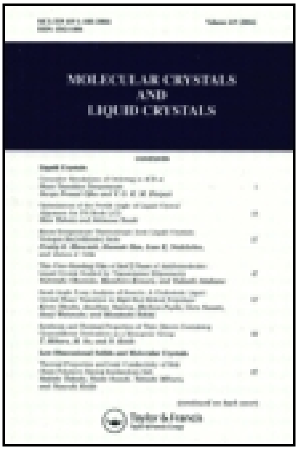

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Preparation of Water Dispersed Indium Tin Oxide Sol Solution

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Preparation of Water Dispersed Indium Tin Oxide Sol Solution

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Indium tin oxide (ITO) nanoparticles with In/Sn = 9:1 (at.%) were synthesized by chemical coprecipitation method in an aqueous solution. The coprecipitate prepared at room temperature showed the crystal structure of indium oxide in X-ray diffraction when it was annealed at the temperature above 300°C under air atmosphere. Reduction process was accomplished to improve the electrical property of ITO powder. Green ITO powder with particle sizes in the range of 20–30 nm was well dispersed by an addition of polyvinylpyrrolidone in an aqueous solution. The dispersibility of ITO sol solution was studied at different conditions by using ζ-potential analyzer. Transmission electron microsopy (TEM) and energy dispersive X-ray spectrometer (EDS) were used to characterize morphology and composition of ITO nanoparticles.

Keywords: dispersibility; indium tin oxide sol solution; polyvinylpyrrolidone

INTRODUCTION

In recent years, considerable effort has been devoted to nano-sized materials in studies of their fundamental mechanism, such as the size effect and the quantum effect, and in applications of these materials. Indium tin oxide, one of transparent conducting oxides, has attracted a great deal of attention due to its remarkable properties

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and technological application. Indium tin oxide (ITO) film has high visible transmittance, high infrared reflectance, good electrical conductivity, excellent substrate adherence and hardness [1–3]. Those properties have made ITO films applied as transparent electrodes for use in LCD (liquid crystal display), PDP (plasma display panel), coating material for use in CRT, transparent conducting thin films, low-emissive windows and solar cells [4]. While several synthesis methods such as sputtering, spray pyrolysis and dip coating methods have been employed for making thin films of TCOs, researches on nanoparticle and its dispersibility in an aqueous solution are still quite sparse [4–6]. It is important to have sol solution with good dispersion because the quality of dispersion affects technical application. In previous researches on ITO nanoparticles, metal alkoxides were used as raw materials for preparing ITO nanoparticles, but it was very difficult to obtain indium and tin alkoxide because of preparation problems, unavailability, or expensive cost. Therefore, we prepared ITO nanoparticles using inorganic metal salts as raw materials. Metal salts are cheaper than metal alkoxides and are very easy to handle [6]. In this work, ITO nanoparticles were synthesized by coprecipitation method to prepare water based ITO sol solution but the particles were not well dispersed in an aqueous solution as other nano-sized particles. The dispersibility of ITO particles in an aqueous solution was improved by using polypyrrolidone as a dispersing agent and was investigated by measuring zeta potential.

EXPERIMENTALS

Materials

Indium nitrate pentahydrate ($In(NO_3)_3 \cdot 5H_2O$, Aldrich 99.9%) and tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Aldrich 98%) as inorganic reactants, and ammonium chloride (Aldrich 99.99%) and ammonium hydroxide (Aldrich 99.99+%) as precipitation agents were used to prepare ITO nanoparticles. Distilled water as dispersing solvent and polyvinylpyrrolidone (Aldrich, M_w 10,000) as dispersing agent were used to prepare ITO sol solution. In all experiments the resistivity of distilled water was 18 MΩ.

Preparation of ITO Nanoparticles by Coprecipitation Method

$In(NO_3)_3 \cdot 5H_2O$ (2.6 g, 6.7 mmol) and $SnCl_4 \cdot 5H_2O$ (0.26 g, 0.74 mmol) were dissolved in 40°C distilled water (10 mL) and the solution was stirred for 30 min. NH_4Cl (0.068 g, 1.3 mmol) was added to the mixture solution and the solution was heated at 40°C for 10 min. A 10 wt.% NH_4OH solution was added to the mixture to be until pH 7 at room temperature and 10 wt.% NH_4OH solution was used as a precipitation agent. After white slurry was formed, it was washed with 50°C distilled water 4–5 times to remove impurities. The washed precipitates were filtered and dried at 70°C for 24 hrs. The dried powder was sintered at 700°C for 3 hrs under air atmosphere. This primary sintering was carried out to crystallize particles and remove impurities. Yellow ITO powder was obtained by this primary sintering. The secondary sintering under hydrogen atmosphere was accomplished at 250°C for 50 min to improve the electrical properties of powder by increasing oxygen vacancy and concentration of carrier. This reduction process affects the color of ITO powders. Finally dark green ITO powder was obtained.

