Hydrolysis reaction on the characterization of wormhole-like mesoporous tungsten oxide

Wei Hao Lai, Lay Gaik Teoh, Yen Hsun Su, Jiann Shieh, Min Hsiung Hon

Abstract

Wormhole-like mesostructures have promising applications in heterogeneous catalysis because channel branching within the wormhole-like mesostructures can facilitate access to active sites on the framework walls. We adopt the poly(alkylene oxide) triblock copolymer of L62 (BASF Pluronic EO8PO30EO8) as a template to form wormhole-like mesoporous tungsten oxide. In the hydrolysis experiment, 10 or 20% anhydrous ethanol was replaced with distilled deionized water (H2O). The crystallinity of wormhole-like mesoporous tungsten oxide decreases when the anhydrous ethanol solvent is replaced with H2O. Such a decrease in the relative strength of O–W–O binding attributes to the hydrolysis of the wormhole-like mesoporous tungsten oxide from Raman spectra. Specific surface area and average pore size of wormhole-like mesoporous tungsten oxide decrease with the amount of H2O replacement. The phenomenon can also be confirmed by nitrogen adsorption–desorption isotherms. These results show that the hydrolysis reactions have great significance and application for the development of wormhole-like mesoporous tungsten oxide in the future.

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1. Introduction

Due to its high potential for photoconductive behavior, tungsten oxide is the most promising candidate for use in electrochromic materials, dye sensitized solar cells, and gas sensors [1–3]. The improved properties of nanostructured materials usually result from their enormous surface area, which provides large quantities of active area to react with, e.g. photochromism, where coloration and bleaching steps are enhanced quickly by irradiating the bare tungsten oxide thin film with light [4,5]. The pore size and distribution can be designed for specific practical applications which have been proposed for these nanostructures [1–3].

It is well known that water plays an important role in the formation of a mesostructured framework. The quantity of water inside the hybrid coating can control the final mesophase. This effect has also been observed in mesoporous silica-based systems [6–8]. In base media, the hydrolysis of silicon alkoxides and their further condensation follows a particles dynamic that leads to a distribution of silicate species in solution with oligomeric species of various degrees of polymerization [9]. Most of the related works are about the preparation of silica, but the references concerning the preparations or characteristics of non-silica-based materials are deficient. Kim et al. [10] developed mesoporous alumina through a post-hydrolysis method to induce the hydrolysis and condensation reactions as the terminal reaction step. Mecheri et al. [11] reported the addition of hydrated tungsten oxide (WO3·2H2O) resulted in a higher proton conductivity, improved heat resistance and lower water solubility for fuel cell applications.

Furthermore, wormhole-like mesostructures have promising applications in heterogeneous catalysis because channel branching within the wormhole-like mesostructures can facilitate access to active sites on the framework walls [12–17]. However, there are few reports of wormhole-like mesoporous tungsten oxide that discuss the influence of hydrolysis reaction. In this work, we adjust the addition of water to investigate the hydrolyzed effect on the characterization of wormhole-like...
mesoporous tungsten oxide by microstructure analyses. We also report on the possible hydrolysis reaction that governs or suppresses the growth of wormhole-like mesoporous tungsten oxide.

2. Experimental

We adopt nonionic surfactants that possess dipolar or zwitterionic headgroups and exhibit substantially lower critical micelle concentrations (CMCs) than the corresponding ionic surfactants. The samples were prepared by a kind of sol–gel process, using colloidal solution of tungstic chloride stabilized by addition of selected organic poly(alkylene oxide) triblock copolymer. 0.5 g of poly(alkylene oxide) triblock copolymers of L62 (BASF Pluronic E08PO30EO8) were dissolved in 5 g of ethanol solvent (purity: 99.8%). To this solution, 2.5 mmol of the anhydrous inorganic chloride precursor, WCl6 (Aldrich), was slowly added and vigorously stirred for 48 h. In the hydrolysis experiment, 10 or 20% anhydrous ethanol was replaced with distilled deionized water (H2O). The resulting solutions were gelled in an open Petri dish at 60°C in air and calcined at 250°C for 12 h to remove the residual triblock copolymer.

Wormhole-like mesoporous tungsten oxide synthesized by sol–gel and incorporating triblock copolymer to generate liquid crystal template was characterized by a variety of analyses. The mesostructure of tungsten oxide obtained was then investigated by X-ray powder diffraction (Rigaku D/Max-IV, using Cu Kα radiation), transmission electron microscopy (Hitachi Model HF-2000, 200 kV), and Raman spectrometer (LabRAM HR, Jobin Yvon). The structure and bonding type of wormhole-like mesoporous tungsten oxide was evaluated by Raman spectra that obtained from the excitation of a 525 nm argon laser focused with a spot diameter of 1 Am. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micrometrics ASAP 2010 system after the samples were vacuum-dried at 150°C for 12 h in a N2 atmosphere. Brunauer–Emmett–Teller (BET) surface areas were estimated over a relative pressure (P/P0) ranging from 0 to 1.0.

