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Carbon-covered Tungsten Carbide Nanoparticles: Solid-state Synthesis and Application as Stable Electrocatalysts for the Hydrogen Evolution Reaction

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Abstract Carbon-covered tungsten carbide nanoparticles(cc-WCNPs) were prepared *via* a one-step solid-state reaction between $W(CO)_6$ and triphenylamine at 850 °C under a sealed Ar atmosphere. As novel electrocatalysts for the hydrogen evolution reaction(HER), cc-WCNPs exhibit an onset potential of –0.14 V *vs.* reversible hydrogen electrode(RHE) and a Tafel slope of 64.6 mV/dec in a 0.5 mol/L H_2SO_4 solution. Additionally, these cc-WCNPs catalysts also show excellent electrocatalytic stability after 1000 cycles.

Keywords Hydrogen evolution reaction; Solid-state synthesis; Nanoparticle; Electrocatalysis

1 Introduction

The worldwide energy crisis has forced people to focus on the expansion of renewable resources[1]. Hydrogen-based energy sources are potential alternatives to petroleum feedstocks because of their high energy and the lack of carbon[2,3]. Electrochemical hydrolysis is a theoretically efficient method of hydrogen production because hydrogen evolution reaction (HER) will dominate over the electrochemical process. However, overpotentials need to be overcome, and advanced catalysts are imperative[4]. Despite having the best catalytic performance for the HER, Pt is quite expensive, which hinders its large-scale utilization[5].

Tungsten carbides have been considered as potential alternative catalysts to Pt for the HER. W_2C and WC have a similar band structure to that of Pt[6,7]. Although tungsten carbides show relatively low HER activity, they have always been used as support materials for Pt[8—10]. For example, Liu and Mustain[9] reported that the Pt/WC exhibited significantly better stability than the commercial Pt/C. However, the use of tungsten carbides/carbon nanostructures as electrocatalysts for the HER has not yet been reported.

In this study, carbon-covered tungsten carbides nanoparticles(cc-WCNPs) were prepared *via* a one-step solid-state reaction under a sealed Ar atmosphere using $W(CO)_6$ and triphenylamine as precursors. The HER properties of the products were investigated in a 0.5 mol/L H_2SO_4 solution without any active processes, demonstrating an onset potential of –0.14 V and a small Tafel slope of 64.6 mV/dec. Additionally, cc-WCNPs exhibited excellent electrocatalytic stability.

2 Experimental

2.1 Synthesis of Carbon-covered Tungsten Carbides Nanoparticles(cc-WCNPs)

To prepare cc-WCNPs, 0.50 g of $W(CO)_6$ and 0.83 g of triphenylamine were ground to form a homogeneous powder. The solid mixture was degassed and sealed under an Ar atmosphere in a glove box and subsequently heated at 850 °C for 3 h. After cooling to room temperature, the products were washed with deionized water three times and then collected *via* centrifugation.

2.2 Characterization

Scanning electron microscopy(SEM) measurements were carried out on an XL30 ESEM FEG microscope. Transmission electron microscopy(TEM) measurements were performed using a Hitachi H-8100 electron microscope(Hitachi, Japan). X-Ray diffraction(XRD) data were recorded on a RigakuD/MAX 2550 diffractometer. The energy-dispersive spectroscopy (EDS) measurements were performed on an IE250X-Max50 (Oxford, Britain).

2.3 Electrochemical Measurements

Electrochemical measurements were performed on a CHI614D electrochemical analyzer(CH Instruments, Inc., Shanghai, China) in a three-electrode cell. A glassy carbon electrode(GCE) with a 0.07 cm^2 geometric area, an Ag/AgCl electrode and a platinum wire were used as the working

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electrode, the reference electrode and the counter electrode, respectively. All the potentials reported in this work were *vs.* the reversible hydrogen electrode(RHE). In a 0.5 mol/L H_2SO_4 solution, E(RHE)=E(Ag/AgCl)+0.059pH+0.21 and the pH of the 0.5 mol/L H_2SO_4 solution is 0.16. The working electrode was prepared as follows: 1 mg of as-prepared catalyst and 10 μL of 5%(mass fraction) Nafion solution were dispersed in a 1 mL of water/ethanol(1:1, volume ratio) mixed solvent, followed by ultrasonic treatment for at least 30 min. Then, 5 μL of the ink was added dropwise onto the glassy carbon electrode. Linear sweep voltammetry(LSV) with a scan rate of 2 mV/s in a range from 0 V to –0.8 V(*vs.* RHE) was performed in the 0.5 mol/L H_2SO_4 solution. A stability test was then carried out using cyclic voltammetry(CV) within the same potential range for 1000 cycles at a scan rate of 100 mV/s.