Preparation of Water Based ITO Sol Solution

Water based ITO sol solution was easily prepared by adding ITO nanoparticles to an aqueous solution containing polyvinylpyrrolidone (PVP). The constant amount of ITO powder (0.4 g) was added to an aqueous solution (5.0 mL) that included different amounts of PVP (1.25%, 20%, 60%, 100% and 200%). These weight percents of PVP in bracket mean weight percent of PVP to the constant amount of ITO powder. Ultrasonication was applied to these ITO sol solutions for 10 mins. After the ultrasonication, ball mill (Shimadzu Vibrating Mill) was applied to the ITO sol solution for 10 min. Zirconium bead with 0.8 mm diameter was used as ball mill. The water based ITO sol solutions with different pH (pH 3–pH 10) were prepared and ammonium solution and hydrochloric acid solution were used to control pH.

Analysis

The crystal structure, morphology, shape and composition of ITO nanoparticles were characterized by X-ray powder diffraction (XRD, Philips, X'Pert-MPD system), transmission electron microscopies (TEM, Hitachi model S-2400 and Jeol model JEM-2010) and energy dispersive X-ray spectrometer (EDS, Hitachi model, H-7500), respectively. Dispersibility of ITO nanoparticles in an aqueous sol solution was characterized by Zeta potential analyzer measurement (Brookhaven Instrument, USA).

RESULTS AND DISCUSSION

Preparation of ITO Nanoparticles by Coprecipitation Method

Figure 1 shows the XRD spectrum of ITO nanoparticles prepared by coprecipitation method. In Figure 1, the crystalline peaks in the XRD spectrum of particles well matched with the diffraction data of cubic indium oxide from the JCPDS card. The number (222), (400), (440) and (622) in the XRD spectrum correspond to the (hkl) values of the genuine indium oxide crystal.

The chemical composition of particles was analyzed with EDS. Figure 2 shows the EDS spectrum for ITO nanoparticles prepared by coprecipitation method. It was observed that In Lα_1(3.2 KeV) peak and Sn Lα_1(3.4 KeV) peak appeared. It indicates the presence of indium and tin elements in the products. It was found that the atomic molar percent of indium to tin was determined as 9:1. Generally, when the In:Sn molar ratio is determined as 9:1, ITO nanoparticles have the highest conductivity [4]. According to XRD and EDS data, it was known that ITO nanoparticles with In:Sn = 9:1 (at. molar%) were well synthesized by coprecipitation method. However ITO particles were

