

Palladium nanoparticles supported on hollow mesoporous Tungsten carbide microsphere as electrocatalyst for formic acid oxidation

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Abstract: Hollow tungsten carbide and cobalt spheres (HTCCS) with cobalt concentration of 6% were prepared by spray conversion and reduction carbonization methods. The HTCCS with diameters of about 8–18 μm were covered with 0.3–1.0 μm microporous. The Pd/WC catalyst was prepared through the replacement reaction between Co nanoparticles on the surface of HTCCS and PdCl_4 . The electro-catalytic performances for formic acid electro-oxidation were investigated by cyclic voltammetry and chronoamperometry. It exhibited the low onset potential, excellent catalytic activity and stability compared with Pd/C due to the larger electrochemical surface area (ECSA) and the synergistic effect between Pd and WC.

Keywords: direct formic acid fuel cell; formic acid oxidation; WC-Co composite spheres; electro-catalyst; mesoporous materials

The direct formic acid fuel cell (DFAFC) has received considerable attention due to its several advantages, such as low toxicity, limited fuel crossover and high practical power density^[1–3]. In recent years, the Pd-based catalysts have shown high activity for the formic acid electro-oxidation (FAEO) by overcoming the CO poisoning effect^[4–6]. But the high price of noble metal catalysts would limit its large-scale commercial applications.

Tungsten carbide (WC) are an interesting class of materials as electro-catalyst supports mainly due to its electrochemical catalytic performance as kind of noble metals, the resistance to CO poisoning and its insolubility in acid solution, especially the FAEO application^[7–11]. So palladium nanoparticles supported on WC (Pd/WC) as electro-catalyst offers a great opportunity for cost reduction in DFAFC applications. Previous studies have proven that Pd catalysts supported on WC have extremely high activity toward the electro-oxidation of formic acid^[12–14]. However, palladium nanoparticles are apt to aggregate on the surface of WC because of its low specific surface area and the lack of anchoring sites for metal particles. Consequently, this will deteriorate the activity and stability of electro-catalyst.

In our previous study, we reported that the large-scale commercial hollow WC-Co composite spheres with the large surface area were fabricated by combining spray conversion with in-situ carbonized synthesis methods^[15]. Here, Pd/WC catalyst was efficiently prepared by the replacement reaction between Co nanoparticles and PdCl_4 . The structure and morphology of Pd/WC catalyst were characterized and the electro-catalytic performances were studied in this work.

1 Experimental

1.1 Preparation of the hollow tungsten carbide & cobalt sphere

Preparation of hollow tungsten carbide & cobalt sphere (HTCCS) with cobalt concentration of 6% was previously reported by our group^[15]. In brief, ammonium metatungstate (AMT), soluble cobalt salt, organic carbon source and deionized water were used as the raw materials and prepared for the mixed solution with carbon concentration of 19.76%. The tungsten cobalt carbon precursor powder was prepared by centrifugal atomization.

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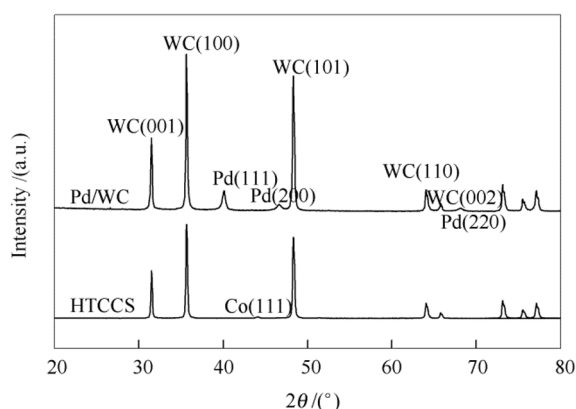


Fig. 1 XRD pattern of HTCCS and Pd/WC catalysts

The centrifugal speed was 1.2×10^4 r/min, the inlet temperature of nitrogen gas was 240°C and the outlet temperature was 120°C . The precursor powder was calcined at 450°C under the protection of nitrogen for 1 h, and then reduction and carbonization treatment were taken at 900°C with hydrogen atmosphere for 2 h.

