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An ion exchange route to produce WO_3 nanobars as Pt electrocatalyst promoter for oxygen reduction reaction

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HIGHLIGHTS

► WO_3 nanobars (3 nm × 10 nm) is synthesized through ion exchange route.
► The long-chain of the ion exchange resin results in the bar shape of WO_3.
► The shape of WO_3 varies with the concentrations of WO_3 precursor.
► WO_3 nanobars give highly promotion effect on Pt/C electrocatalyst.
► Pt/WO_3 has higher electrochemical stability than Pt/C.

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ABSTRACT

WO_3 nanobars with the length of 10–50 nm and the width of 3–6 nm on carbon (C-WO_3) are synthesized through an ionic exchange route to locally anchor the metatungstate ions ($W_7O_{24}^{6-}$). The structures, morphologies and catalytic performance of the as-synthesized nanomaterials are characterized by various physical and electrochemical methods. The results indicate that Pt nanoparticles supporting on C-WO_3 (Pt/C-WO_3) are highly active and stable as cathode electrocatalyst for fuel cells. On one hand, a mass activity of 174.6 mA $mg^{-1}{}_{Pt}$ at 0.9 V is obtained for oxygen reduction reaction (ORR), which is much higher than that on commercial Pt/C electrocatalyst (98.6 mA $mg^{-1}{}_{Pt}$). On the other hand, Pt/C-WO_3 electrocatalyst shows excellent electrochemical stability than Pt/C. The origin of these improvements in the catalytic activity can be attributed to the synergistic or promotion effect of WO_3 on Pt. The improvement in the electrochemical stability is due to and also explains the stronger interaction force between Pt and WO_3 than that between Pt and C. The present method is simple and effective, which can be readily scale up for the production of other nanomaterials as well as WO_3.

1. Introduction

Low temperature fuel cell technology has been considered as one of the important ways to decrease the energy crisis of the world for its high-energy conversion efficiency, so it has great and potential economic value [1–5]. The electrocatalyst is the critical part of the low temperature fuel cells. Owing to the sophisticated synthesis technologies, relatively good electrochemical activity and stability, noble metals such as Pt and Pd have been remaining the main active ingredients of the electrocatalysts [2,6–9]. However, the high cost of the noble metals restricted the popular application of the low temperature fuel cells, especially for the cathode side which need more amount of noble metals to promote the kinetics of the oxygen reduction reaction (ORR) [10–12]. On the other hand, the carbon support corrosion remains the major challenges for high potential on fuel cell ORR electrocatalysts [13]. Therefore, many efforts such as structure design, alloy synthesis and crystal parameter alteration on the noble metal have been made to obtain improved electrocatalytic activity, stability and use ratio [2,8,14–16]. On the above basis, graphitization or composite synthesis on the carbon support to achieve more stable catalyst structure and performance was also exposited [3,7,17,18].

Metal oxides have aroused much attention and been studied in various fields including light-emitting diodes [19,20], coating materials [21], photocatalysis [22–24], flame retardants [25], chemi-sensors [26,27], solar cells [28,29] and catalytic reaction [30,31]. Due to their promotion effect on noble metal electrocatalyst, metal oxides were also investigated with interesting as electrocatalyst promoter for fuel cells, which have been approved to be able to improve the overall catalytic activity to a large degree

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[32–34]. Specially, it has been reported that tungsten oxides have excellent CO tolerance and higher catalytic activity when being loaded with Pt nanoparticles as electrocatalysts [35–41]. According to Savadogo's report, the electrocatalytic activity of Pt supporting on WO_3 for ORR in acidic media was twice as high as that of Pt supporting on carbon [42].

There have been many methods for the synthesis of tungsten oxides with various shapes including nanowires [39,40], nanofilms [43], nanoclusters [44], microfibers [45], etc. It is believed that the big particles of promoter catalyst are difficult to exert the promotion effect on noble metal electrocatalysts. The reason is that they have too heavy density and low specific surface area to perform the promotion effect efficiently and disperse the noble metal particles uniformly [46,47]. So it is of great significance to develop nanosized metal oxides with a controllable size down to 10 nm or less.

Here, we synthesized WO_3 nanobars with the length of 10–50 nm and the width of 3–6 nm that were uniformly dispersed on carbonized resin (C-WO_3) through ionic exchange route [3,7,18]. The WO_3 nanobars synthesized here were used as Pt electrocatalyst promoter for ORR in acidic media and showed excellent electrochemical stability as well as remarkable catalytic promotion effect.

2. Experimental

Typically, the D201 × 1 cinnamic strong alkali anion exchange resin (10 g, Hebi Power Resin Factory, China) was impregnated in 100 ml of AMT (ammonium metatungstate, $(NH_4)_6W_7O_{24}\cdot 6H_2O$, A.R., Tianjin Jinke Fine Chemicals Co., China) solution with the W atom concentrations of 0.50, 0.05 and 0.005 mol L^{-1} for 5 h, respectively (W atom concentration equals 1/7 AMT concentration, for one AMT molecule having seven W atoms). The exchanged resin was washed with deionized water and dried at 80 °C overnight. The dried resin was then heated at 600 °C for 1 h in N_2 atmosphere. After cooling down to room temperature, the resulting product was grinded into powders and the final tungsten oxide on carbonized resin composite (C-WO_3) was obtained. The C-WO_3 prepared with the W atom concentrations of 0.50, 0.05 and 0.005 mol L^{-1} were denoted as C-WO_3(0.50), C-WO_3(0.05) and C-WO_3(0.005), accordingly.

