

表面形状制御による水分散性 ITO ナノ粒子の作製

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Water-Dispersible ITO Nanoparticles Prepared by Surface Shape Control[†]

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近年フレキシブルディスプレイなどの有機基板を用いたデバイスが発展している。有機基板上への透明導電膜の作製においては低温成膜プロセスの確立が重要である。本論文では、このようなプロセスに好適な新形状の酸化インジウムスズ (Indium Tin Oxide, ITO) ナノ粒子の作製について報告する。従来報告されている立方体型 ITO ナノ粒子の作製方法を応用し、核生成・粒子成長プロセスを制御することによって表面に突起を有する ITO ナノ粒子を得た。この ITO ナノ粒子は立方体型 ITO ナノ粒子よりも比表面積が大きく多くの水分子が吸着可能であることから、親水性が高く、非常に高い水分散性を有していることが分かった。この ITO ナノ粒子水分散液はミスト成膜法、スピンコート法、ブラシ塗布法などの低温成膜プロセスへの適用が期待される。

Devices that use an organic substrate, such as flexible displays, have recently become widespread. A low-temperature deposition process is considered an important factor for preparing a transparent conductive film on an organic film. In this paper, we report uniquely shaped indium tin oxide (ITO) nanoparticles (NPs) that exhibit a uniform crystal orientation and are appropriate for use in a low-temperature deposition process. These ITO NPs have numerous protrusions on their surface. These protrusions were formed through control of the nucleation and particle growth of NPs prepared using a method previously developed for preparing cubic ITO NPs. The ITO NPs with protrusions had a larger specific surface area than the cubic ITO NPs because of their shape and could adsorb a greater number of water molecules. Therefore, the ITO NPs with protrusions exhibited greater hydrophilicity and greater dispersibility in water. We expect aqueous dispersions of the ITO NPs with protrusions to find applications in low-temperature deposition processes such as the mist deposition, spin coating, and brush coating methods.

Key words ナノ粒子, ITO, ソルボサーマル法, 水分散性, 透明導電性酸化物
nanoparticle, ITO, solvothermal synthesis, water dispersibility, transparent conductive oxide

1 Introduction

Indium tin oxide (ITO) is a widely used *n*-type semiconductor [1] that performs important roles in various electronic devices, including displays [2], because of its low resistivity, appropriate chemical stability, and transparency toward visible light [3]. Most ITO thin films have been prepared by a dry process such as sputtering [4]. ITO thin films prepared by such processes exhibit low resistivity; however, the equipment required for dry processing is expensive and the process itself requires high temperatures. Wet processes such as coating methods using inks containing ITO nanoparticles (NPs) also have problems, including

high resistivity of the resultant films because of remaining dispersant and organic solvent [5].

The affinity between the surface of NPs and their dispersion medium is known to be a key factor governing the stability of NP dispersions [6]. Therefore, in the present work, we controlled the surface shape of ITO NPs to increase their stability in an aqueous dispersion without a dispersant. Specifically, the formation of numerous protrusions on ITO NP surfaces increased their specific surface area and the amount of water molecules they adsorbed, resulting in highly hydrophilic ITO NPs.

The surface shape of NPs has been controlled using various methods. Controlling particle growth *via* adsorption

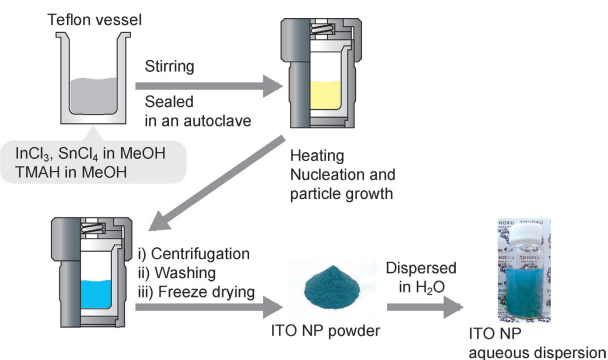
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additives [7] has been a focal point. In previous studies, amines and ions were found to be effective for controlling the shape of α - Fe_2O_3 NPs [8], [9]. Also, Kanie *et al.* developed a solvothermal one-pot method to prepare cubic ITO NPs, whose morphology reflects their crystal system, with a uniform crystal orientation [10], [11].

Inspired by these previous reports, we attempted to control the surface shape of ITO NPs by varying their synthesis conditions. We speculated that changing the nucleation and particle growth process by varying the concentration of the metal chloride used as a metal source could promote the heterogeneous nucleation of generated cubic ITO NPs, resulting in NPs with protrusions and a uniform crystal orientation. We also investigated the formation process and water dispersibility of the ITO NPs.

