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Porous Single-Crystalline TaON and Ta_3N_5 Particles

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Nitrides have attracted considerable attention in many fields. Recently, the present authors have reported a tantalum oxynitride, TaON, and a tantalum nitride, Ta_3N_5, as visible light-responsive photocatalysts.[1−3] These photocatalysts exhibit a high quantum efficiency (QE) for water oxidation into O_2 under visible-light irradiation, up to 34% and 10% for TaON and Ta_3N_5, respectively. As nitrides are known to typically contain significant amounts of defects in the crystal structure, which would seem to be an undesirable property for electronic and photoelectronic applications, the high QE for oxidation of water by TaON and Ta_3N_5 photocatalysts is unexpected. Further detailed study of the TaON and Ta_3N_5 structures is therefore warranted.

Although there have been a few reports on TaON[4−7] and Ta_3N_5[5,6,8] synthesized from Ta_2O_5 powder in an ammonia atmosphere, the crystal habits of these materials have yet to be examined in detail. In this study, TaON and Ta_3N_5 particles prepared by nitriding Ta_2O_5 powder (99.9%, rare metallic) under a flow of NH_3 (flow rate of 20 mL/min for TaON and 1 L/min for Ta_3N_5) at 1123 K for 15 h were investigated by X-ray powder diffraction (RINT 2000/PC, Rigaku Corporation) and high-resolution field emission transmission electron microscopy (JEM-2010F, JEOL, 200 kV).

Figure 1 shows the schematic structures of Ta_2O_5, TaON, and Ta_3N_5. Ta_2O_5 has an orthorhombic structure (a = 43.997 Å, b = 3.894 Å, c = 6.209 Å), while TaON assumes a monoclinic structure (a = 4.968 Å, b = 5.037 Å, c = 5.185 Å, β = 99.560°) similar to baddeleyite (ZrO_2).[9] The structure of Ta_3N_5 is orthorhombic (a = 3.8862 Å, b = 10.2118 Å, c = 10.2624 Å) and consists of TaN_6 octahedra, with a structure similar to that of anisovite (Ti_3O_5).[10] In the present synthesis, Ta_2O_5 nitrided under a flow of 20 mL/min ammonia for 15 h was revealed by X-ray diffraction (XRD) to form TaON, whereas preparation under 1 L/min ammonia for the same period produced Ta_3N_5 (Figure 2).

TEM observation revealed that the Ta_2O_5 powders consisted of well-dispersed primary particles of submicrometer size (Figure 3a) and that each particle produced a sharp SAED (selected area electron diffraction) pattern, indicating high crystallinity (Figure 4a).

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(1) Hitoki, G.; Takata, T.; Kondo, J. N.; Hara, M.; Kobayashi, H.; Domen, K. *Chem. Commun.* **2002**, 1698.

(2) Hitoki, G.; Ishikawa, A.; Takata, T.; Kondo, J. N.; Hara, M.; Domen, K. *Chem. Lett.* **2002**, *7*, 736.

(3) Hara, M., Hitoki, G., Takata, T.; Kondo, J. N.; Kobayashi, H.; Domen, K. *Catal. Today* **2003**, *78*, 555.

(4) Brauer, G.; Weidlein, J. R. *Angew. Chem.* **1965**, *77*, 913.

(5) Brauer, G.; Weidlein, J. R.; Straehle, J. *Z. Anorg. Allg. Chem.* **1966**, *348*, 298.

(6) Swisher, J. H.; Read, M. H. *Metall. Trans.* **1972**, *3*, 489.

(7) Orhan, E.; Tessier, F.; Marchand, R. *Solid State Sci.* **2002**, *4*, 1071.

(8) Brauer, G.; Weidlein, J. R. *Angew. Chem.* **1965**, *77*, 218.

(9) Armytage, B.; Fender, B. E. F. *Acta Crystallogr. B* **1974**, *30*, 809.

(10) Strähle, J. *Z. Anorg. Allg. Chem.* **1973**, *402*, 47.

