Nanoparticle Synthesis of Transition Metal Oxynitride by Induction Thermal Plasma

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Abstract: Titanium oxynitride nanoparticles are synthesized from titanium powder injection into induction thermal plasma. Nitridation is expected to be promoted by NH_x radicals from NH_3 addition in the quenching gas. Molar ratio of Ti/O is controlled by oxygen addition in the sheath gas to understand the effect of oxygen source amount on the composition. The results indicate that precise control of mole ratio of Ti/O at large amount of nitrogen source injection leads to precise control of titanium oxynitride composition.

Keywords: thermal plasmas, oxynitride, photocatalysts, capacitors

1. Introduction

Transition metal oxynitrides have several advantages, such as low bandgap and excellent conductivity compared to its corresponding oxides and nitrides. Titanium oxynitride (TiO_xN_y) nanoparticles have attracted considerable attentions. Their potentials in many applications such as photocatalysts [1], capacitors [2], and electrodes [3] have been reported. Typically, TiO_xN_y nanoparticles are produced by annealing TiO_2 with ammonia at high temperature [1], or alternative methods such as sol-gel process [3], plasma-enhances atomic layer deposition [4], and laser pyrolysis [5]. However, the above methods possess critical issues such as time-consuming or low production rate.

Thermal plasma has been utilized to synthesize nanoparticles for a long time because of high chemical reactivity and high enthalpy. Therefore, thermal plasma has the advantage of high production rate. Induction thermal plasma is a suitable thermal plasma source for nanoparticles production since impurity generation from electrodes can avoided owing to electrodeless discharge. The purpose of this study is to synthesize TiO_xN_y nanoparticles by induction thermal plasma.

2. Experiment

The experimental setup of induction thermal plasma for the synthesis of TiO_xN_y nanoparticles, which is shown in **Fig. 1**. The apparatus mainly consists of powder feeder, RF power supply at 4MHz, induction plasma torch with water-cooling, reaction chamber, quenching tube, and powder collection filter.

Pure titanium powder with 45 μm in diameter as raw material is introduced into the plasma torch with Ar as carrier gas at the flow rate of 3 L/min. The feed rate is adjusted at 0.2~0.3 g/min. Ar is also used as sheath gas at 60 L/min and as inner gas at 5 L/min. NH_3 and Ar are injected as counter flow through the quenching tube at the flow rate of 8 L/min and 5 L/min, respectively. Nitridation is expected to be promoted by NH_x radicals as nitrogen source from NH_3. Mole ratio of nitrogen source to Ti is larger than 100 because nitridation is rather difficult to compare oxidation of titanium. Hence, limited oxygen source is injected as O_2 sheath gas at different gas flow rates to control precise mole ratio of Ti/O as 10:4, 10:8, 10:12, 10:16, 10:20.

The synthesized particles are oxidized gradually under an Ar atmosphere with 2vol % of O_2 to prevent from rapid oxidation in air. As synthesized particles are finally collected at the inner wall of the chamber and the filter.

X-ray diffraction (XRD, Rigaku Smartlab) is applied to determine the crystal structure of particles. The chemical bonding states are confirmed by X-ray photoelectron spectra (XPS, Shimadzu, Kratos AXIS Ultra). Elemental mapping is analysed by scanning TEM-energy dispersive X-ray spectrometry (STEM-EDS, JEOL JEM-ARM200F).

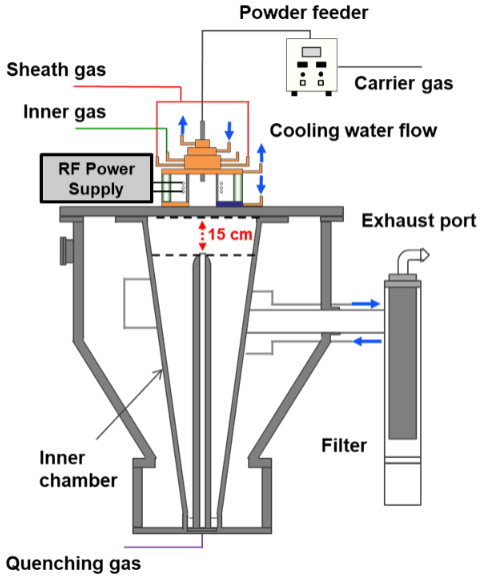

Fig. 1. Experimental setup of induction thermal plasma

3. Results and discussion

The XRD patterns of the synthesized particles without oxygen source and with oxygen source at Ti/O molar ratio of 10:4, 10:8, 10:12, 10:16, and 10:20 are shown in **Fig. 2**. Standard card of cubic TiN and TiO are also included. The XRD patterns of the particles correspond to cubic structure. The diffraction peaks from the product without oxygen source are nearly close to the reference pattern for cubic TiN. The peaks shift toward cubic TiO is confirmed when increasing oxygen molar ratio. Lattice constant for cubic crystal system can be calculated by the following equation.

$$a = \frac{\lambda \times \sqrt{h^2+k^2+l^2}}{2\sin\theta} \quad (1)$$

where λ represent the X-ray beam wavelength, *h*, *k* and *l* indicate the miller index of facet, θ represent the diffraction angle. Calculated lattice constants of the synthesized particles are shown in **Fig. 3**. The lattice constant decreased as increasing oxygen molar ratio. The lattice constants are less than the 4.247 Å found for cubic TiN and greater than the 4.176 Å observed for cubic TiO. This trend suggests the formation of cubic titanium oxynitride [6].

