JOURNAL OF MATERIALS SCIENCE **40** (2005) 4133–4135 LETTERS

Polyelectrolyte adsorption and rheological behavior of ITO nanoparticles in ethanol with ammonium polyacrylate as a surfactant

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In recent years, transparent conducting oxides (TCOs) deposited on glass are important materials for optoelectronic devices. Among all the TCOs investigated, indium tin oxide (ITO) thin films have been used widely [1], owing mainly to their extraordinary capability in providing a high work function and a nearly metallic electrical conductivity. Additionally, ITO thin films also provide excellent optical properties such as a high optical transparency in visible wavelength region and a high reflectance in infrared wavelengths.

Most of the ITO thin films are prepared by dry processes, e.g., sputtering and chemical vapor deposition [1]. Goebbert *et al.* [2] recently propose an interesting processing scheme; to which, ITO thin films were prepared via a solution route using crystalline ITO nanoparticles as a starting material. The nanoparticles were dispersed in water or alcohol with a surface modifying agent to facilitate the nanoparticle dispersion. Rheological behavior of the ITO suspensions is found critically important to the success of the film-forming process, but has been rarely reported in the literature [3]. Shear viscosity of many powdered suspensions generally decreases with a minor concentration of appropriate surfactant [4–9]. Siladitya *et al.* [10] yet proposed that shear viscosity and particle size strongly depend on the critical micelle concentration (CMC) in given carrier liquid. They found that the mean particle size decreases remarkably from 25 μm to 20 nm below the CMC, but above CMC, the mean particle size increases 20 times when the surfactant concentration is increased 50 times. In this study, we report similar findings, to which the suspension viscosity of ITO nnaoparticles in alcohol is increased with NH_4PA surfactant concentration beyond a critical level. An adsorption-isotherm experiment was then carried out to help assess possible adsorption mechanisms contributing to the viscosity increase. A hypothetical model is then proposed.

Commercially available ITO nanoparticles (PKD-ITO-n P01, Titanex Corporation, Taiwan) were used as the starting material. The ITO nanoparticles present a chemical purity >99%, an average particle size of ∼30 nm, and are spherical in shape with an apparent agglomeration (Fig. 1). Ammonium polyacrylate (NH_4PA, Toagoshi Co., Ltd., Japan) was used as a surfactant. The NH_4PA is considered as a "weak" polyelectrolyte due to its weak carboxylic acid group, which dissociates easily in water but not in neutral solvent such as ethanol [7]. The NH_4PA was yet added in proportions with respect to the particulate weight. Reagent-grade ethanol was first mixed with NH_4PA before the ITO nanoparticles were added and ball-mixed altogether for 24 hr.

The flow behavior of the ITO suspensions was carried out using a strain-controlled concentric viscometer (VT550, Gebruder HAAKE Gmbh, Germany) at a constant temperature (25 °C). The working shear rate used in this experiment varied from 1 to 1000 s^{-1}.

Some ITO suspensions were centrifuged at 10,000 rpm for 10 min. The clear supernatants were decanted, leaving behind the sediment cakes. The sediments were then remixed with fresh ethanol in an ultrasonic bath before being subjected to another centrifugal process. This washing process was repeated four times before the final sediments were oven-dried at 55 °C for 48 hr to remove ethanol. The dried cakes were then subjected to thermal gravimetric analysis (TGA, Pyris 6 TGA, Perkin Elmer Instruments, USA) at a heating rate of 10 °C min^{-1} in air to determine the adsorbed polyelectrolyte amount.

Shear viscosities of 10 vol% ITO suspensions (i.e., $\phi = 0.10$) consisting of different NH_4PA concentrations are shown in Fig. 2. The viscosity decreased with the increasing NH_4PA concentration. The 5 wt% of NH_4PA concentration appears to be a transition point for the nanoparticle suspensions. Below the "critical" NH_4PA concentration, the slurries showed a monotonous shear-thinning flow behavior over the entire shear-rate range examined, while above the critical concentration the suspensions exhibited a shear-thinning character followed then by a shear-thickening behavior. This shear-thickening flow is generally manifested by a transition of suspension structure from a homogeneous state to become a rather heterogeneous state of particulate arrangement in the liquid upon the shear-rate increase. This suggests that the slurries were relatively well dispersed when the surfactant concentration exceeds 5 wt%, so that the interparticle forces were outweighed by the external stress field which allows the particles to arrange themselves into a more uniform configuration at low shear rates. As shear rate was further increased, the particles were forced to leave their equilibrium position so that a voluminous flow resulted, leading to the increased viscosity.