3. Results and discussion

The synthesized factors of wormhole-like mesoporous tungsten oxide precursor solution, including surfactant concentration, pH, and temperature, are important in promoting the stability of liquid-crystal micelles as a mesostructure director. It has been demonstrated [18] that the triblock copolymers of L62 are completely are removed and form wormhole-like mesoporous tungsten oxide upon calcination at 250°C. However, the recent studies of the mesostructured crystallinity of tungsten oxide do not have detailed discussion of this. Fig. 1 shows X-ray powder diffraction patterns of wormhole-like mesoporous tungsten oxide samples prepared by (a) full anhydrous ethanol, (b) 10%, and (c) 20% replaced with H2O and calcined at 250°C. The crystalline structure in Fig. 1a is the cubic type of nanocrystals (JCPDS-ICDD 41-0905, \(a = b = c = 3.714\) Å). Three peaks can be identified at 2θ values of 24.08°, 34.01° and 55.41° by a spectral deconvolution analysis of the X-ray spectra. These peaks are consistent with the cubic crystalline structure and correspond to 100, 110 and 210 diffractions, respectively. Tungsten oxide exists in many polymorphic modifications, but monoclinic \(\gamma\)-WO3 is the only polymorph from 290 to 600 K [19,20]. Furthermore, the crystal phases which were replaced with 10% (Fig. 1b) and 20% H2O (Fig. 1c) are both monoclinic crystalline, as seen from the position of the peak and the broadness of the peak. The crystallinity of wormhole-like mesoporous tungsten oxide decreases when the anhydrous ethanol solvent was replaced with H2O due to the full-width at half-maximum (FWHM).

Raman spectroscopy is a powerful tool to investigate the bonding structure of wormhole-like mesoporous tungsten oxide. The Raman spectra of wormhole-like mesoporous tungsten oxide are presented in Fig. 2. The spectra yield information concerning the existence of different phases and bonds of the wormhole-like mesoporous tungsten oxide crystals. The wormhole-like mesoporous tungsten oxide synthesized with full anhydrous ethanol (Fig. 2a) has a better crystallinity than that of the 10% (Fig. 2b) or 20% H2O replacement (Fig. 2c) as shown in Raman spectra. The degree of crystallinity of wormhole-like mesoporous tungsten oxide powder with the cubic phase prepared with full anhydrous ethanol is in agreement with the confirmed results of XRD (Figs. 1a and 2a). However, the broad profile of the samples synthesized with 10% H2O replacement (Fig. 2b) is indicative of the defects of mesopores that are abundant in n-type semiconductors. The Raman spectra of wormhole-like mesoporous tungsten oxide samples in Fig. 2a and b show
features of wormhole-like tungsten oxide with main bands in the regions 200–400 and 600–850 cm\(^{-1}\); the three strongest wavenumbers of which are located at 261, 704, and 803 cm\(^{-1}\). The wavenumber that appears at 266 cm\(^{-1}\) corresponds to the O–W–O binding modes of the bridging oxygen. The wavenumbers that appear at 713 and 803 cm\(^{-1}\) are both assigned to the W–O stretching modes\(^{[21,22]}\). Wormhole-like mesopores were destroyed with the replacement of 20\% H\(_2\)O, which can be found as agglomerated particles appeared in the TEM observation in Fig. 3c. Non-uniform tungsten oxide nanoparticles with short-ranged order are dispersed, which makes the background intensity increase due to chaotic light scattering in the Raman spectra (Fig. 2c). Compared with the 20\% H\(_2\)O replacement of sample, more uniform tungsten oxide nanoparticles with the smaller wormhole-like mesopores are seen in the TEM observation in Fig. 3b, and the background intensity reduces and the ideal oscillator mode of the Raman spectrum is present in Fig. 2b. The bands of wormhole-like mesoporous tungsten oxide synthesized with 10\% H\(_2\)O replacement (Fig. 2b) is a little left-shifted as compared with that of anhydrous ethanol (Fig. 2a). There are all smooth curves over the 1000 cm\(^{-1}\) in Fig. 2, which is no evidence for the presence of carbon at 1390 or 1591 cm\(^{-1}\) in the spectra (data not shown), indicating the complete combustion of the organic additive during the calcined processes\(^{[23]}\). From Fig. 2, the W–O bond is first formed at 803 cm\(^{-1}\) and followed by the O–W–O binding modes of the bridging oxygen at 266 cm\(^{-1}\). Such an increase in the relative strength of O–W–O binding attributes to the hydrolysis of the wormhole-like mesoporous tungsten oxide\(^{[22]}\). Baker et al.\(^{[24]}\) noted the appearance of a peak and/or shoulder at approximately 800 cm\(^{-1}\), which can be attributed to O–W–O binding from the FTIR spectra, indicates hydrolysis and polycondensation reaction. The grain size of wormhole-like mesoporous tungsten oxide also has the same trend, the grain growth of which can be seen in Teoh et al.\(^{[25]}\).

