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Porous Tungsten Carbide Nanoplates Derived from Tungsten Trioxide Nanoplates

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Porous WC nanoplates (PWCPs) were synthesized by a nitridization-carbonization process using WO_3 nanoplates as the precursor for morphological control. The WO_3 nanoplates were derived from tungstate-based inorganic-organic hybrid belts. The synthesis of PWCPs involved a nitridization reaction of WO_3 nanoplates in NH_3 at 650°C for 2 h, followed by a carbonization reaction in a CO/CO_2 (10:1, v/v) mixture at 750°C for 10 h. The as-obtained product is a pure hexagonal WC phase with a plate-like and porous morphology. The aggregates of the PWCPs with dimensions of (100–300) × (10–30) nm form a house-of-card structure with open channels and high-specific surface areas, and can act as potential supports of electrocatalysts for high-performance fuel cells.

I. Introduction

TUNGSTEN carbide (WC) nanostructures and their nanocomposites have attracted increasing attention in electrocatalytical applications for fuel cells due to their Pt-like electrical structure and their synergistic effect with other metal clusters.[1–3] For electrocatalytical applications, high surface areas and good dispersibility are essential requirements. To achieve this purpose, many groups have developed various methods to prepare nanoscale WC nanocrystals, including WC nanoparticles on support,[4–6] free-standing WC nanoparticles,[7,8] mesoporous WC nanochains,[9] WC nanofibers,[10] WC nanorods and nanopatelets,[11] hollow WC microspheres,[12] three-dimensionally ordered macroporous WC,[13] hierarchical WC micro/nanocrystals,[14] and inverse opal WC nanostructures.[15] However, morphology-controlled synthesis of low-dimensional tungsten carbide nanostructures (e.g., nanoplates) with high surface areas and high redispersibility is still a harsh challenge.

We here introduce an efficient approach to synthesize porous WC nanoplates (PWCPs) with large diameter-to-thickness ratios and high specific surface areas on the basis of topochemical conversion and intercalation chemistry.[16–18] Essentially, the PWCPs are synthesized via a two-step nitridization-carbonization method using two-dimensional WO_3 nanoplates as intermediates for morphological control. This method is cost-effective, easy to control, and suitable for large-scale production.

II. Experimental Procedure

The WO_3 nanoplates were synthesized according to our previous report.[17] Typically, $H_2W_2O_7{\cdot}xH_2O$ (~5 g) was dispersed in a mixture of *n*-octylamine (~33 mL) and heptane (160 mL) under magnetic stirring, and kept reacting for 3 d. After the reaction, a white solid, i.e., the THBs, was collected and dried. The as-obtained THBs (~5 g) were dispersed in a HNO_3 aqueous solution (~6 mol/L, 150 mL) and kept stirring for 2 d at room temperature. The solid was collected, washed, and dried at 120°C. The yellow powders obtained, H_2WO_4 nanoplates, were calcined at 400°C for 2 h in air to synthesize WO_3 nanoplates.

The WO_3 nanoplates (~0.5 g) were uniformly covered on the surface of a rectangular Al_2O_3 plate (128 mm × 29 mm × 4 mm), which was then horizontally put in a semicylindrical Al_2O_3 boat (φ 42 mm × 29 mm × 5 mm). The boat with WO_3 nanoplates was carefully pushed to the center of a quartz tube (φ 46 mm × 600 mm) of a horizontal tubular furnace. After sealing carefully, the furnace was firstly purged with CO_2 gas (100 mL/min) for 20 min to discharge the residual air. Then, the CO_2 gas was switched to NH_3 gas (100 mL/min), and the furnace was heated to 500°C with a rate of 25°C/min, and then to 650°C with a rate of 10°C/min. The nitridization reaction was kept for 2 h at 650°C. The NH_3 gas was then changed to a CO/CO_2 mixture (100 mL/min, V_{CO}:V_{CO2} = 10:1) and the temperature was increased to 750°C (heating rate: 10°C/min), at which the carbonization reaction was kept for another 10 h. Finally, the sample (e.g., PWCPs) was cooled and collected for characterization.

