Synthesis of Highly Ordered Mesoporous Tantalum Oxide

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The pore arrangement of mesoporous tantalum oxide prepared with a block copolymer surfactant as a structure-directing agent is remarkably improved by optimizing the amounts of metal source and water content. In contrast to the wormhole-like pore structure observed in the mesoporous tantalum oxide prepared under standard conditions, a highly ordered mesoporous structure is formed under optimized conditions.

Tantalum oxide (Ta_2O_5) and its mixed oxides (MTa_2O_6, M = Ca, Mg etc.) have been studied as highly active photocatalysts for overall water decomposition under ultraviolet (UV) irradiation.[1] As a new class of photocatalyst, our group previously synthesized mesoporous Ta_2O_5 by the ligand-assisted templating (LAT) method reported by Ying et al.[2,3] This material exhibited high, stable activity for water decomposition under UV irradiation despite its amorphous framework, which limits the mobility of evolved electrons and holes. Mesoporous Ta_2O_5 is, therefore, of particular interest because of its unique photocatalytic ability. However, the mesoporous structures realized to date are disordered and are of only low thermal stability, prohibiting detailed analysis and further modification. Recently, a neutral templating route using a block copolymer as a structure-directing agent was applied by Yang et al. in the synthesis of some pure and mixed mesoporous metal oxides.[4] While some of those materials had low pore regularity and uniformity, the neutral templating route in general affords materials with thick pore walls, providing high structural strength with respect to thermal and hydrothermal treatment. This communication reports the synthesis of highly ordered mesoporous Ta_2O_5 via the neutral templating route using a modified sol–gel method with block copolymer surfactant P123 as a structure-directing agent. A two-dimensional (2D) hexagonal mesoporous structure is successfully achieved by synthesis under optimized conditions of metal source and water content. To the best of the authors' knowledge, this is the first report of the reproducible synthesis of 2D-hexagonally ordered mesoporous Ta_2O_5.

Mesoporous Ta_2O_5 was prepared by an improved version of the method reported by Yang et al.[4] The triblock copolymer P123 ($HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}OH$, BASF; 1 g) was dissolved in 10 g of ethanol with constant stirring for 10 min. To this solution was added 4–15 mmol of $TaCl_5$ with vigorous stirring for 10 min, followed by the addition of 0–60 mmol of deionized water with stirring for more than 1 h to promote hydrolysis. The resulting sol solution was transferred to a Petri dish for aging at 313 K for 7 days to obtain a gel precursor. The gel was then calcined at 773 K for 5 h to remove the template.

Standard mesoporous Ta_2O_5 reported by Yang et al.[4] was synthesized with 10 mmol of metal source in 10 g of ethanol solution containing 1 g of P123. The influence of the amount of metal source in range 4–15 mmol was investigated in the absence of added water. Figure 1A shows the XRD patterns of mesoporous Ta_2O_5 synthesized with various amounts of the metal source. Under standard conditions, only the intense diffraction peak associated with the wormhole-like structure is observed (Figure 1A(c)). However, this diffraction peak gradually weakens as the amount of metal source is increased above 10 mmol, indicating that the mesoporous periodicity becomes gradually weaker with increasing amount of metal source (Figure 1A(a) and (b)). As the amount of metal source was reduced, however, an additional broad peak appeared at around 3°, implying the formation of hexagonally ordered mesoporous structure (Figure 1A(d)–(g)). This result reveals that an ordered mesoporous structure can be successfully formed with the addition of only a small amount of metal source. Thus, it is clear that mesoporous periodicity of Ta_2O_5 is strongly affected by the metal source content. Comparing the intensity of first diffraction peaks among samples synthesized with small amounts of metal source (Figure 1A(d)–(g)), the most intense peak was observed for the sample prepared with 6 mmol of metal sources. Therefore, this sample is considered to form the most regular periodic structure. Figure 1b compares the BET surface area, d-spacing value, and wall thickness of these samples prepared with various amounts of metal source. Although the wall thickness continuously decreases with decreasing metal source content, the d-spacing value remains constant at about 7 nm. That is, the mesopore diam-

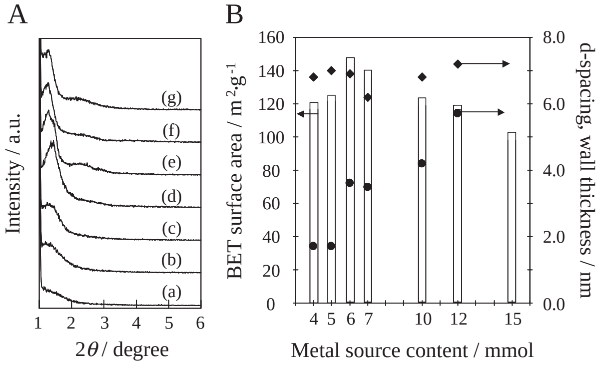

Figure 1. (A) Low-angle XRD patterns and (B) changes in BET surface area, d spacing, and wall thickness for mesoporous Ta_2O_5 prepared with various amounts of metal source: (a) 15, (b) 12, (c) 10, (d) 7, (e) 6, (f) 5, and (g) 4 mmol. Diamonds denote d spacing, and circles denote wall thickness which was calculated by the equation as follow: $(2 \times (d\text{-spacing value})/1.73)$–(mesopore diameter).