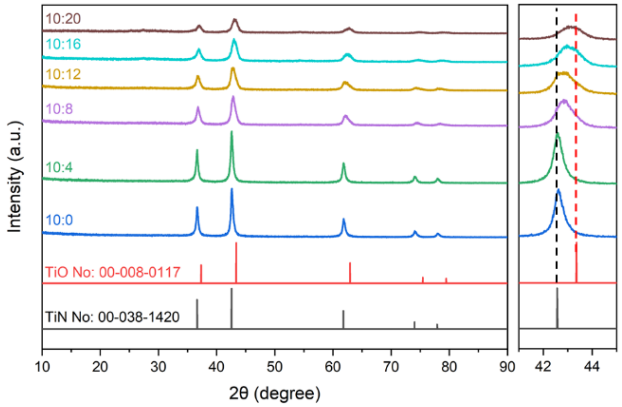

Fig. 2. XRD patterns of the synthesized particles

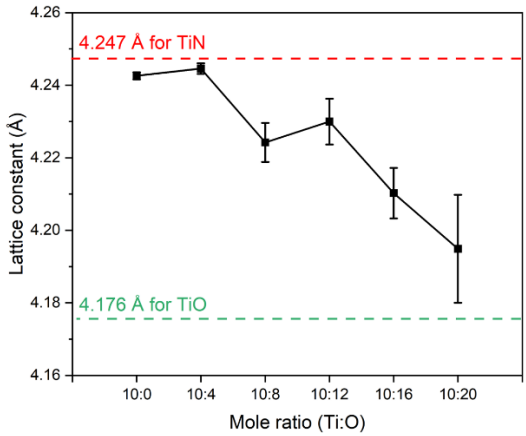

Fig. 3. Lattice constants of the synthesized particles

XPS survey spectrums of the synthesized particles at different Ti/O molar ratios revealed the existence of O 1s, Ti 2p, and N 1s peaks in all conditions. The narrow-scan XPS spectrum of Ti 2p can be deconvoluted into six peaks as shown in **Fig. 4**. The deconvolution yields three major doublets ($2p_{3/2}$ and $2p_{1/2}$) in each condition. The set of three $2p_{3/2}$ peaks represent TiN at 455.6 eV, TiO_xN_y at 457.2 eV, TiO_2 at 458.2 eV. The other set of three $2p_{1/2}$ peaks indicate TiN at 461.6 eV, TiO_xN_y at 463.2 eV, TiO_2 at 464.2 eV. Obtained results of XPS and XRD revealed that the successful formation of titanium oxynitride.

The result of elemental mapping image of the synthesized particles with oxygen source at Ti:O molar ratio of 10:20 is shown in **Fig. 5**. The size of particles is around 20 nm. Oxidation layer of core-shell structure is not observed on the particles. The composition on the surface of the particles is thus closed to the composition of the core.

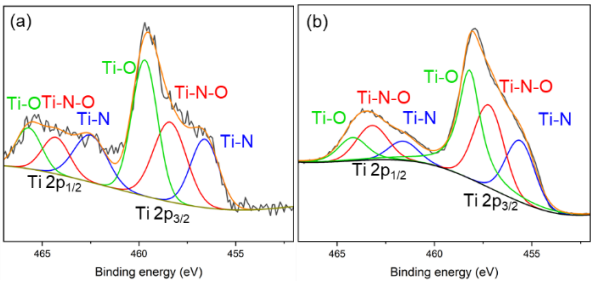

Fig. 4. Ti 2p narrow-scan XPS spectrum of the synthesized particles (a) without oxygen source; (b) with oxygen source at Ti:O molar ratio of 10:20

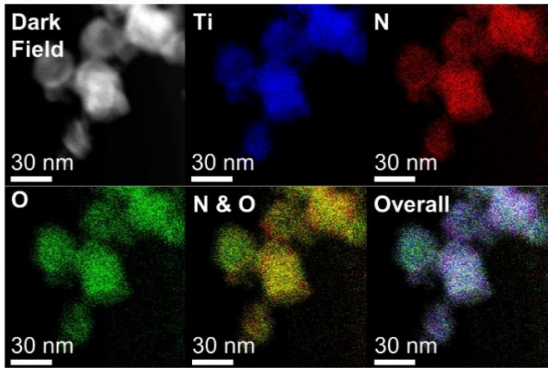

Fig. 5. The elemental mapping image of the synthesized particles with oxygen source at Ti:O molar ratio of 10:20

4. Conclusion

Titanium oxynitride nanoparticles with cubic structure are synthesized successfully by induction thermal plasma. Precise control of mole ratio of Ti/O at large amount of nitrogen source injection leads to precise control of titanium oxynitride composition. Obtained remarks suggest that thermal plasma is a promising route to produce high purity metal oxynitride nanoparticles at high processing rate.

Acknowledgement

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