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Research Article

Synthetic Conditions and Color Characteristics of Tantalum Oxynitride Prepared via Liquid-NH₃ Process

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Tantalum oxynitrides, such as TaON, exhibit promising color properties and can be employed as nontoxic yellow pigments containing no heavy metals. We have developed a process for preparing nitrides or oxynitrides involving the vacuum-calcination of a precursor material obtained via reaction between a metal halide and liquid NH₃. Herein, we describe the synthetic conditions of the liquid-NH₃ process that affect the color, and thus the color characteristics, of the resulting pigments. Reaction and postreaction treatment conditions were adjusted to obtain the desired yellow color. The liquid-NH₃ process was performed using 1.0 eq of H₂O (relative to TaCl₅) as the oxygen source and 30.0 eq of KCl (relative to TaCl₅) as flux. Calcination of the precursor at 1073 K under vacuum was followed by recalcination from room temperature to 973 K at rate of 10 K min⁻¹ under air. A powder with a color index of $L^* = 84.20$, $a^* = -2.71$, and $b^* = 44.07$ was obtained.

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1. Introduction

The development of green chemical processes is not only desirable but expected for creating a sustainable society in harmony with nature. Tantalum oxynitrides, such as TaON, have shown promise as nontoxic yellow pigments containing no heavy metals, which are similar to praseodymium yellow and cerium zirconium bismuth based oxide [1]. To date, these materials have been prepared via a gas nitriding process, in which tantalum oxide is transformed into the nitride under a flow of NH₃ gas under high temperatures [1]. In contrast, the liquid-NH₃ process affords the nitride or oxynitride through vacuum-calcination of a precursor material obtained by the reaction between a metal halide and liquid-NH₃ [2–4]. Because the liquid-NH₃ process allows for the precise control of the elemental composition of the starting materials, the process is suitable for screening new pigment compositions. In one case, the color of the tantalum oxynitride prepared via the liquid-NH₃ process was different from the color of TaON (Yellow TaON) prepared via the gas nitriding process using a flow of moist NH₃ gas, but was similar to that of green TaON [5]. Our aim is to clarify the conditions of the liquid-NH₃ process that control the color of the products, and to understand the color characteristics

of the resulting pigments. Because the liquid-NH₃ process involves the circulation of an inert gas within a glove box, the atmosphere is reductive and thus the oxidation number of Ta can be lower than expected. To prevent this, an additional recalcination step in air was carried out *after* the vacuum-calcinations.

2. Experimental Methods

2.1. Glove Box Operations for Precursor Synthesis. To minimize the effects of atmospheric moisture, the reactions were carried out inside a vacuum glove box (UNICO, UN-650F), based on a previously reported synthetic method [2], in which the water vapor concentration was less than 23.8×10^{-4} wt% (dew point: 223 K) under a N₂ atmosphere. Accordingly, precautions were taken with the commercially available reaction reagents. The bottles were opened inside the glove box, and the reagents were allowed to stand at room temperature (rt) for over 24 hours before use. The precursor for the nitride was prepared in the absence of an oxygen source inside a glove box, as previously reported, as follows. Under a N₂ atmosphere, TaCl₅ (3 mmol, Aldrich, 99.99%) and KCl (30 mmol, Wako Pure Chemical Industries,

special grade) as flux were placed in a 100 mL three-necked flask equipped with a glass stirrer, then sealed with a pair of two-way stopcocks and a Teflon plug. The flask was then placed in a low-temperature constant temperature bath (EYELA, PSL-1800; 1-propanol cooling medium, set at 193 K) under a flow of Ar gas ($2,000 \text{ cm}^3 \text{ min}^{-1}$). High-purity NH_3 gas (Sumitomo Seika Chemicals, 99.9%) was flowed at $3,000 \text{ cm}^3 \text{ min}^{-1}$ over the contents of the flask until 50 cm^3 of liquid NH_3 was condensed. Next, H_2O (3 mmol) was injected into the flask with a microsyringe. After stirring the cooled mixture for 30 minutes, the flask was warmed to rt, which allowed the unreacted NH_3 to evaporate. The resulting product was dried for 1 hour under vacuum ($5 \times 10^3 \text{ Pa}$) using a vacuum line.

2.2. Vacuum Calcination. The crude mixture of the precursor (described above), containing both the byproduct NH_4Cl and flux KCl, was transferred under a N_2 atmosphere into a quartz reaction tube ($\phi 12 \times 300 \text{ mm}$) with one end sealed. After inserting quartz wool for the prevention of powder scattering, the reaction tube was sealed using a two-way stopcock with a Teflon plug. The reaction tube was placed in a small muffle furnace (KDF S-70, Denken Co., Ltd.), then heated from rt to 1073 K at rate of 20 K min^{-1} and held at 1073 K for 10 minutes under vacuum using an oil rotary vacuum pump (SATO SW-150). Immediately after the vacuum/heat treatment, the quartz reaction tube was removed from the electric furnace, and the product was separated from the NH_4Cl and KCl by washing, filtering, and drying.

