Preparation and Enhanced Electrochromic Property of Three-dimensional Ordered Mesostructured Mixed Tungsten–Titanium Oxides

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Ordered three-dimensional (3-D) cage-like mesoporous mixed tungsten–titanium oxides (WO_3–TiO_2) with relatively high surface area (152 m^2g^{-1}) have been synthesized by employing Pluronic F108 triblock copolymer as a structure-directing agent via "acid-base pairs" strategy. Such materials exhibit enhanced electrochromic properties with the contrast ratio (T_b/T_c) of $\approx$1.8 at 550 nm.

During the past decade, electrochromic materials have attracted considerable interest for their applications such as automobile sector rear view mirrors, sunroofs, optical displays and so on.[1–10] Tungsten oxide, one of the good electrochromic materials, has received the most attention.[2–6] Further research shows that the electrochromic reversibility and lifetime can be improved by adding titanium to tungsten oxide.[7,8] Recent reports have shown that mesoporous WO_3 materials possess enhanced electrochromic properties, which may be due to their high surface area and special pore structure.[3,4] However, the synthesis of mesoporous mixed tungsten–titanium oxides WO_3–TiO_2 have not been reported yet, probably because it is difficult to control the homogeneous gellation of multicomponent inorganic precursors and the complex biphasic self-assembly. Herein, we have successfully prepared ordered mesoporous WO_3–TiO_2 materials with 3-D cage-like structure by using Pluronic F108 triblock copolymer as a structure-directing agent according to the "acid-base pairs" strategy.[11] Such mesoporous materials with relatively high surface area and 3-D open framework can facilitate the ion intercalation/deintercalation process. The photoelectrochemical experiments show their potential application in electrochromic field.

For the preparation of ordered mesoporous WO_3–TiO_2, tungsten hexachloride (WCl_6) and titanium isopropoxide [$Ti(OPr)_4$] were used as inorganic precursors. In a typical synthesis, 1 g of Pluronic F108 ($EO_{132}PO_{50}EO_{132}$, Mav = 14600, BASF) was dissolved in 10 g of ethanol, then 0.8 g of WCl_6 and 1.1 g of $Ti(OPr)_4$ were added in the solution and the mixture was further stirred for 2 h. The mesoporous WO_3–TiO_2 films were prepared by spin coating of the solution with ITO glass as a substrate. The as-deposited films were left in air (relative humidity: 30–70%) to evaporate the solvent. After dried for 2 days, the template was removed by calcination at 350 °C in air and then the final electrochromic films (about 100 nm thick) were obtained. The nonporous WO_3–TiO_2 material as a reference was prepared by similar preparation approach except that no block copolymer template was used.

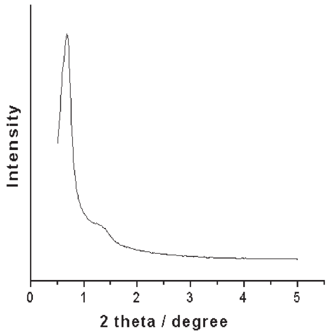

Figure 1. XRD pattern for the calcined mesoporous WO_3–TiO_2 sample synthesized using F108 as structure-directing agent.

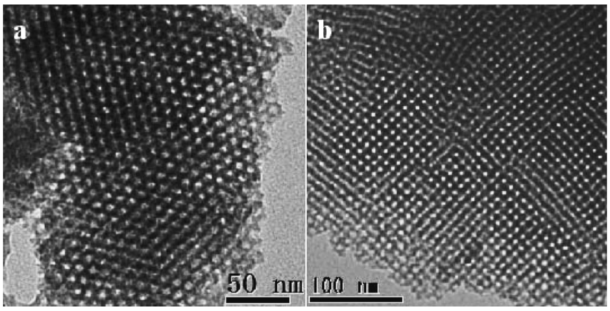

Figure 2. TEM images of calcined mesoporous WO_3–TiO_2 samples synthesized using F108 as structure-directing agent along (a) [111] direction and (b) [110] direction.

X-ray diffraction (XRD) pattern (Figure 1) for the calcined mesoporous WO_3–TiO_2 materials prepared by using triblock copolymer F108 as a structure-directing agent exhibits an intense reflection at 2θ value of 0.68 and a broad peak with lower intensity in the 2θ range of 1.1–1.6, implying that the materials possess mesoscale regularity. No distinguishable diffraction peaks in the wide-angle region (2θ of 20–80) for the mesoporous mixed oxides are observed, indicating that the wall of mesoporous WO_3–TiO_2 products has amorphous feature. Transmission electron microscopy (TEM) images in Figure 2 reveal that the mesoporous WO_3–TiO_2 products have ordered 3-D caged mesostructure (possible space group of $Im3m$) similar to the previous report.[12] In addition, the energy dispersive X-ray spectroscopy (EDX) for the mesoporous WO_3–TiO_2 shows that W element is uniformly dispersed within WO_3–TiO_2 frameworks with the ratio of 1:1.9, which is approaching the initial adding amount. N_2 adsorption/desorption isotherm (Figure 3) for the calcined mesoporous WO_3–TiO_2 products exhibits a typical type IV curve with an H2 hysteresis loop, which is typical feature for 3-D cage-like mesostructure. The pore size distribution (Figure 3 inset) is rather narrow with a mean value of 6.0 nm (calculated by BJH model). The calcined mesoporous WO_3–TiO_2 products have a BET surface area of 152 m^2g^{-1} and a pore volume of 0.20 cm^3g^{-1}, which are much larger than 20 m^2g^{-1} and 0.03

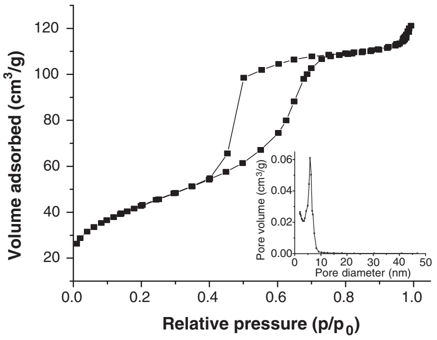

Figure 3. Nitrogen adsorption/desorption isotherm plot and pore size distribution curve (inset) for the calcined mesoporous WO_3–TiO_2 sample.