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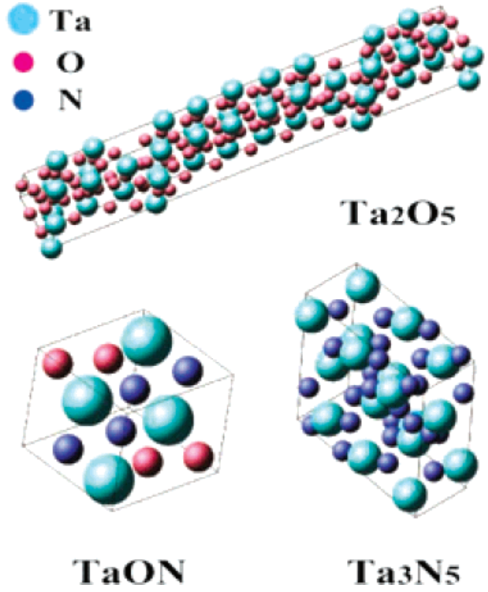

Figure 1. Schematic structures of Ta_2O_5, TaON, and Ta_3N_5.

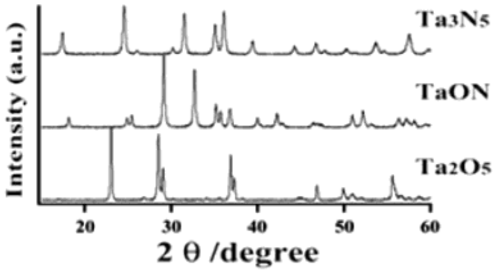

Figure 2. X-ray diffraction patterns of Ta_2O_5, TaON, and Ta_3N_5.

After nitridation of Ta_2O_5 to TaON, many pores of 10−20 nm in size emerged within the particles (Figure 3b). Similar pore formation was also observed for Ta_3N_5 (Figure 3c). The apparent particle size of the primary particles of Ta_2O_5 was maintained after nitridation to TaON or Ta_3N_5. However, the BET surface area was increased from 1.8 m^2/g for Ta_2O_5 to 6.5 m^2/g for TaON and 11.4 m^2/g for Ta_3N_5, attributable to the emergence of pores in the nitriding process.

During nitridation, substitution of N^{3-} for O^{2-} takes place while maintaining the valence state of Ta^{5+}. As three O^{2-} anions would be replaced by two N^{3-} anions, it seems reasonable for the primary particles of Ta_2O_5 to become porous given that the apparent size of primary particles remained unchanged after nitridation.

Figure 4c,e shows examples of TaON and Ta_3N_5 particles along with SAED patterns for the full samples. Surprisingly, these diffraction patterns exhibit sharp spots similar to that of the original Ta_2O_5 (inset of Figure 4a), indicating that the TaON and Ta_3N_5 particles are still single-crystalline primary particles. High-magnification images of the TaON and Ta_3N_5 particles (Figure 4d,f) show that the fringe patterns run coherently across the pores, again confirming the single-crystalline nature of these porous particles. After checking over 100 particles of TaON and Ta_3N_5, all particles appear to be single crystals similar to those shown in Figure 4c or 4e.

