O_2 plasma.

Figure 4C and D shows the XPS spectra of treated WC and Pt ML-treated WC before and after HER measurements. No oxidation of WC after the HER was observed for either sample.

There was no apparent change in the Pt4f intensity before and after HER, suggesting the Pt ML was stable under HER measurements. Our HER performance is consistent with a more detailed report that a Pt monolayer supported on WC containing less additional surface carbon had much higher activity than that on WC with more surface carbon,[13] and so clearly shows that atomic oxygen can be used to pretreat the WC substrate before Pt deposition to enhance the HER activity.

In conclusion, we report that O_2 plasma treatment of WC substrates at room temperature is a highly effective technique for removing graphitic carbon at WC surfaces without causing oxidation of WC. These results were obtained by controlling the O_2 plasma conditions, such as the atomic oxygen flux, ion flux, exposure time, etc. Two electrochemical reactions (MOR and HER) were selected to evaluate the effects of O_2 plasma treatment on electrocatalytic activity. After removal of graphitic carbon, MOR activity of WC foils and HER and MOR activities of WC foils and Pt ML/WC foils were improved significantly. These results suggest that preparation of WC surfaces free of graphitic carbon is important for producing active WC electrocatalysts. The results also indicate that O_2 plasma treatment has potential for applications in optimizing catalytic performance or regenerating catalysts that are deactivated by carbon deposition.

AUTHOR INFORMATION

Corresponding Author

*E-mail: bkoel@princeton.edu (B.E. Koel); jgchen@udel.edu (J.G. Chen).

Notes

The authors declare no competing financial interest.

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