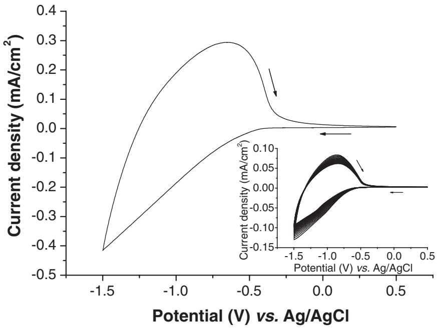

Figure 4. Cyclic voltammogram for the mesoporous WO_3–TiO_2 film in 1.0 mol·L^{-1} $LiClO_4$/1,2-propanediol carbonate electrolyte with the scan rate of 10 mV·s^{-1} and evolution of the cyclic voltammogram (inset) for the same film with the scan rate of 2 mV·s^{-1}. The reference and counter electrodes were solid Ag/AgCl electrode with a reference potential of 0.2065 V vs. normal hydrogen electrode at 298 K, and platinum wire, respectively.

cm^{3}g^{-1} of the nonporous WO_3–TiO_2 prepared in the absence of F108, respectively.

Figure 4 shows the typical cyclic voltammogram of mesoporous WO_3–TiO_2 films deposited on ITO glass at a scan rate of 10 mV·s^{-1}. There are no sharp current peaks in the cyclic voltammogram, suggesting that the mesoporous WO_3–TiO_2 films with amorphous wall features might have a broad distribution of energetically different intercalation sites.[10] As shown in Figure 4 inset, the amount of the inserted electrons reaches a relatively stable value of 1.7×10^{-4} C after 20 cycles with a reduced ratio of only 15%, indicating that 3-D cage-like mesostructured WO_3–TiO_2 materials feature a reversible process of charge insertion.

In situ spectroelectrochemical experiments were performed to monitor the electrochromic process for the mesoporous WO_3–TiO_2 films (Figure 5). The values of the transmittance for mesoporous WO_3–TiO_2 films in the original state (curve *a*) and the colorated state (curve *b*) are around 85–95% and 48–60%, respectively. The colorated WO_3–TiO_2 films bleach entirely by a positive potential of 0.5 V (applied for 50 s) and the transmittance spectrum (curve *c*) returns to the initial state, suggesting that the electrochromic process is highly reversible. The contrast ratio of mesoporous WO_3–TiO_2 oxides calculated[10] by T_b (transmittance for the bleaching)/T_c (transmittance for the coloration) is ≈1.8 at 550 nm, which is 1.5 times the value of nonporous WO_3–TiO_2 materials (≈1.2). The coloration efficiency of the materials is ≈22.1 cm^{2}C^{-1}, which is 2.2 times the value of the nonporous WO_3–TiO_2 materials (≈9.8 cm^{2}C^{-1}). Moreover, it is noticeable that the contrast ratio for mesoporous films keeps relatively constant value in the wide wavelength range from 400 to 800 nm, suggesting that such materials possess good electrochromic response at short wavelength as well as long wavelength, which is different from the previous reports.[4,9] This new feature is probably attributed to the special component and structure of the mesoporous materials, which might be beneficial to the potential application in "smart windows."

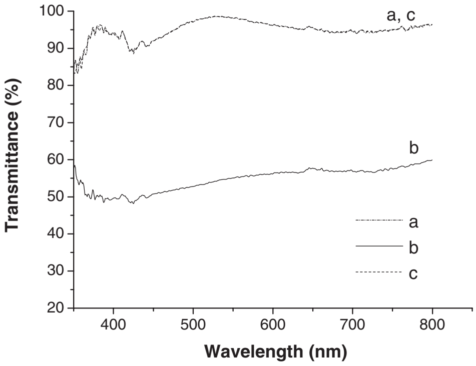

Figure 5. Optical transmittance spectra for the mesoporous WO_3–TiO_2 film: (a) (dash dot line) for original state (calcined mesoporous WO_3-TiO_2/ITO film); (b) (solid line) for colorated state (−1.5 V applied for 200 s); (c) (dash line) for bleached state (0.5 V applied for 50 s after b).

The improved electrochromic properties of the mesoporous WO_3–TiO_2 films might be attributed to the 3-D cage-like structure of the mesoporous WO_3–TiO_2 materials, in which the interconnected pores and other structural features (such as large surface area) might contribute to the diffusion and insertion process of ions.[3–6]

In summary, 3-D cage-like mesoporous mixed oxides WO_3–TiO_2 have firstly been synthesized utilizing the "acid-base pairs" strategy with triblock copolymer F108 as a template. Such mesoporous WO_3–TiO_2 materials show potential application in the eletrochromic field due to the amorphous framework, large surface area and 3-D interconnected mesoporous structure.

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