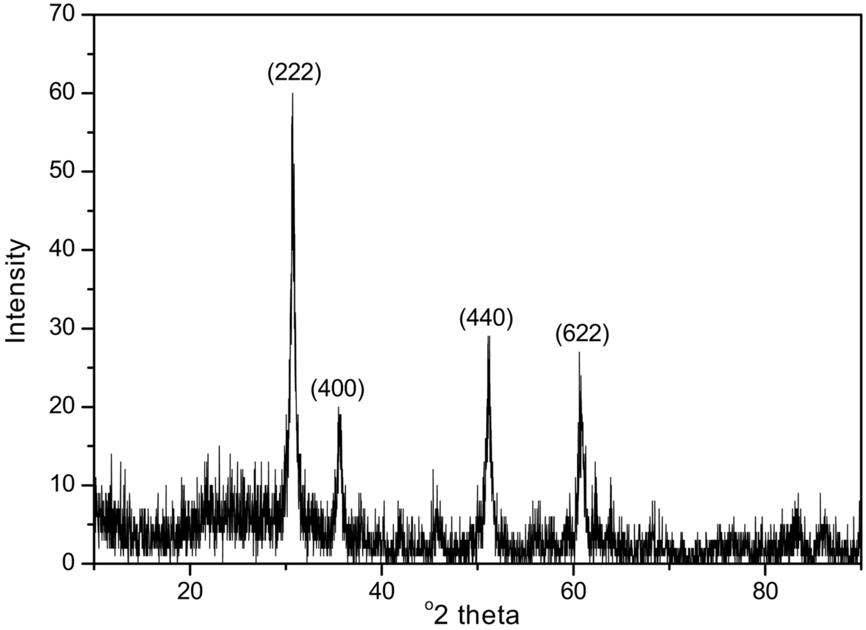

FIGURE 1 XRD spectrum of ITO nanoparticles: annealed at 700°C under air atmosphere and then annealed at 250°C under hydrogen atmosphere.

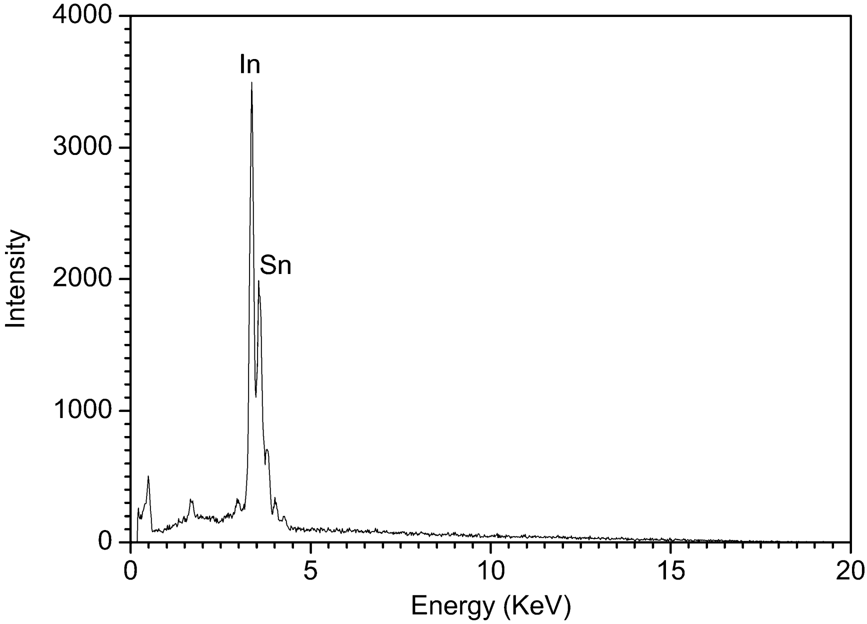

FIGURE 2 EDS spectrum of ITO nanoparticles: annealed at 700°C under air atmosphere and then annealed at 250°C under hydrogen atmosphere.

not well dispersed as other nano-sized particles. It is imperative to have well dispersed ITO nanoparticles in an aqueous sol solution for application.

Dispersibility of ITO Nanoparticles in an Aqueous Sol Solution

The dispersibility of ITO nanoparticles at different weight percent of PVP and at different pH was investigated by measuring the zeta potential of the ITO sol solution. Figure 3 shows the zeta potential vs. concentration (wt.%) of PVP in the ITO sol solution. The absolute value of zeta potential was the highest when concentration of PVP was 20 wt.%. In general, the dispersion of ceramic powder in solution can be improved when the absolute value of the zeta potential is increased after an addition of dispersing agent [7]. According to this, it was known that ITO sol solution which included 20 wt.% of PVP had the best dispersibility. Figure 4 shows the zeta potential vs. pH of sol solutions. These ITO sol solutions had different value of pH but contained the same amount of PVP (20 wt.%). ITO sol solution had the best dispersibility when the value of pH was 3–5. The dispersibility of ITO