The correlation of crystallinity and Raman spectra would be interpreted in stimulated Raman scattering described through use of the polarization\(^{[26]}\). We assume that the vibrational mode can be described as a simple harmonic oscillator of resonance frequency \(\omega_V\) and damping constant \(\gamma\), and we denote the internuclear distance with \(q\) and the reduced nuclear mass with \(m\).
Near the Raman resonance, the Raman susceptibility can be approximated as

\[
\chi_R(\omega_S) = \frac{(N/12m\omega_c)(\partial\chi/\partial q)^2}{[\omega_S - (\omega_L - \omega_V)] + i\gamma}
\]  

(1)

Here \(\alpha\) is the polarizability of a molecule in which the internuclear distance is held fixed at its equilibrium value. The exact Raman resonance of \(\omega_S = \omega_L - \omega_V\), as defined in Eq. (1). According to Beer’s law, we then find that the evolution of the field amplitude \(A_S\) is given in the slowly varying-amplitude approximation by

\[
\frac{dA_S}{dz} = -\alpha_S A_S
\]  

(2)

where

\[
\alpha_S = -12\pi n_S \chi_R(\omega_S)|A_L|^2
\]  

(3)

is the Stoke wave “absorption coefficient”. We insert Eq. (1) into Eq. (3), which becomes

\[
\alpha_S = \left\{-\frac{\pi\gamma(N/m\omega_c)(\partial\chi/\partial q)^2(\omega_S/n_Sc)|A_L|^2}{[\omega_S - (\omega_L - \omega_V)]^2 + \gamma^2}ight\}
+ \left\{-\frac{\pi(N/m\omega_c)(\partial\chi/\partial q)^2(\omega_S - (\omega_L - \omega_V))(\omega_S/n_Sc)|A_L|^2}{[\omega_S - (\omega_L - \omega_V)]^2 + \gamma^2}\right\}i
\]  

(4)

The real and imaginary part are both negative, the real part of the absorption coefficient is negative, implying that the Stokes wave actually experiences exponential enhancement on the modulus of the complex amplitude of the Raman field. The absorption coefficient \(\alpha_S\) depends only on the damping constant of \(\gamma\), since the other factors can be regarded as constant in this study. From the results of Eq. (4) and Beer’s law (Eq. (2)), we would conclude that the damping constant of \(\gamma\) induces the absorption coefficient of \(\alpha_S\) to increase, then the peak intensity of the Raman spectra rises with exponential growth [26].

The promotion of crystallinity is due to the long-range order in the crystal structure of the materials, so the ideal oscillator mode and intensity of wormhole-like tungsten oxide appears (Fig. 2a). Furthermore, the crystallinity reduces with the decreasing of the long-range order and random arrangement of atoms in the materials, which tend to lower the amplitude of the oscillators in the Raman spectra. We suggest that if the damping constant of \(\gamma\) is raised, then the peak intensity significantly increases in the Raman spectra. So, we can find the correlation between crystallinity and the Raman spectra.

These results are consistent with TEM observations, as shown in Fig. 3. The TEM images show the wormhole-like mesoporous tungsten oxide prepared for anhydrous ethanol (Fig. 3a), and 10% and 20% replaced by \(H_2O\) (Fig. 3b and c) and calcined at 250°C. Tungsten oxide prepared by anhydrous ethanol (Fig. 3a) shows the wormhole-like distribution of mesopores with the average size of 10 nm. There is no long-range order in the pore structure. Only three-dimensional (3D) mesoporous tungsten oxide with long-range order has prepared to date by using SBA-15 as template [21,27]. However, wormhole-like structures are destroyed as synthesized with 10 or 20% replacement of \(H_2O\), especially in Fig. 3c. If anhydrous ethanol solvent is replaced by \(H_2O\) during the hydrolysis or condensation reaction, wormhole-like mesopores of tungsten oxide would be harmfully formed. It is very interesting to note the regularly rectangular shape of wormhole-like mesoporous tungsten oxide produced by pure ethanol and calcined at 250°C (Fig. 3a). There were similar morphologies in some other reported articles [28,29]. This may be because the cubic phase of the mesostructure in that of adjacent axes is close to 90° [30]. From the XRD in Fig. 1a, the wormhole-like mesoporous tungsten oxide calcined at 250°C has a cubic phase (JCPDS-ICDD 41-0905). Adding \(H_2O\) in the precursor of tungstic solution may retard the condensation rate of the mesostructure during hydrolysis reaction, which is significant for applications of wormhole-like mesoporous materials.