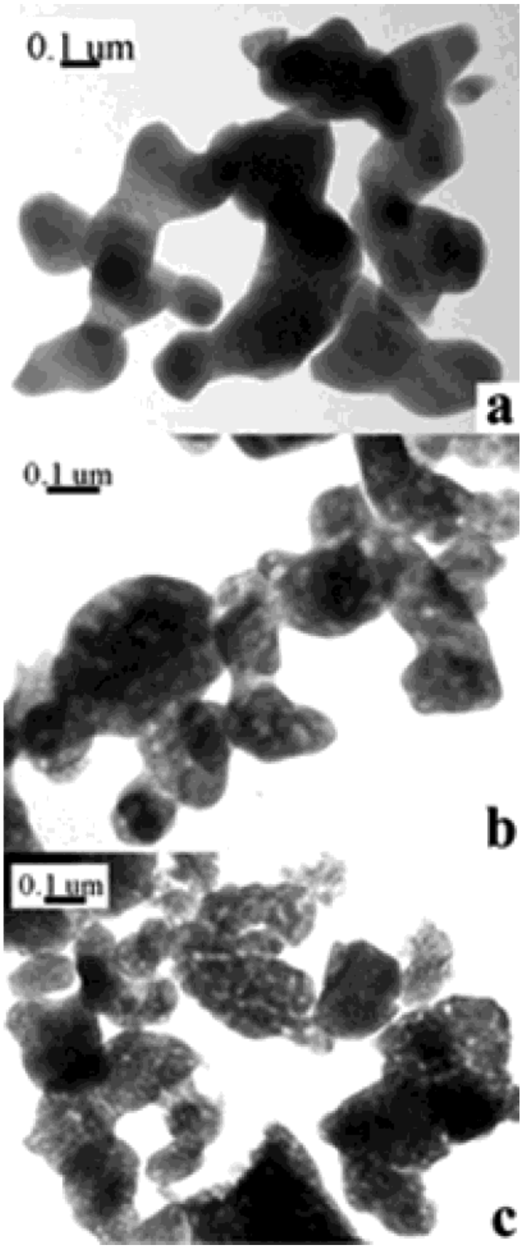

Figure 3. TEM images of (a) Ta_2O_5, (b) TaON, and (c) Ta_3N_5.

A solid-state transformation is pseudomorphic if the external geometry and size of the precursor are retained in the product. When the solid product is formed in one or several crystallographically equivalent orientations relative to the parent crystal as a consequence of a solid-state transformation, the process is called topotactic. A typical example of pseudomorphism and topotactism is the transformation of a MoO_3 platelet to a Mo_2N platelet by reaction with NH_3: the {100} planes of Mo_2N are parallel to the{010} planes of MoO_3.[11−13] The nitride Mo_2N product consists of 3−4-nm particles aggregated in a spongy relic of the parent crystals, in which the average pore size lies below 3 nm. It has also been known that the transformation of V_2O_5, MoO_3, and Nb_2O_5 reacted with NH_3 to porous nitride VN,[14,15]

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(11) Volpe, L.; Oyama, S. T.; Boudart, M. *Stud. Surf. Sci. Catal.* **1983**, *16*, 147.

(12) Volpe, L.; Boudart, M. *J. Solid State Chem.* **1985**, *59*, 332.

(13) Li, S.; Kim, W. B.; Lee, J. S. *Chem. Mater.* **1998**, *10*, 1853.

(14) Oyama. S. T.; Kapoor, R.; Oyama, H. T.; Hofmann, D. J.; Matijević, E. *J. Mater. Res.* **1993**, *8*, 1450.

(15) Kwon, H.; Choi, S.; Thompson, L. T. *J. Catal.* **1999**, *184*, 236.