3 Results and Discussion

Fig.1(A) shows the XRD pattern of cc-WCNPs. The obvious diffraction peaks at 34.7°, 38.3°, 39.7°, 52.4°, 61.8°, 69.7°, 75.1° and 75.9° can be assigned to the (110), (002), $(\bar{1}\bar{1}1)$, $(\bar{1}\bar{1}2)$, (3,0,0), $(\bar{1}\bar{1}3)$, (3,0,2) and $(\bar{2}\bar{2}1)$ faces of W_2C(JCPDS No. 65-3896), respectively. The other three peaks at 31.5°, 35.6° and 48.3° correspond to the (001), (100) and (101) faces of WC(JCPDS No. 51-0939), respectively. The XRD results reveal the well-formed crystallographic structure of tungsten carbides in cc-WCNPs. The EDS of the cc-WCNPs reveals the abundant existence of W and C elements[Fig.1(B)]. The observed Au peak originates from the sputtered Au conductive coating. The atom ratio of W/C was measured to be 56.16/24.73[10].

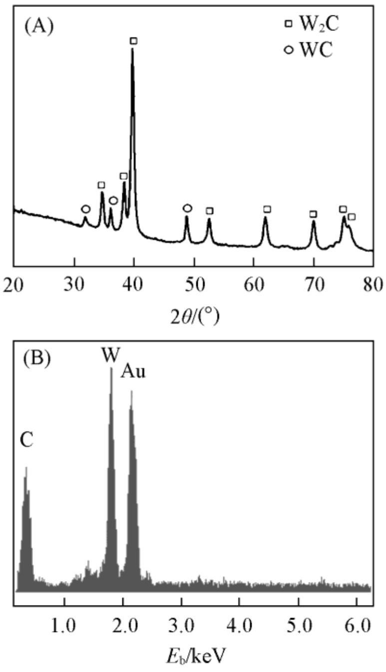

Fig.1 XRD pattern(A) and EDS spectrum(B) of cc-WCNPs

The morphology of cc-WCNPs was determined by SEM and TEM. Fig.2(A) and (B) display the low- and high-magnification SEM images of cc-WCNPs, showing the morphology of microspheres with different diameters ranging from 500 nm to 1 μm. Fig.2(C) and (D) are TEM images of cc-WCNPs. The surface is clearly coated by a thin layer of carbon. Fig.2(E) illustrates a high-resolution TEM(HRTEM) image of the surface of one sphere. The observed lattice fringes with an interplanar distance of 0.23 nm correspond to the $(\bar{1}\bar{1}1)$ plane of W_2C. Fig.2(F) shows the magnified image of the selected area of Fig.2(E). The interface contrast between carbon and tungsten carbide can be readily observed[11]. Meanwhile, clear hexagonal atomic lattices in the W_2C are also found in Fig.2(F). All these observations indicate the successful formation of tungsten carbide nanoparticles coated with carbon[12].

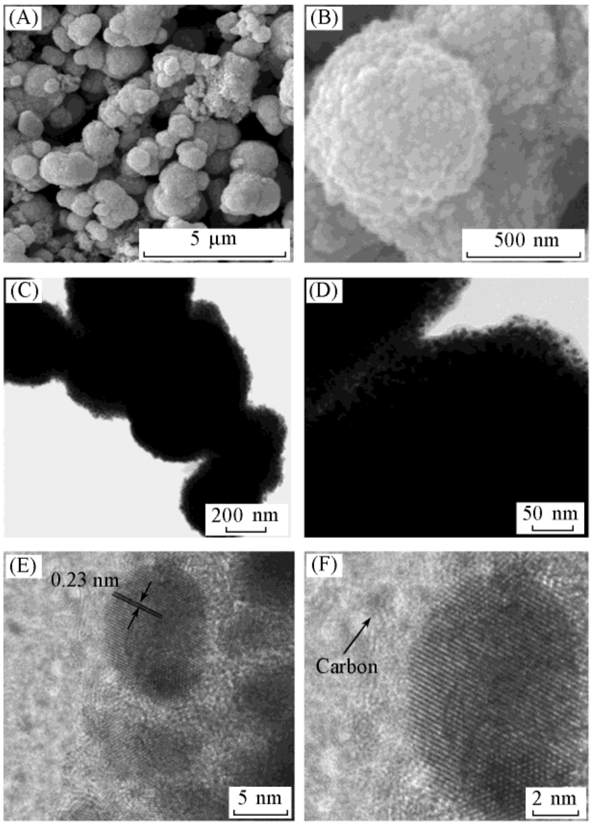

Fig.2 Low-(A) and high-magnification(B) SEM images, low-(C) and high-magnification(D) TEM images and low-(E) and high-magnification(F) HRTEM images of cc-WCNPs