2 Experimental Procedure

The basic condition used to prepare the ITO NPs are described herein. First, a 1.8 M tetramethylammonium hydroxide (TMAH) methanol solution (7.5 mL) was added to a Teflon-made vessel. Then, a methanol solution of 0.36 M indium (III) chloride (InCl_3) and 0.04 M tin (IV) chloride (SnCl_4) (7.5 mL) was added, and the resultant mixture was stirred for 10 min at room temperature. The resultant solution was sealed in an autoclave and heated at 190°C for 24 h. The products were centrifuged and washed twice with ethanol and twice with water. The product (ITO NP powder) was then freeze-dried. In addition, an ITO NP aqueous dispersion was prepared by adding 40 mL of water to the ITO NP powder and dispersing the mixture by ultrasonication. (Scheme 1)



Scheme 1 Preparation of ITO NP powder and an ITO NP aqueous dispersion.

3 Results and Discussion

Effect of Heating Temperature

Fig. 1 shows XRD patterns of products prepared under the basic conditions at various temperatures from 100°C to

200°C. When the reaction temperature was 100°C (Fig. 1a), 130°C (Fig. 1b), and 150°C (Fig. 1c), no diffraction peaks assignable to In_2O_3 were observed. However, when the reaction temperature was 190°C (Fig. 1d) and 200°C (Fig. 1e), all of the observed peaks were assignable to In_2O_3 . Thus, the XRD results indicate that a reaction temperature greater than 190°C was necessary to obtain a crystalline In_2O_3 phase.

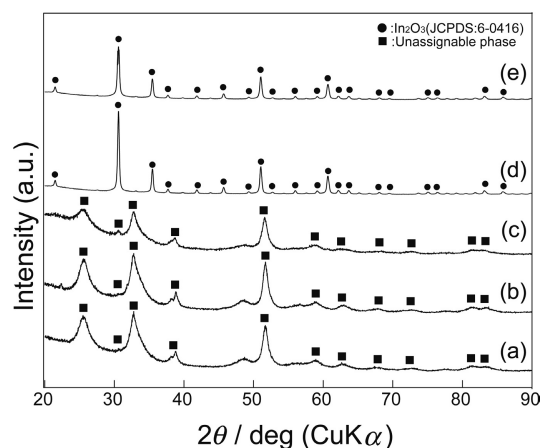


Fig. 1 XRD patterns of products obtained at various reaction temperatures: (a) 100°C, (b) 130°C, (c) 150°C, (d) 190°C, and (e) 200°C.

Effect of Metal Chloride Concentration

The concentration of the metal source was varied to investigate its effect on the surface shape of the ITO NPs. Under all of the investigated conditions, the Sn/In molar ratio for the sources was maintained at 11.1 mol%. Fig. 2a shows XRD patterns of the products obtained when the metal source concentration under the basic conditions was $[\text{InCl}_3] = 0.18$ M (i) and $[\text{InCl}_3] = 0.36$ M (ii). All of the peaks in both diffraction patterns were assignable to In_2O_3 . Also, the Sn/In molar ratio, as determined from inductively coupled plasma (ICP) analysis results, was 10.3 mol% and 11.6 mol% for the products corresponding to $[\text{InCl}_3] = 0.18$ M and $[\text{InCl}_3] = 0.36$ M, respectively. These results show that ITO was obtained under both conditions. In both cases, the Sn/In ratio in the product matched that of the metal sources.

Fig. 2b and Fig. 2c show transmission electron microscopy (TEM) images of products prepared at $[\text{InCl}_3] = 0.18$ M and $[\text{InCl}_3] = 0.36$ M, respectively. Cubic-shaped ITO NPs were observed at $[\text{InCl}_3] = 0.18$ M, and ITO NPs with protrusions were observed at $[\text{InCl}_3] = 0.36$ M. The TEM images indicated that the sizes of the cubic NPs and the NPs with protrusions were 39 ± 12 nm and 38 ± 10 nm, respectively. These sizes are consistent with the crystallite size, 34 nm and 33 nm of the cubic NPs and the NPs with protrusions, respectively, calculated from the XRD results using

Scherrer's formula.