\XRD (Cu$K\alpha$; ZHJ XPERT PRO, China), SEM (JEOM-6700F, Japan), TEM (200 kV; Tecnai-G20), N_2 adsorption-desorption (Nova 4200a), TG-DTA (Netzsch STA409PC, Germany), and FT-IR (Nicolet460) were used to characterize the as-obtained PWCPs and their precursors.

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III. Results and Discussion

Figure 1(a) shows an XRD pattern of the WO_3 nanoplates obtained from a tungstate-based inorganic-organic hybrid compound, formed via acid-base reactions between $H_2W_2O_7{\cdot}xH_2O$ and *n*-octylamine.[18] As the XRD pattern in the inset of Fig. 1(a) shows, the hybrid has a serials of peaks located in the low 2θ range (less than 25°), and the peaks are attributable to (00*l*) deflections, characteristic of a highly-ordered lamellar structure with an interlayer distance of 2.597(2) nm.[18] As the SEM image in Fig. 2(a) shows, the as-obtained hybrid consists of a one-dimensional belt-like structure, being 10–50 μm long and 0.5–1 μm in apparent diameter. The TG-DTA and FT-IR analyses (not shown) indicated that the belts are of an inorganic-organic hybrid lamellar structure, alternately stacking inorganic W–O layers and organic amine layers.[18] The WO_3 nanoplates were synthesized by selectively removing the organic species from the hybrid belts.[17] The as-obtained WO_3 nanoplates are indexed to a monoclinic WO_3 phase (JCPDS no. 43-1035) according to the XRD pattern [Fig. 1(a)]. Figure 2(b) shows a SEM image of the as-obtained WO_3 nanoplates, which is loosely assembled to form a house-of-card structure with high surface areas.[17]

The WC sample (PWCPs) derived from the as-obtained WO_3 nanoplates shows three strongest peaks located at 31.4°, 35.6°, and 48.3° in its XRD pattern [Fig. 1(b)], being indexed to (001), (100), and (101) deflections of a hexagonal WC phase (JCPDS no. 25-1047, a = 2.9062 and c = 2.8378 Å), respectively. Other weak peaks (not shown) in the XRD pattern are also in good agreement with the hexagonal WC phase, and no peaks belong to impurities. The calculated cell parameters [a = 2.896(3) and c = 2.847(8) Å] are close to the literature data. The SEM image in Fig. 2(c) shows that the WC sample consists of uniform plate-like particles, similar to their precursor of WO_3 nanoplates [Fig. 2(b)]. The high-magnification SEM image in Fig. 2(d) indicates that the WC nanoplates, with dimensions of 200–500 nm in areas and 10–30 nm in thicknesses, are of pores with various sizes.

Figure 3 shows the TEM observatons of the porous WC nanoplates (PWCPs). A low-magnification TEM image in Fig. 3(a) confirms that a WC nanoplate consists of small particles overlapped on one another, forming a quasi two-dimensional and porous morphology. The corresponding high-magnification TEM image [Fig. 3(b)] indicates that the PWCPs consist of interconnected nanoparticles with a size range of 10–20 nm. A high-resolution TEM image in

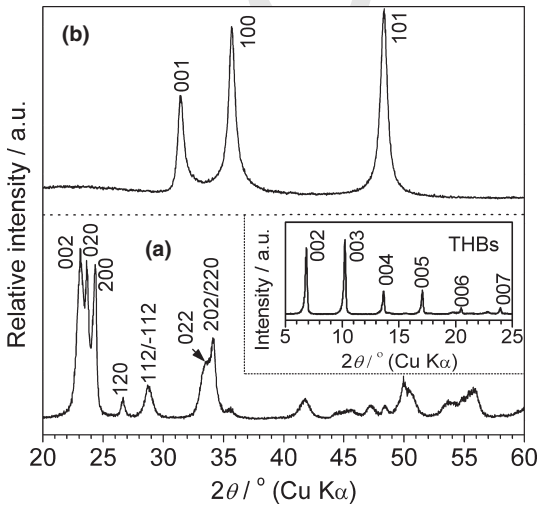

Fig. 1. (a) XRD pattern of the WO_3 nanoplates derived from the tungstate-based inorganic–organic hybrid belts (THBs); (b) XRD pattern of the porous WC nanoplates (PWCPs) derived from the WO_3 nanoplates. The inset is the XRD pattern of the (THBs).