2.3. Postreaction Treatment: Recalcination in Air. For the postreaction recalcination in air, a portion of the calcined sample was poured into a porcelain crucible at rt, then heated to 973 K at rate of 10 K min^{-1} using an electric muffle furnace (KDF S-70, Denken Co., Ltd.). After maintaining the mixture at the elevated temperature, the sample was removed and characterized.

2.4. Characterization. XRD was measured using a Rigaku RINT2500 diffractometer. For reference, XRD patterns of Ta_3N_5 and TaON and single crystal data of Ta_3N_5 [6] and TaON [7] were calculated using CrystalMaker and CrystalDiffract software [8].

The color ($L^*a^*b^*$ color index) of the synthesized powder samples was measured using a JASCO UV-Vis spectrophotometer (V-650) attached to an ISV-22 integrating sphere. The samples were positioned in a PSH-001 powder sample holder such that the rubber plate section was completely covered.

Diffuse reflectance spectra (800–200 nm) were measured at 200 nm min^{-1} using Spectralon standards [9]. The $L^*a^*b^*$ values were calculated using the included color calculation program software (JASCO Corporation, viewing: 2 degrees, light source: D65, data interval: 5 nm, color matching function: JISZ8701-1999).

The binding energies determined by XPS (SHIMADZU ESCA-850) were corrected in reference to the $\text{C}1s$ peak for each sample. Ta_2O_5 (Wako Pure Chemical Industries, special grade) was used as a reference for the Ta 4f peak.

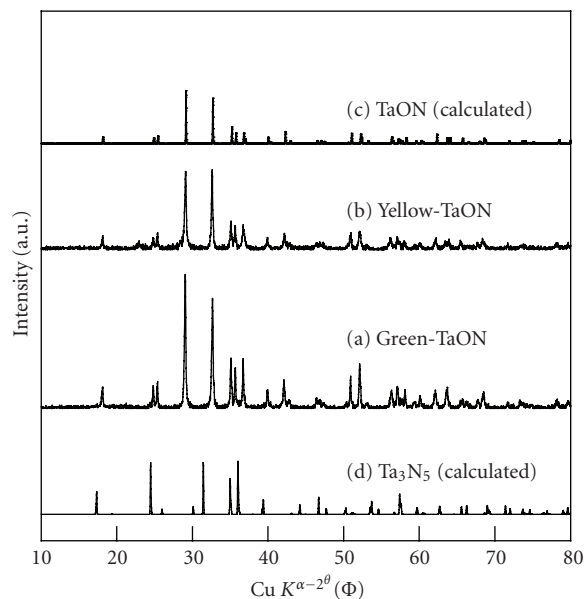


FIGURE 1: XRD patterns in (a) green TaON synthesized via liquid- NH_3 process, (b) yellow TaON synthesized via liquid- NH_3 process, (c) TaON (calculated), and (d) Ta_3N_5 (calculated).

3. Results and Discussion

The XRD pattern of the green TaON powder (synthesized via the liquid- NH_3 process) before the postreaction recalcination is shown in Figure 1(a). The positions of all diffraction peaks were in good agreement with those of the calculated TaON (Figure 1(c)) [7]. No minor peaks assignable to calculated Ta_3N_5 (Figure 1(d)) [6] were observed. The XRD pattern of the yellow TaON powder (synthesized via the liquid- NH_3 process) after the postreaction recalcination is shown in Figure 1(b). The XRD pattern of the yellow TaON powder gives the same XRD pattern as the green TaON. This result indicates that the crystal phase of the TaON powder samples synthesized via the liquid- NH_3 process is not influenced by the postreaction recalcination at 973 K in air. Diffuse reflectance spectra for the green and yellow TaON powders synthesized via the liquid- NH_3 process are shown in Figures 2(a) and 2(b), respectively. These diffuse reflectance spectra are similar to the reported green and yellow TaON spectra observed by Orhan et al. [5]. According to these researchers, the difference in the reflectance spectra between the yellow and green TaON is caused by the difference in composition of the TaON. The yellow TaON has slightly more oxygen atoms than nitrogen atoms ($\text{TaO}_{1.02}\text{N}_{0.99}$).

XPS spectra for the green and yellow TaON powders synthesized via the liquid- NH_3 process are shown in Figures 3(a) and 3(b), respectively. The green TaON produces a photoelectron signal at lower energy than Ta_2O_5 (Figure 3(c)) and yellow TaON, which can be explained in terms of the difference in bond polarities of Ta-O and Ta-N as mentioned above, that is, the Ta-N bond is more covalent than the Ta-O bond [10]. This suggests that the green TaON has more Ta-N bonds than Ta-O bonds, while the yellow TaON has more Ta-O bonds than Ta-N bonds.