Fig. 2d shows a high-resolution TEM (HR-TEM) image and an electron diffraction (ED) pattern of one of the NPs shown in Fig. 2c. The NP shown in Fig. 2d appears to have a uniform crystal orientation, and a spot pattern assignable to the (200)

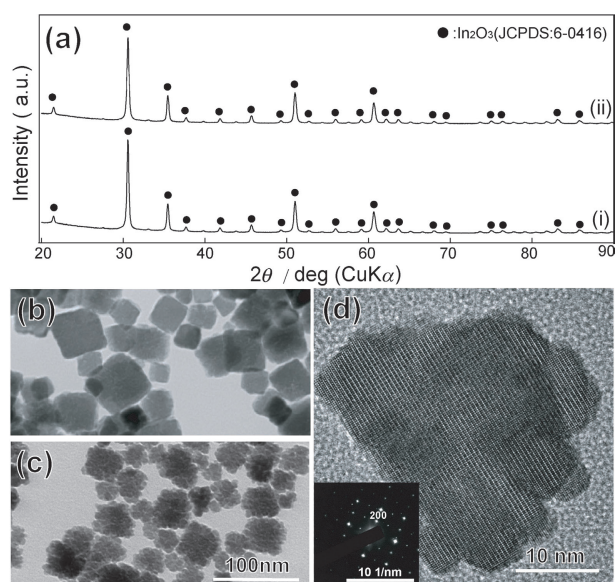


Fig. 2 (a) XRD patterns for products prepared under $[\text{In}^{3+}] =$ (i) 0.18 M and (ii) 0.36 M. TEM images of products prepared under $[\text{In}^{3+}] =$ (b) 0.18 M and (c) 0.36 M. (d) HR-TEM image of an ITO NP prepared under $[\text{In}^{3+}] =$ 0.36 M. The inset shows the ED pattern for the corresponding ITO NP.

crystal planes of In_2O_3 is observed. These results show that ITO NPs with protrusions that exhibit a uniform crystal orientation were obtained via control of the metal source concentration.

Effect of Heating Time on the Shape of ITO NPs

To investigate the formation process for the ITO NPs with protrusions, we varied the heating time. Fig. 3 shows TEM images of the products obtained as the heating time was varied from (a) 3 h to (b) 6 h, (c) 9 h, (d) 12 h, (e) 48 h, and (f) 168 h. For a heating time 3 h, NPs were not observed; an indeterminate form were obtained (Fig. 3a). In the XRD patterns, peaks assignable to In_2O_3 were not observed (results not shown). For a heating time 6 h, a few cubic particles were observed (Fig. 3b) and some of the XRD peaks were assignable to In_2O_3 . When the heating time was 12 h or longer, all peaks in the XRD patterns were assignable to In_2O_3 . In the TEM image for a heating time of 12 h (Fig. 3c), not only NPs with protrusions but also particles with an indeterminate form were observed. When the heating time was 18 h and 48 h (Fig. 3d and 3e, respectively), only NPs with protrusions

were observed. When the heating time was extended to 168 h (Fig. 3f), the protrusions on the NP

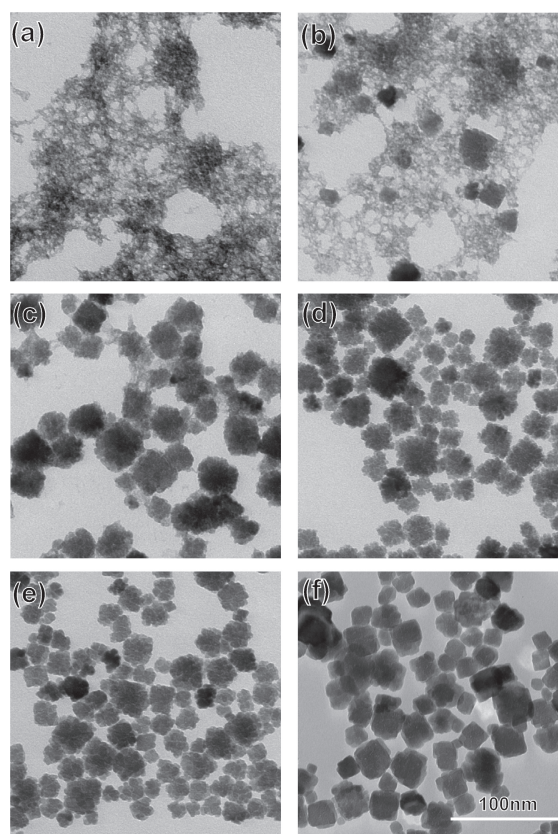


Fig. 3 TEM images of ITO NP products obtained at reaction times of (a) 3 h, (b) 6 h, (c) 9 h, (d) 12 h, (e) 48 h, and (f) 168 h.

surfaces disappeared. The Sn/In molar ratio for the products in Fig. 3a–3f are shown in Table 1. The Sn/In ratio decreased as the heating time was increased beyond 48 h.