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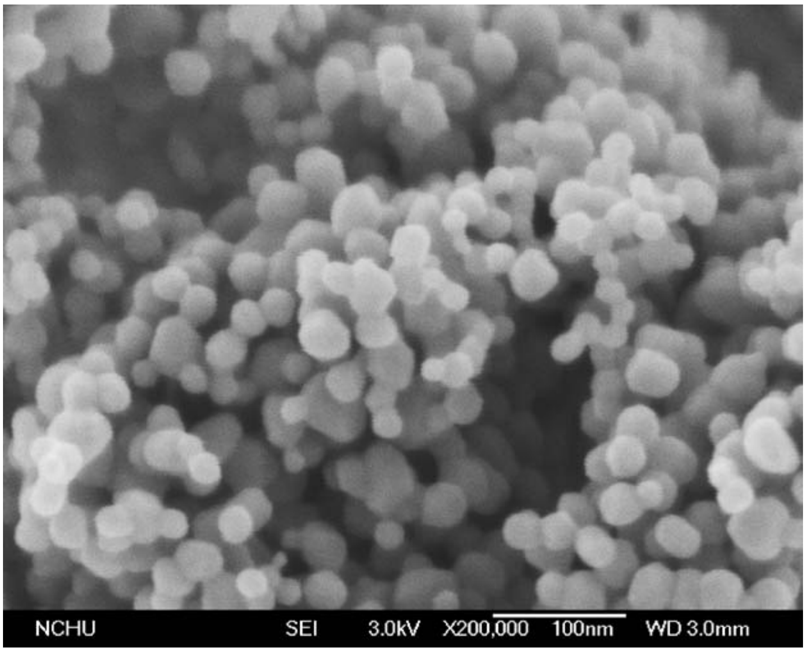

Figure 1 Morphology of the as-received ITO nanoparticles.

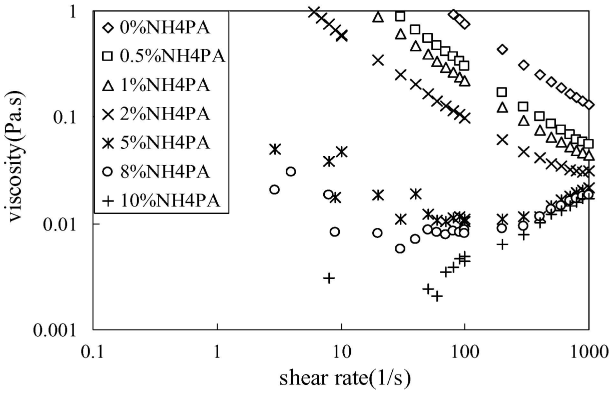

Figure 2 Flow behavior of suspensions with different weight percents of NH_4PA. The solids concentration (ϕ) was held at $\phi = 0.1$.

In Fig. 3, the viscosity appeared to increase adversely with NH_4PA concentration for the $\phi = 0.15$ suspensions. For a particle suspension with increased surfactant concentration, viscosity generally decreases because the surfactant molecules tend to disperse the particles by surmounting the van der Waals force between particles so that particle flocculation in liquid was prohibited by steric and/or electrostatic forces. It may be interesting to note that, in this experiment, the NH_4PA surfactant dissolve poorly in ethanol liquids when the solid ITO nanoparticles were not present. The suspensions at a relatively low solids fraction ($\phi = 0.1$) yet showed a dispersed flow character upon the surfactant addition, which is drastically different from that of the 15 vol% ITO suspensions. In an attempt to explain this phenomenon, thermal gravimetric analysis was carried out to examine the adsorption isotherm of NH_4PA on the ITO nanoparticles.

Fig. 4 is the adsorption isotherm which shows the specific adsorption of NH_4PA molecules with respect to its concentration in ethanol solvent. There seems to be no saturation point, indicating that the polyelectrolyte surfactant appeared to continuously adsorb on the nanoparticles preferentially. This finding might be explained by a hypothesis that a multiple coating of the NH_4PA occurs upon the polyelectrolyte addition, hence contributing to the "monotonous" increase in the specific adsorption. We expect that the adsorption process is likely

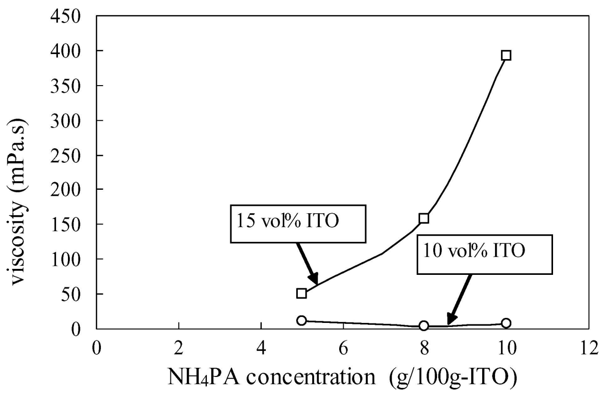

Figure 3 Viscosity of ITO suspensions ($\phi = 0.1$ and 0.15) at shear rate of 100 s^{-1}. The NH_4PA concentration varies from 5 to 10 wt%.