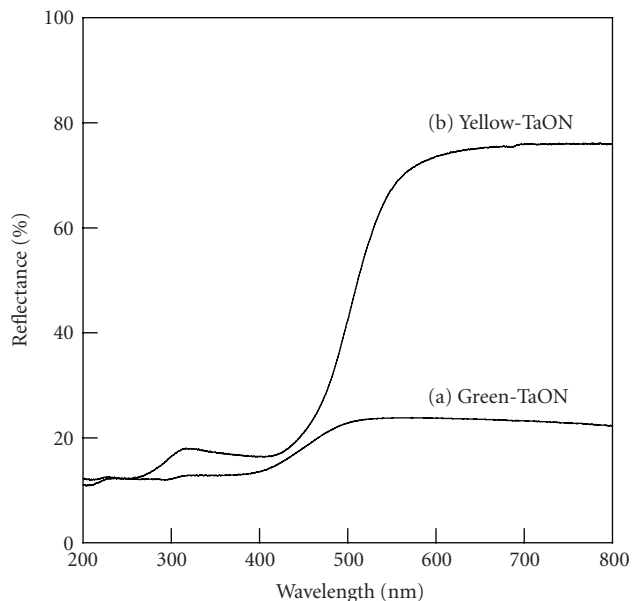


FIGURE 2: Diffuse reflectance spectra of TaON synthesized via liquid-NH₃ process: (a) green TaON and (b) yellow TaON.

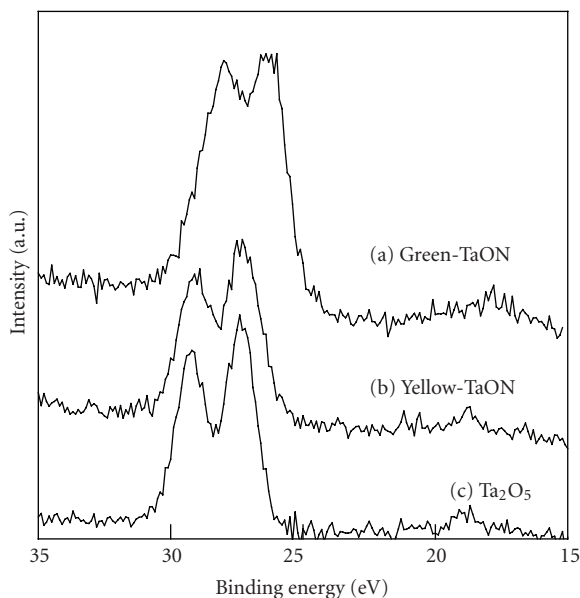
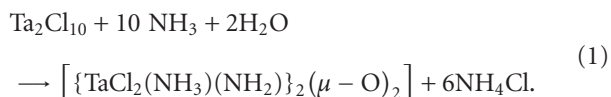


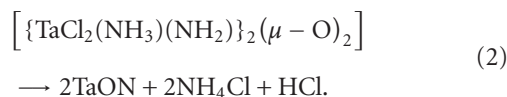
FIGURE 3: XPS spectra for Ta 4f in (a) green TaON synthesized via liquid-NH₃ process, (b) yellow TaON synthesized via liquid-NH₃ process, and (c) Ta₂O₅.

We have previously reported that the precursor of TaON synthesized via the liquid-NH₃ process consists of a dimer complex $[\{\text{TaCl}_2(\text{NH}_3)(\text{NH}_2)\}_2(\mu - \text{O})_2]$ [4], as described in the following equation:



During vacuum calcination (at 973 K) within the liquid-NH₃ process, this precursor can transform to TaON, as described

in the following equation:



This reaction mechanism implies that the TaON synthesized via the liquid-NH₃ process has more Ta-N bonds than Ta-O bonds resulting in the green color. Alternatively, during the postreaction recalcination in air, the Ta-N bonds in the green TaON transform to Ta-O bonds, resulting in a color change from green to yellow. The color change, however, does not result in broadening of the XRD peaks in the yellow TaON (Figure 1(b)), which indicates that recalcination in air does not deform the crystal lattice of the green TaON powder samples synthesized by the liquid-NH₃ process. From the diffuse reflectance spectrum (Figure 2(b)), $L^*a^*b^*$ data for yellow TaON powders synthesized using the liquid-NH₃ process after postreaction recalcination was calculated to be $L^* = 84.20$, $a^* = -2.71$, and $b^* = 44.07$. For the green TaON, values of $L^* = 43.82$, $a^* = -1.83$, and $b^* = 3.31$ were obtained from the diffuse reflectance spectrum (Figure 2(a)). Such a drastic color change in TaON is different from the case of the small binding energy shift of Ta 4f that has been reported by Maeda et al. [11].

4. Conclusion

Using a liquid-NH₃ process, we have prepared a TaON powder that can be employed as a nontoxic yellow pigment containing no heavy metals. The preparation involves the vacuum-calcination of a precursor material obtained via reaction between a metal halide, H₂O and liquid NH₃. Calcination of the precursor at 1073 K under vacuum was followed by recalcination at 973 K under air. The reaction conditions were adjusted to afford a powder with a color index of $L^* = 84.20$, $a^* = -2.71$, and $b^* = 44.07$.

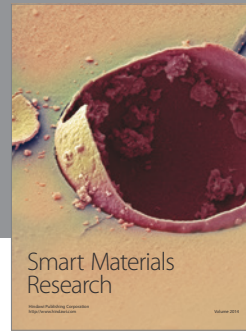
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