To investigate the HER performance of cc-WCNPs, ink containing well-dispersed cc-WCNPs was added dropwise to GCE with a loading density of 0.36 mg/cm^2. Without any active process, the HER properties of cc-WCNPs were directly determined in a 0.5 mol/L H_2SO_4 solution. Fig.3(A) presents the polarization curves of cc-WCNPs, Pt/C and bare GCE measured by LSV at a rate of 2 mV/s. The cc-WCNPs catalyst exhibits an onset potential of –0.14 V. Typically, Pt/C exhibits the highest HER catalytic performance with a near zero overpotential, while the bare GCE exhibits little HER activity[13]. An overpotential(η) of 0.15 V is required to achieve a current density(j) of 1 mA/cm^2. When j=10 mA/cm^2, η=0.31 V. HER activities of several metal carbide-based catalysts are listed in Table 1. The cc-WCNPs catalysts yield comparable current densities at the same overpotential even with a small loading.

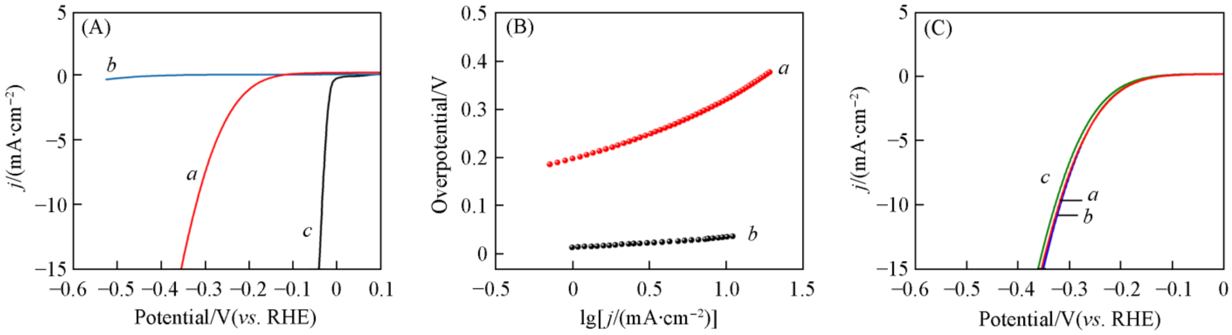

Fig.3 Polarization curves of cc-WCNPs(*a*), bare GCE(*b*) and Pt/C(*c*) with a scan rate of 2 mV/s in a 0.5 mol/L H_2SO_4 solution(A), Tafel plots of the cc-WCNPs(*a*) and Pt/C(*b*) catalysts(B) and durability test for the cc-WCNPs by cyclic voltammograms for 1000 cycles at a scan rate of 100 mV/s in a 0.5 mol/L H_2SO_4 solution(C)

(C) *a*. Initial; *b*. 500 cycles; *c*. 1000 cycles.

Table 1 Comparison of HER activity of several metal carbides-based catalysts

Catalyst	Loading/(mg·cm^{-2})	Electrolyte	j/(mA·cm^{-2})		Ref.
			η= 200 mV(*vs.* RHE)	η= 300 mV(*vs.* RHE)	
cc-WCNPs	0.36	0.5 mol/L H_2SO_4	2	6	This work
Mo_2C	2	0.1 mol/L $HClO_4$	Less than 1	*ca.* 8	[14]
WCN	0.4	H_2SO_4(pH=1)	Less than 3	*ca.* 7.5	[15]
TaC	0.5	0.05 mol/L H_2SO_4	Less than 0.1	Less than 0.3	[16]
WC	—	0.1 mol/L $HClO_4$	Less than 2	Less than 2	[17]

The Tafel slope is often utilized to indicate the dominant mechanism of the HER process. As shown in Fig.3(B), the Tafel slope of cc-WCNPs is 64.6 mV/dec, indicating that the electrochemical desorption step is the primary rate-determining step[18]. As expected, the commercial Pt/C catalyst yields a Tafel slope of 30.2 mV/dec. Fig.3(C) shows that after 1000 cycles, the cc-WCNP catalyst retains a similar polarization curve, and negligible HER current has been lost, demonstrating its high cycling stability in an acidic electrolyte[19].

4 Conclusions

In this study, cc-WCNPs were successfully synthesized *via* a solid-state reaction at 850 °C under a sealed Ar atmosphere using $W(CO)_6$ and triphenylamine as W and C sources, respectively. Tungsten carbides/carbon composites were studied as efficient and stable electrocatalysts for HER. The cc-WCNPs electrocatalysts exhibited an onset potential of –0.14 V and a Tafel slope of 64.6 mV/dec in a 0.5 mol/L H_2SO_4 solution. Furthermore, the cc-WCNP catalysts demonstrated excellent electrocatalytic stability. This study provides a method for the preparation of transition-metal-carbide/carbon nanostructures for HER applications.

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