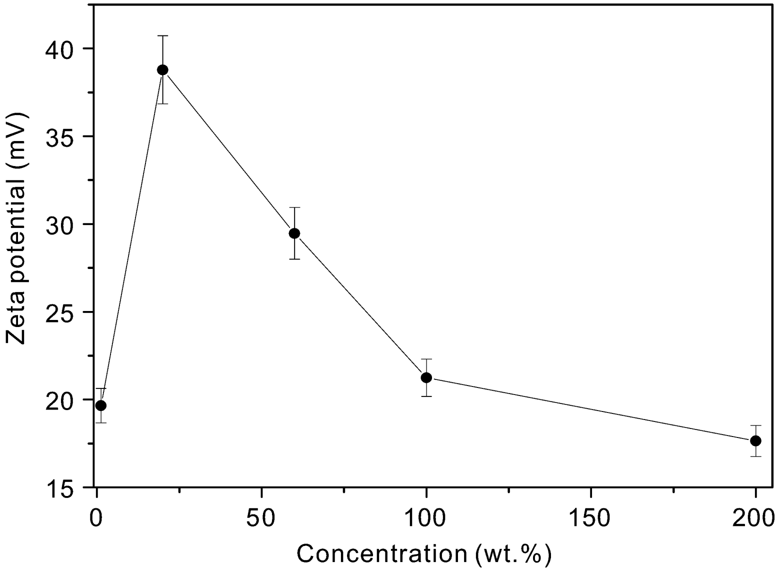

FIGURE 3 Zeta potential versus concentration (wt.%) of PVP in the water based ITO sol solution.

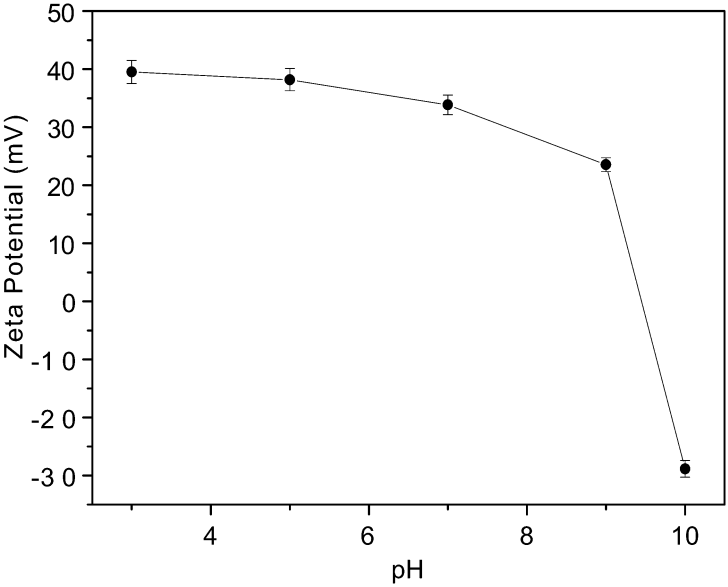

FIGURE 4 Zeta potential versus pH of the water based ITO sol solution.

sol solution was also confirmed by following TEM images in Figure 5. Figure 5(A) is the TEM images of ITO sol solution with 20 wt.% PVP and Figure 6 is the TEM images of ITO sol solution without PVP as dispersing agent. In the both images the diameter of particles was determined as about 20–30 nm. However dispersibility of ITO nanoparticles were better in Figure 5(A) than that in Figure 6 and the aggregation of ITO nanoparticles was seen in Figure 6. According to this, it was known that dispersion of nanoparticles related to the role of the dispersing agent. A few reports introduce the preparation of ITO powder by emulsion technique or coprecipitation method [1,8]. However ITO nanoparticles prepared by both methods were not well dispersed despite use of surfactant and the size of those was much larger as about 45–75 nm [1,8]. In this work, PVP was used to improve dispersibility of ITO nanoparticles in an aqueous solution. The image in upper side of Figure 5(A) was enlarged image of ITO particle. It was observed that PVP was continuously coated on the particle surface in the images of Figure 5(A). TEM image was measured after staining of the sample with uranyl acetate (2%) to observe organic polymer such as PVP. According to TEM image, it was known that the addition of dispersing agent such as PVP gave good dispersibility of particles by coating on the particle surface. It was confirmed that the particle was indium oxide by Figure 5(B). Figure 5(B) shows high-resolution TEM image of ITO nanoparticles. In Figure 5(B), indium oxide lattice spacing of 2.92 Å was consistent with the lattice spacing of (222) plane in the XRD spectrum of indium oxide crystal. The existence of lattice planes on the HR-TEM image means the crystalline of indium oxide. From both Figure 5(A) and (B) it was known that the particle was indium tin oxide particle and PVP was coated on the surface of ITO particles. The thickness of PVP coated on the surface was estimated as about 6–7 nm. In general, polymer coating on the surface of particles makes steric repulsive force by positive surface charge increase and results in an improved dispersibility of particles [9,10]. PVP coating on the surface of ITO particles improved the dispersibility of ITO particles in an aqueous solution.