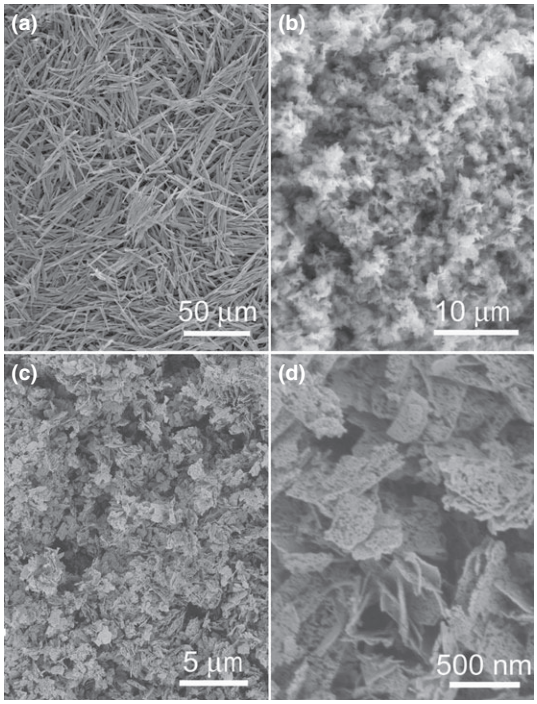

Fig. 2. SEM images of (a) the tungstate-based inorganic–organic hybrid belts (THBs) and the corresponding (b) WO_3 nanoplates and (c–d) porous WC nanoplates (PWCPs) derived from the THBs.

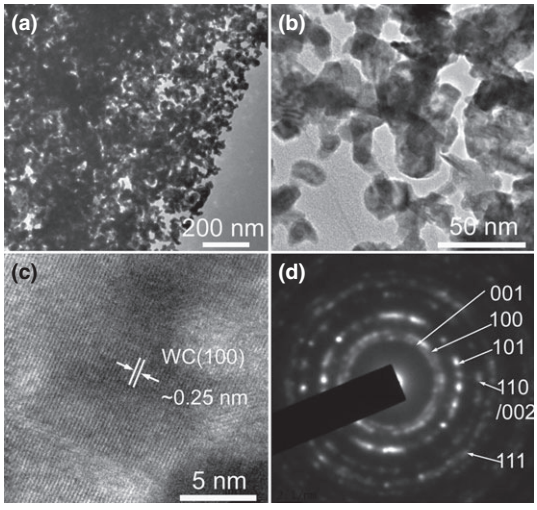

Fig. 3. (a–b) TEM images, (c) HR-TEM image, and (d) SAED pattern of the porous WC nanoplates derived from the tungstate-based hybrid belts.

Fig. 3(c) shows ordered lattice fringes with a lattice spacing of ~0.25 nm, attributable to the (100) planes of hexagonal WC phase. The corresponding SAED pattern in Fig. 3(d) shows a series of discontinuous diffraction rings belonging to hexagonal WC phase. The elements of the sample determined by EDS spectra are W and C. The TG-DTA curves (not shown) of the PWCPs had a mass gain of 12.4% and exothermic peak at 420°C–486°C, mainly due to the oxidation of WC, besides a small amount of residual carbon. The mass fraction of the residual carbon was calculated to be ~4.5 wt% according to the TG-DTA analysis.