Table 1 Sn/In molar ratio for ITO NPs prepared at various aging times

Aging time / h	Sn/In / mol%
3	12.7
6	12.7
9	12.0
12	12.1
48	9.3
168	8.4

Effect of Cl^- Concentration on Shape of ITO NPs

In a previous study [8], [9], the concentration of Cl^- was found to affect the shape of NPs. Therefore, the effect of Cl^- on the shape of the ITO NPs prepared in the present work was investigated. Tetramethylammonium chloride (TMACl) was added to the starting mixture used to prepare cubic ITO NPs (Fig. 2b). Fig. 4 shows TEM images of the obtained

products. In the TEM image corresponding to $[TMACl] = 0.18$ M (Fig. 4a), cubic NPs and NPs with slight protrusions on their surface were observed. When the concentration of TMACl was further increased in the range 0.27–0.54 M, the number of protrusions increased with increasing TMACl concentration (Fig. 4b–4d).

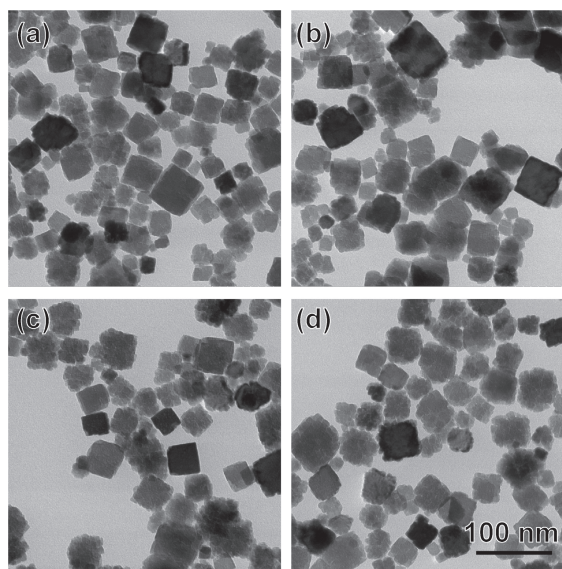
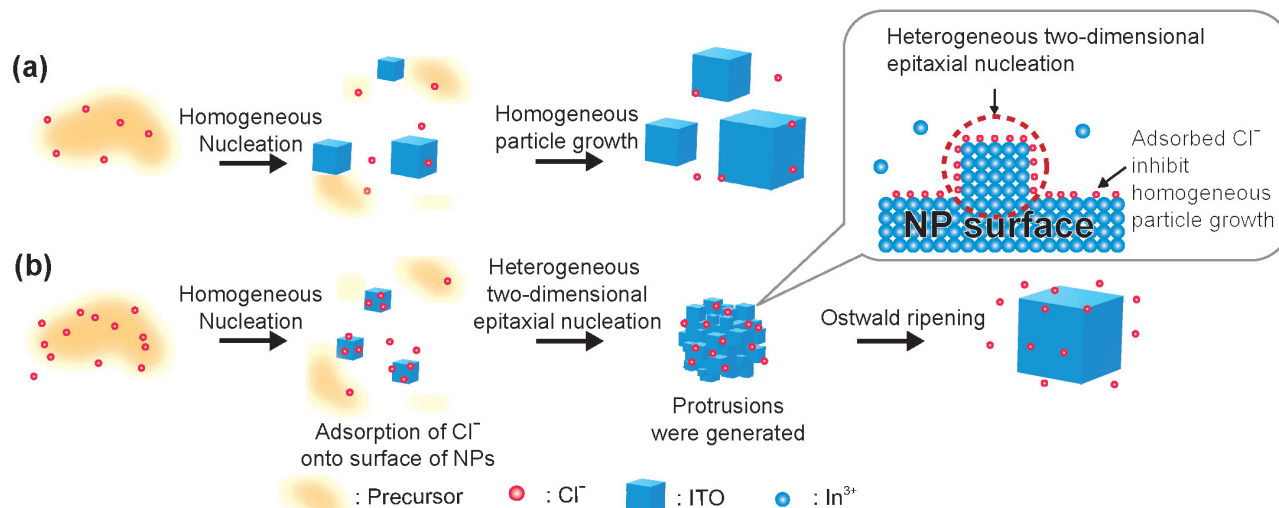


Fig. 4 TEM images of ITO NPs obtained when TMACl was added to the reaction mixture at a concentration of (a) 0.18 M, (b) 0.27 M, (c) 0.36 M, and (d) 0.54 M.