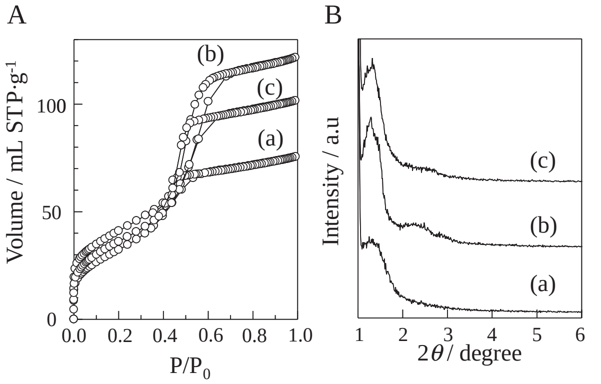

Figure 2. (A) N_2 adsorption–desorption isotherms and (B) low-angle XRD patterns of mesoporous Ta_2O_5 prepared with various amounts of metal source and water: (a) 6 mmol of metal source, no water, (b) 6 mmol of metal source, 6 mmol of water, (c) 10 mmol of metal source, no water (standard condition).

eter becomes smaller with increasing metal source content. Since the assembly mechanism of mesoporous metal oxide synthesized by amphiphilic block copolymer as a template is originated from the electrostatic interaction between metal ions and ethylene oxide groups around the rod micelle, the metal source content is considered to affect the thickness of pore walls and mesopore ordering. As stronger interactions among micelle rods results in more regular mesoporosity, a highly ordered mesoporous structure could be formed in the range with small metal source content. Mesoporous Ta_2O_5 prepared with 6 mmol of metal source has a BET surface area of 147 $m^2 \cdot g^{-1}$, which is also the highest among these samples. Although the regularity of the mesoporous structure of samples prepared with 4 and 5 mmol of metal source is close to that of the 6 mmol sample, the BET surface area of the 4–5 mmol samples was lower, indicating partial destruction of the mesoporous structure in the calcinations step owing to thinner walls (<2 nm). Therefore, 6 mmol of metal source is concluded to be the most suitable for obtaining highly ordered mesoporous Ta_2O_5.

The addition of water to the sol solution to control the rate of hydrolysis and polycondensation of the metal source is a key factor for achieving reproducible syntheses of mesoporous transition-metal oxides.[5] We optimize the amounts of added water to produce a better ordered mesoporous structure. The optimal amount of added water for the synthesis of mesoporous Ta_2O_5 with 6 mmol of metal source was found to be 6 mmol. Figure 2A compares the N_2 adsorption–desorption isotherms and low-angle XRD patterns of samples synthesized with 0 and 6 mmol of added water, with the results for mesoporous Ta_2O_5 synthesized under standard conditions shown for reference. All the isotherms are assignable to a type-IV pattern, characteristic of mesoporous materials. A relatively large increase in N_2 adsorption uptake derived from capillary condensation of mesopores is observed for samples synthesized under the optimized conditions (Figure 2A(b) and (c)). The isotherms of these two samples also have an H1-type hysteresis loop, associated with the formation of cylindrical mesopores. However, the pore-size distribution of the sample prepared with 6 mmol water is narrower than that of the sample prepared without water, demonstrating that the uniformity of mesopore diameter is improved by the addition of water.

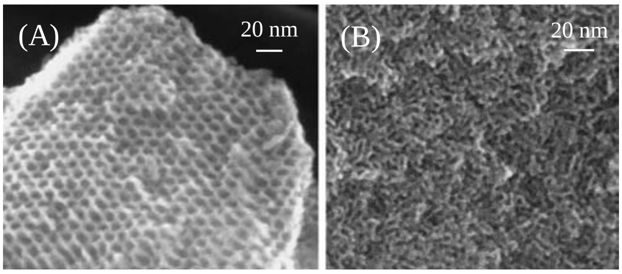

Figure 3. SEM image of mesoporous Ta_2O_5 synthesized under (A) optimized conditions and (B) standard conditions.

An SEM image of the surface of the optimized mesoporous structure is shown in Figure 3A, clearly revealing the formation of a regular arrangement of uniform hexagonal mesopores with an open pore system. In contrast, the SEM image of mesoporous Ta_2O_5 prepared under standard conditions (Figure 3B) has wormhole-like mesopore structure. This type of channel system was also formed in the MSU-X materials synthesized by Pinnavaia et al.[6,7]

In conclusion, Ta_2O_5 with a highly ordered hexagonal mesoporous structure was successfully prepared through the optimization of metal source and water content in synthesis using a block copolymer as a structure-directing agent. The open porous structure of the mesoporous Ta_2O_5 was confirmed by SEM analysis. This highly ordered mesoporous structure with open pore system will have advantages in various applications as a catalyst, as well as for the incorporation and encapsulation of large functional molecules.

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