1.2 Preparation of Pd/WC catalyst

Subsequently, Pd/WC catalyst was prepared through the replacement reaction between Co nanoparticles and PdCl_4 . In a typical procedure, 50 mg HTCCS was first dispersed in 25 mL deionized water to prepare a suspended solution in a flask. After the pH was adjusted to nearly 6 by dropping 1 mol/L NaOH solution, 20 mL 5 mmol/L PdCl_2 was added to the above flask, followed by heating at 50°C in oil bath for 6 h. The resulting solution was filtered, washed and dried at 85°C for 10 h in a vacuum oven. The result sample was added into a freshly prepared solution of NaBH_4 under vigorous stirring for 2 h, handled by hydrochloric acid for 30 min, filtrated and dried at 70°C for 10 h. The as-prepared product was denoted as Pd/WC. According to the replacement reaction between Co nanoparticles and PdCl_4 , the theoretical loading amounts of Pd were nearly 10%. For comparison, the home-made Vulcan XC-72R carbon supported Pd catalyst with the same Pd loading was denoted as Pd/C reported by our group^[16].

1.3 Characterizations

The samples were characterized by XRD, SEM and TEM, respectively. XRD was performed with a Thermo ARL SCINTAG X'TRA X-ray at room temperature using quartz monochromatic $\text{Cu } K\alpha_1$ radiation source ($\lambda = 0.154$ nm) under a voltage of 45 kV and a current of 40 mA. The XRD patterns were recorded with a step size of 0.04° from 10° to 80° at the speed of $2.4^\circ/\text{min}$. TEM was carried out on a Tecnai G2 F30 S-Twin (Philips-FEI).

1.4 Electrochemical measurements

Electrochemical measurements were performed with an Ivium electrochemical workstation and a standard three-electrode cell. A Pt foil and saturated calomel electrode (SCE) were respectively used as counter and reference electrodes. To form a working electrode, 2 mg of electro-catalyst sample was ultrasonically mixed in 200 μL of ethanol-water solution (1:1, volume ratio) to form a homogeneous ink followed by dropping 2.6 μL of the electro-catalyst ink onto the surface of a glassy carbon electrode (GCE, with a diameter of 3 mm), and 5 μL of Nafion solution of 1.0% in ethanol was added to fix the electro-catalyst on the GCE surface. All electrochemical measurements were carried out in a nitrogen-saturated 0.5 mol/L H_2SO_4 solution with or without 1 mol/L HCOOH at a scan rate of 50 mV/s.

2 Results and discussion

2.1 XRD

The XRD patterns of HTCCS and Pd/WC were presented in Figure 1. The diffraction peak at 39.4° , 45.8° and 66.8° are reflections of the face-centered cubic crystal lattices of the Pd. Except for the reflections of the Pd fcc-phase, the reflections for the WC (001), WC (100), WC (101), WC (110), WC (002) and so on crystal faces with rather intense peak of Pd/WC catalyst displayed from the XRD pattern, which correspond to the hexagonal phase of WC. A slight diffraction peak at 44.1° is attributed to the Co(111) planes in the Figure 1. What has been discussed above indicates that Co has been replaced completely after the preparation of Pd/WC.

Figure 2(a) shows that the diameter of HTCCS is about 8–18 μm and the surface are rough and covered with 0.3–1.0 μm microporous (Figure 2(b)). After ultrasonic dispersion for 30 min in the process of preparation of Pd/WC catalyst, some microspheres are split and the hollow structure is indicated in Figure 2(c). Figure 2(d) is a magnified image of the sphere surface shown in Figure 2(c). Compared with the surface of HTCCS (Figure 2(b)), it is obvious that the fine particles are uniformly deposited on the surface of WC, showing that Co particles are replaced by Pd nanoparticles.

TEM image (Figure 2) shows a lattice spacing of 0.28 nm with the lattice orientation of (001) of WC and a lattice spacing of 0.23 nm with the lattice orientation of (111) of Pd. It also indicates that Pd nanoparticles with an average crystallite size of 5.0–6.0 nm are dispersed on the surface of WC. Figure 2(f) shows the EDS spectra of Pd/WC confirming the Pd loading concentration of 9.8%, which is close to theoretical loading amounts of Pd.

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