Pt supported on C-WO_3 (denoted as Pt/C-WO_3) was prepared and used as electrocatalyst for ORR. A total of 50 mg of C-WO_3 was added in a mixed solution with H_2PtCl_4 (58 mg) and formic acid and treated in ultrasonic bath for 30 min to form uniform ink. After the ink was dried, we got Pt/C-WO_3 electrocatalyst. The Pt contents in the resulting products were targeted at 40 wt%. The actual Pt contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP, IRIS (HR), USA).

For electrode preparation, Pt/C-WO_3 (5 mg) or commercial Pt/C (4 mg, 47.6 wt % Pt, TKK, Japan) were dispersed in 1.95 ml of ethanol and 0.05 ml of 5 wt% Nafion suspension (DuPont, USA) under ultrasonic agitation to form the electrocatalyst ink. The electrocatalyst ink (5 μl) was deposited on the surface of a rotating disk electrode and dried at room temperature. The total Pt loadings were controlled at 0.02 mg cm^{-2}.

The electrochemical measurements were carried out in an oxygen-saturated 0.1 mol L^{-1} $HClO_4$ solution scanned between 0 and 1.1 V (vs. RHE) at a scan rate of 5 mV s^{-1} at 25 °C controlled by a water-bath thermostat. A platinum foil (1.0 cm^2) and a reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively.

All chemicals were of analytical grade and used as received.

The morphologies and sizes of the C-WO_3 and Pt supported electrocatalysts were characterized by transmission electron microscopy (TEM, JOEP JEM-2010, JEOL Ltd.) operating at 200 kV. The structure of C-WO_3 and electrocatalysts were determined on a X-ray diffractometer (XRD, D/Max-IIIA, RigakuCo., Japan,CuK1, $\lambda = 1.54056$ Å radiation) and a X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250, Thermo-VG Scientific).

3. Results and discussion

Fig. 1a and b show the XRD patterns of C-WO_3(0.50), C-WO_3(0.05) and C-WO_3(0.005). All the patterns match the characteristics of WO_3 crystal (PDF#20-1324) by comparing JCPDS cards. The peak intensities of the WO_3 weakened with the decreasing concentration of AMT, which related to the particle size.

Fig. 2 shows the TEM images of the WO_3 nanoparticles on carbonized resin, which were prepared at different concentrations of AMT. As shown in Fig. 2a, the C-WO_3(0.50) prepared at higher concentration of AMT carried large and congregated bulks of WO_3 crystals. The morphology of the WO_3 crystals could transform to less sized nanobars with the length of 10–50 nm and width of 3–6 nm with the reduction in AMT concentrations (Fig. 2b). And the less concentration is AMT, the more sparse distribution is WO_3 nanoparticles (Fig. 2c). Fig. 2d shows the HRTEM image of C-WO_3(0.05), the crystal lattice of WO_3 (200) is clearly shown.

The reason for the different shape of WO_3 particles at different AMT concentrations is tried to explain as follows. The D201 × 1 cinnamic strong alkali anion exchange resin has long-chain structure (see Fig. 3), which would combine the $W_7O_{24}^{6-}$ ions linearly through ion exchanging. After the exchanged resin is carbonized, the bar-shaped WO_3 particles will accordingly form. But if the concentration of AMT is too low, the formed WO_3 particles could not link each other to form bars. So there are lots of dot-shaped

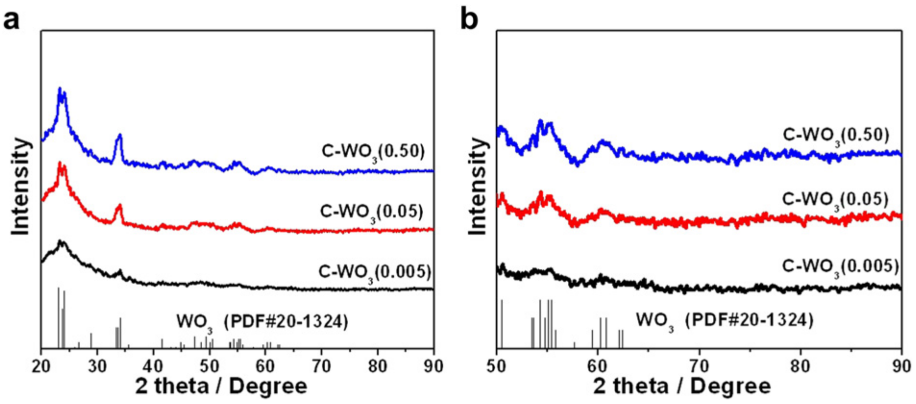

Fig. 1. (a) XRD patterns of C-WO_3 composite with different AMT concentrations and (b) the corresponding XRD patterns at high angle range.