CONCLUSION

We described preparation of an aqueous sol solution of polymer – inorganic nanoparticles. The water based ITO sol solution was easily prepared by adding ITO nanoparticles to an aqueous solution containing polyvinylpyrrolidone as dispersing agent. This ITO sol solution had good dispersibility with the absolute value of zeta potential of 38 mV when weight percent of PVP to ITO powder is 20 wt.%. In this

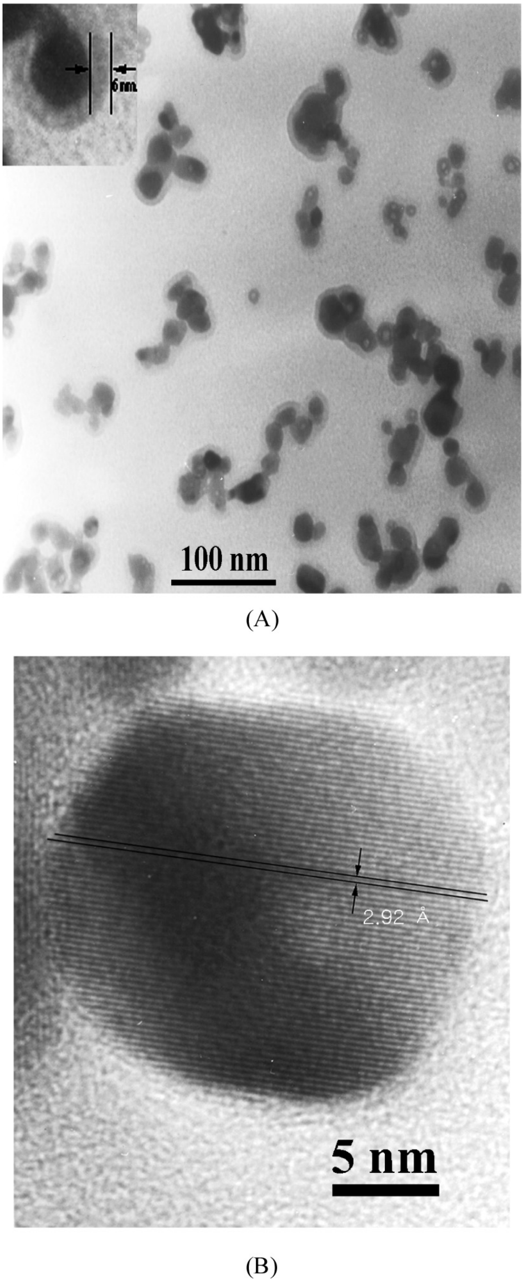

FIGURE 5 TEM image of ITO nanoparticles in an aqueous solution with PVP as a dispersing agent (A) and HR-TEM image of ITO nanoparticles (B).

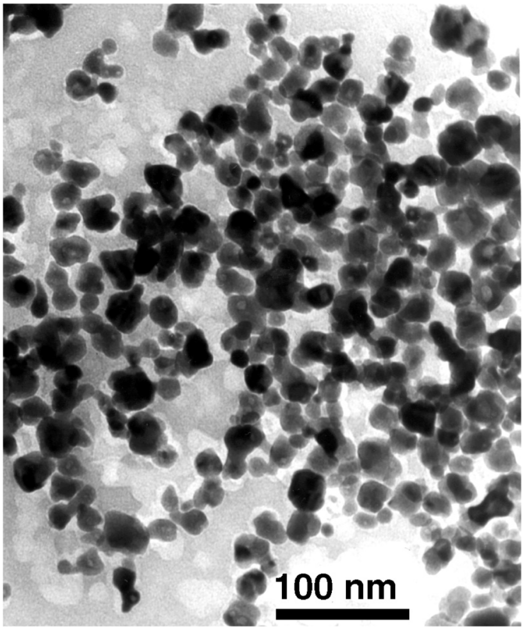

FIGURE 6 TEM image of ITO nanoparticles in an aqueous solution without PVP.

work, it was known that an increase of steric repulsive force by coating polyvinylpyrrolidone on the surface of ITO particles improved the dispersibility of ITO particles in an aqueous sol solution.

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