Since the TEM images only show the local regions, the overall mesoporosity of the samples is also measured by \(N_2\) adsorption/desorption isotherms. The shape of the curves in Fig. 4 is similar with that of typical wormhole-like mesoporous materials [25,31]. The Brunauer–Emmett–Teller (BET) specific surface area of wormhole-like mesoporous tungsten oxide synthesized with anhydrous ethanol is 133 m²/g in Fig. 4(a), for 10% replaced by \(H_2O\) is 102 m²/g in Fig. 4(b), and 20% replaced by \(H_2O\) is 107 m²/g in Fig. 4(c). Mesoporous tungsten oxide would have enhanced sensitivity or optochromic properties with high surface area after the introduction of mesopores. In the behavior of the surfactant in binary surfactant/solvent systems, the concentration of surfactants, aging rate, pH value in precursor solution, and calcined temperature, are all the key factors for the controlled preparation of organic or inorganic mesostructures [18,32]. The performance of such structures can be identified from the result of BET analyses and the microstructured morphologies from TEM observation. Among the TEM images in Fig. 3, the number of wormhole-like mesopores is most abundant in Fig. 3a, the next is in Fig. 3b, and the last is in Fig. 3c. The specific surface area and average pore size of wormhole-like mesoporous tungsten oxide samples decrease, which correspond with the number of wormhole-like mesopores from

![Fig. 4. Nitrogen adsorption–desorption isotherms of wormhole-like mesoporous tungsten oxide samples prepared with (a) full anhydrous ethanol, (b) 10%, and (c) 20% replaced with \(H_2O\) and calcined at 250°C.](image-url)
Fig. 5. High-resolution lattice-image of wormhole-like mesoporous tungsten oxide sample synthesized with triblock copolymer of L62 and calcined at 250 °C.

TEM observation when increasing the amount of H2O replacement. The phenomenon is also confirmed by the enhancement of the hydrolysis reaction by adding H2O to the precursor of the tungsten solution.

The HRTEM image of the wormhole-like mesoporous tungsten oxide produced by the anhydrous ethanol is presented in Fig. 5. According to the study of Woodward and Sleight [20] and JCPDS card no. 41-0905, the wormhole-like mesoporous tungsten oxide has a cubic structure with the lattice constant of 3.714 Å. The SAD spots are recorded through the [0 1 0] zone axis (data not shown), which corresponds to the fcc crystal structure. Well-crystallized lattices can be seen in Fig. 5, which grow along the [1 0 0] direction with the atomic lattice constant of 3.71 Å, and the side surface is perpendicular to {0 1 0}. The aligned lattices are interrupted at the location of mesopores formed by triblock copolymers. The average size of mesopores in tungsten oxide nanowire is about 8 nm. Wormhole-like mesoporous tungsten oxide is characterized with the cubic single-crystal structure with the discontinuous lattice at the mesopores in wormhole-like mesoporous semiconductor oxide. These results show that the hydrolysis reactions have great influence and application for the development of wormhole-like mesoporous tungsten oxide in the future.

4. Conclusions

In summary, the crystal phase of wormhole-like mesoporous tungsten oxide sample replaced with H2O is monoclinic crystalline, as seen from the position and the broadness of the peak. The crystallinity of wormhole-like mesoporous tungsten oxide decreases when the anhydrous ethanol solvent was replaced with H2O. Such a decrease in the relative strength of O–W–O binding attributes to the hydrolysis of the wormhole-like mesoporous tungsten oxide from the Raman spectra. Adding H2O in the precursor of tungstic solution may retard the condensation rate of the mesostructure during the hydrolysis reaction. The specific surface area and average pore size of wormhole-like mesoporous tungsten oxide decrease with the amount of H2O replacement. The phenomenon can also be confirmed by nitrogen adsorption–desorption isotherms. We also first find that the mesoporous tungsten oxide is characterized with the cubic single-crystal structure with the discontinuous lattice at the mesopores in wormhole-like mesoporous semiconductor oxide. These results show that the hydrolysis reactions have great influence and application for the development of wormhole-like mesoporous tungsten oxide in the future.

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