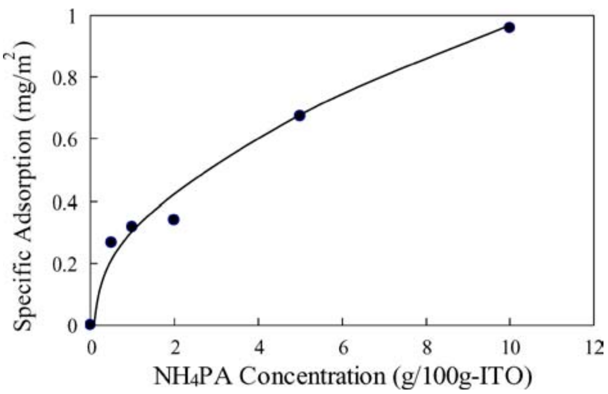

Figure 4 Adsorption isotherm of NH_4PA on ITO nanoparticles in ethanol.

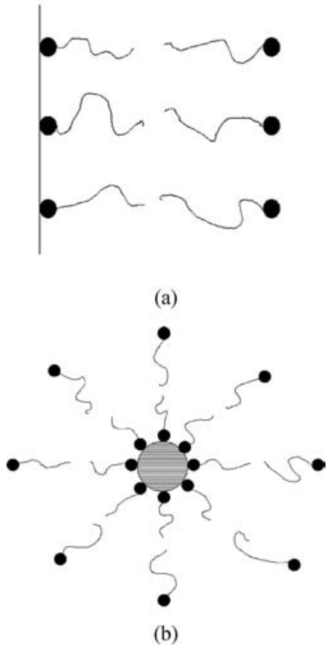

Figure 5 Schematic model of predicted adsorbed configuration: (a) on surface. (b) as a whole.

to continue with more polymer layers being formed as each potential adsorption site on surface of the nanoparticles is filled. This ultimately increases the "effective" solid fraction in liquid, creating more viscous solution as observed.

Albano and Garrido [4] have used the NH_4PA as a surfactant to enhance the dispersion of micron-sized α-Si_3N_4 in water. From their adsorption analysis, a clear saturation around 0.6 wt% was found. This reveals that the polyelectrolyte adsorption and hence the resultant flow behavior are highly dependent on the solvent nature of the liquid carriers. Siladitya *et al.* [10] pointed out that a critical micelle concentration (CMC) of surfactant plays an important role in determining the dispersion quality. But, here we can neglect the weakly attached dispersant on the particle surface and possibly micellar colloid consisting of surfactants. The reasons lie upon our experimental observations as follows. First, the preparation of TGA samples for the adsorption-isotherm determination was conducted by repeated washing/centrifuging separation four times; therefore, only the nanoparticles with strongly adsorbed surfactants were left for the analysis and possibly micelle that might exist in the liquid were separated from the sediment cakes. Second, the CMC of ionic-surfactant is usually about 1 mmol, which is substantially lower than the concentration used in this experiment. In contrast with hemi-micelle configuration proposed by Liu *et al.* [11], the surfactants used have a saturation point for adsorption. Their model is hence not suitable for our modal suspension system. A hypothetical model shown in Fig. 5 is proposed to explain the "abnormal" adsorption of the NH_4PA polyelectrolyte on ITO particles in ethanol. The figure shows a two-layer configuration, and the number of layers might increase with the surfactant concentration. The polyelectrolyte molecules are expected to assume a train or loop configuration upon the preferential adsorption on the nanoparticles. The tail ends then tangle with the tails of other polyelectrolyte molecules, forming multiple coating on the particle surface. The polymer adsorption literally increases the physical size of the nanoparticles, as well as the effective solid concentration, resulting in a reduced interparticle separation.

Acknowledgment

This work is financially supported by the National Science Council (Taiwan, ROC) under contract NSC 92-2216-E-005-020.

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Received 14 December
and accepted 17 December 2004