The results were used to evaluate the process by which protrusions form on ITO NPs (Scheme 2). Cubic ITO NPs were generated through homogeneous nucleation followed by particle growth. By contrast, ITO NPs with protrusions were generated through the growth of homogeneous particles, the adsorption of Cl^- , which inhibited particle growth, onto the cubic ITO NP surfaces, followed by heterogeneous and epitaxial particle growth. As a result, ITO NPs with protrusions and a uniform crystal orientation were obtained.



Scheme 2 Generation of (a) cubic ITO NPs and (b) ITO NPs with protrusions.

The protrusions on the NP surfaces disappeared and the Sn/In molar ratio decreased with increasing heating time, indicating that Ostwald ripening occurred.

Dispersibility in Water

The water dispersibility of the ITO NPs with protrusions and that of the cubic ITO NPs were compared. Fig. 5a shows two ITO NP dispersions in the as-dispersed state. Both samples were homogeneously dispersed in water. Fig. 5b shows the two dispersions 2 weeks after they were prepared. The cubic ITO NPs were sedimented on the bottom of the vessel. By contrast, the ITO NPs with protrusions remained homogeneously dispersed in water, similar to the as-prepared dispersions shown in Fig. 5a. These results indicate that the ITO NPs with protrusions exhibited greater

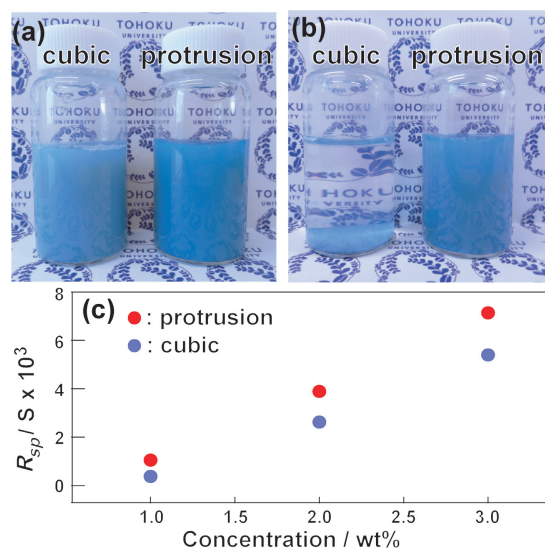


Fig. 5 Appearance of ITO NP dispersions (a) as dispersed and (b) after 2 weeks. (c) Relation between the concentration of the ITO NP dispersions and the R_{sp} normalized specific surface area S of the ITO.

water dispersibility than the cubic ITO NPs.

Further analysis was conducted by measurement of the ITO NP relaxation times using ^1H NMR (Fig. 5c). The hydrophilicity parameter R_{sp} calculated from the results indicates the amount of water molecules adsorbed on the NP surfaces [12]. The relationship between the concentration of the ITO NP dispersions and the R_{sp} normalized specific surface area (S) of the ITO NPs contained in dispersions (R_{sp} / S) is shown in Fig. 5c. At each concentration, the ITO NPs with protrusions exhibited a larger R_{sp} / S value than the cubic ITO NPs. These results indicate that the ITO NPs with protrusions have more water molecules adsorbed on their surface than the cubic ITO NPs. Therefore, the cubic ITO NPs exhibited a more hydrophilic surface. The S of the ITO NPs with protrusions and that of the cubic ITO NPs, as determined by Brunauer–Emmett–Teller (BET) analysis of N_2 adsorption data, were $37.0 \text{ m}^2/\text{g}$ and $26.3 \text{ m}^2/\text{g}$, respectively. The increase in specific surface area likely increased the hydrophilicity of the NPs.

4 Conclusion

ITO NPs with abundant protrusions on their surface and which could be dispersed in water for an extended period without a dispersant were successfully prepared *via* a solvothermal method. The ITO NPs with protrusions could be generated by heterogeneous particle growth induced by Cl^- adsorbed on cubic ITO NPs generated in the initial stage of the reaction. Therefore, the crystal orientation of ITO NPs with protrusions was uniform. Furthermore, the ITO NPs with protrusions were highly hydrophilic because of their shape and could form stable dispersions in water. The preparation of high-performance transparent conductive films using aqueous inks containing ITO NPs with protrusions without a high-temperature treatment may be feasible. We also expect our ITO NPs with protrusions will find applications in electrodes for flexible substrates.

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