Figure 4 shows the N_2 adsorption-desorption isotherm curves and pore-size distribution of the as-obtained PWCPs. The N_2 adsorption-desorption isotherm is of type IV, and the high absorption at high relative pressure (P/P_0) range (approaching 1.0) suggests the formation of large mesopores

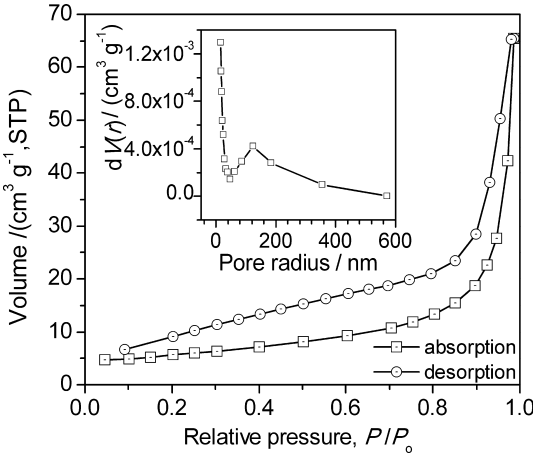

Fig. 4. Nitrogen adsorption–desorption isotherm curves and the pore-size distribution based on the BJH method adsorption (the inset) of the porous WC nanoplates derived from the tungstate-based hybrid belts.

(2–50 nm) and macropores (>50 nm) in the PWCPs sample.[19–21] The shape of hysteresis loops is of type H3, associated with aggregates of plate-like particles, giving rise to slit-like pores.[21] The low-pressure hysteresis also indicates that the PWCPs contain some micropores (<2 nm).[21] Actually, the pore-size distribution (the inset of Fig. 4) confirms that there are three types of pores: macropores ($50 < \varphi < 500$ nm), micropores, and mesopores (φ <50 nm).[21] The micropores and mesopores mainly are due to the in-plane pores of an individual WC nanoplate [Figs. 3(a)–(b)], whereas the macropores are mainly caused by the house-of-card structure of the aggregated PWCPs [Fig. 2(d)]. The specific surface area of the PWCPs is 19.5 m^2/g according to the multipoint BET plot.

The formation of the PWCPs may involve the essential reactions as shown in Eqs. 1–2.[8,16–18] The plate-like shape is inherited from the WO_3 nanoplates to WC nanoplates via a tungsten nitride.[16] The formation mechanism of the micropores and mesopores in PWCPs can be understood from the following aspects: (1) the shrinkage in volume during the conversion from monoclinic WO_3 (7.2 g/cm^3) to β-W_2N, and then to hexagonal WC (15.6 g/cm^3) due to the difference in density and (2) the framework support effect of the solid plate-like morphology which prevent the mass transfer during the nitridization and carbonization reactions. The synergistic effect of the shrinkage in volume and the steric hindrance of plate-like morphology in mass transfer facilitate the formation of porous WC nanoplates from WO_3 nanoplates.[8,16]

$$\text{W-containing hybrid belts} \xrightarrow{\text{HNO}_3\text{, then } 400^\circ\text{C}} \text{WO}_3 \text{ nanoplates} \quad (1)$$

$$\text{WO}_3 \text{ nanoplates} \xrightarrow{\text{NH}_3,\,650^\circ\text{C}/2\text{ h}} \beta - \text{W}_2\text{N} \xrightarrow{\text{CO/CO}_2(10{:}1),\,750^\circ\text{C}/10\text{ h}} \text{porous WC nanoplates} \quad (2)$$

The carbonization temperature and CO_2/CO ratios have important effects on the formation of pure WC phase, and low temperature (<750°C) or high CO_2/CO ratios (>10:1) are unfavorable in the synthesis of WC. The subprocess of nitridization plays a key role in the formation of porous morphology by refining the grains of WC phase.[8,16] The plate-like shape of the WO_3 precursor is necessary for the formation of WC nanoplates via a topochemical conversion, and the precursors with other morphologies are not easy to produce porous WC nanoplates.[8,11,14]

IV. Conclusions

Porous WC nanoplates with high surface areas have been synthesized for the first time by a topochemical conversion process, involving a nitridization reaction at 650°C in NH_3 and a carbonization reaction at 750°C in a mixture of CO/CO_2. The WC nanoplates obtained have in-plane micropores, mesopores (<50 nm), and macropores from their aggregates with a house-of-card structure. The porous WC nanoplates can be used as potential supports for high-performance electrocatalysts.

Acknowledgments

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