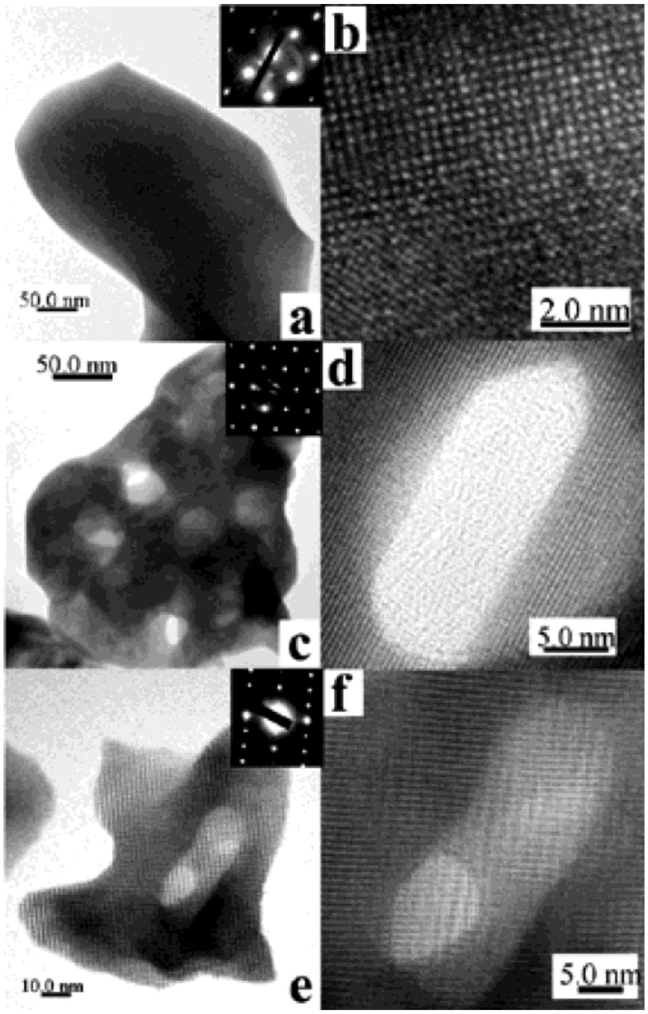

Figure 4. TEM images of (a) single-crystal Ta_2O_5 particle viewed along the [010] direction with diffraction pattern inset and (b) a high-magnification image of a part of (a); (c) single-crystal TaON particle viewed along the $[11\bar{1}]$ direction with diffraction pattern inset and (d) a pore in (c); and (e) single-crystal Ta_3N_5 particle viewed along the [100] direction with diffraction pattern inset and (f) a pore in (e).

MoO_xN_y,[16] NbN,[17] and NbO_xN_y,[18,19] respectively, is pseudomorphous and topotactic.

In this experiment, the morphologies between the parent Ta_2O_5 particles and the product TaON or Ta_3N_5 particles are identical, and each particle of the three materials is single crystalline. It can be suggested that the solid-state transformation of Ta_2O_5 by reaction with NH_3 to either TaON or Ta_3N_5 is pseudomorphic and topotactic. Because all particles of these three materials have a spherical habit, the crystalline orientation relationship between the precursor and product is not clear.

The porous Mo_2N platelets prepared from the transformation of MoO_3 consist of nanoparticles, and the platelets are regarded as single crystals from the SAED pattern in that most nanoparticles take the same crystalline orientation.[11] The pores in the platelets can be considered to be formed by the intervals of the nanoparticles. It is interesting to find that the porous TaON and Ta_3N_5 particles prepared in our experiment are different from those porous Mo_2N platelets. From the bright images and corresponding SAED patterns of TaON and Ta_3N_5 particles (Figure 4), it is clear that each single-crystalline particle of TaON and Ta_3N_5 is one particle rather than consisting of smaller nanoparticles. The pores in the TaON and Ta_3N_5 particles were caused by the voids that appeared in the nitridation process, which link to each other to form larger worm-hole-like pores, rather than being formed by the aggregation of nanoparticles.

A similar material consisting of mesoporous single-crystal particles of a Nb−Ta mixed oxide was recently prepared by the present authors.[20,21] However, that material was prepared by a very different process, involving the crystallization of an amorphous mesoporous precursor. To the best of the authors' knowledge, this is the first report of the formation of porous single-crystalline TaON and Ta_3N_5 particles from a pseudomorphous and topotactic transformation of Ta_2O_5 reacted with NH_3. For photocatalytic applications, this kind of well-crystallized and well-dispersed material is expected to achieve even higher QE for water oxidation under visible-light irradiation.

In conclusion, we have observed that the solid-state transformation of Ta_2O_5 reacted with NH_3 to TaON as well as Ta_3N_5 is pseudomorphous and topotactic. The single-crystalline particles of TaON and Ta_3N_5 were formed from the single-crystalline Ta_2O_5 particles. Each single-crystalline particle of TaON and Ta_3N_5 was one particle, not formed by the aggregation of nanoparticles. The worm-hole-like pores appeared in these particles during the nitridation process.

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(16) Kim, H. S.; Sayag, C.; Bugli, G.; Djéga-Mariadassou, G.; Boudart, M. *Proc. Mater. Res. Soc. Symp.* **1994**, *368*, 3.

(17) Oyama, S. T.; Schlatter, J. C.; Metcalfe, J. E.; Lambert, J. M., Jr. *Ind. Eng. Chem. Res.* **1988**, *27*, 1639.

(18) Kim, H. S.; Shin, C. H.; Bugli, G.; Bureau-Tardy, M.; Djega-Mariadassou, G. *Appl. Catal. A* **1994**, *119*, 223.

(19) Schwartz, V.; Oyama, S. T. *Chem. Mater.* **1997**, *9*, 3052.

(20) Lee, B.; Lu, D.; Kondo, J. N.; Domen, K. *Chem. Commun.* **2001**, 2118.

(21) Lee, B.; Yamashita, T.; Lu, D.; Kondo, J. N.; Domen, K. *Chem. Mater.* **2002**, *14*, 867.