Water-soluble polyethylenimine as an efficient dispersant for gallium zinc oxide nanopowder in organic-based suspensions

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ABSTRACT

Appropriate dispersants for the dispersion of gallium zinc oxide (GZO) nanopowder in the commonly used organic medium-dimethylacetamide (DMAC) are proposed by this study. The dispersion efficiencies and stabilization mechanisms of three dispersants—the organic-based dispersant tris(2-butoxyethyl) phosphate (OP_3) and two water-based dispersant polyethylenimines (PEIs) with different molecular weights—are compared. Surprisingly, the water-based PEI polyelectrolytes exhibit greater efficiency than the organic-based OP_3 for the dispersion of GZO nanopowder in the organic-based suspensions. This is because that the stabilization mechanism of GZO in the very polar DMAC is primarily related to steric repulsion rather than to electrostatic repulsion according to the theoretical and experimental analyses.

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1. Introduction

Zinc oxide (ZnO)-based powders have attracted considerable interest as transparent conducting oxide (TCO) materials in recent years because of their competitive advantages of high natural abundance, low cost, nontoxicity, low resistance, high transparency, and good chemical and thermal stabilities [1–10]. The traditional TCO is indium tin oxide (ITO), which is a very expensive material that is unstable in hydrogen plasma [2,9,10]; thus, numerous doped ZnO compounds, including In_2O_3-doped ZnO, Al_2O_3-doped ZnO (AZO), and Ga_2O_3-doped ZnO (gallium zinc oxide, GZO), have been proposed as replacements for ITO [1–10]. Among the doped ZnO powders, AZO is the most common; however, GZO is the most chemically stable because Ga is less reactive than Al toward environmental oxygen and because the ZnO lattice is less distorted by the substitution of Zn^{2+} with Ga^{3+} than by the substitution of Zn^{2+} with Al^{3+} [11–13].

TCO materials are generally and extensively manufactured as films for use in optical and electrical devices [2,14,15] such as solar cells, flat panels, liquid crystal displays, transistors, light-emitting diodes, and window coatings. Several approaches have been used for preparing TCO films [1,2,16–20], including various physical vapor deposition, sputtering, chemical vapor deposition, epitaxy, ion plating, spray pyrolysis, and solution growth processes. Among these techniques, the method of sol-gel spin coating, which is a solution growth process, has

attracted the interest of numerous research groups [21–24]. Interest in sol-gel spin coating stems from its distinct advantages of cost effectiveness, simplicity, and suitability for mass production because of its high deposition rate. Nevertheless, disadvantages and drawbacks of this method include the challenging conditions needed to control the homogeneity of the sol-gel reaction and the difficulty associated with simultaneously optimizing a chemical reaction and achieving a uniform coating. A new approach using a well-dispersed suspension has been proposed as a simple alternative method of depositing TCO films; this method also features the advantages of low cost and suitability for mass production [10].

Although the preparation of uniform films through the use of well-dispersed powder suspensions is advantageous, most commercially available doped ZnO powders such as AZO and GZO are very fine, with particle sizes of <50 nm. Such fine particles undergo severe aggregation in suspension and are not easily deagglomerated and dispersed. The demand for doped ZnO powders has increased for a wide range of products, including paints and coatings that provide heat-insulating or antistatic functions [25] and various optical and electrical devices; consequently, techniques for preparing stable suspensions of these powders are reasonably expected to increase in importance and to attract increased attention in the near future. Thus far, few reports regarding the dispersion of these powders or the development of appropriate dispersants have been published.

In this work, appropriate dispersants for the dispersion of doped ZnO in organic-based suspensions are proposed and explored. GZO powder and dimethylacetamide (DMAC), a common solvent in

industrial processes, were adopted as a model for this investigation. The purpose is to identify an effective dispersant for GZO powder and to achieve a stable dispersion of GZO in an organic suspension with a high solid content. Moreover, the dominant stabilization mechanism for the dispersion of GZO in suspensions is discussed and clarified.

2. Materials and methods

High-purity GZO nanopowder (54W-GZ10, ITRI, Taiwan) with a hexagonal wurtzite crystal structure was used. The content of gallium oxide (Ga_2O_3) in GZO powder was 1.3 wt%, as determined by inductively coupled plasma atomic emission spectroscopy (ICAP-9000, Jarrell-Ash, USA). The primary particle size of GZO was approximately 20 nm, as characterized by transmission electron microscopy (JEM-2100, JEOL, USA). The surface area of GZO was 47 m^2/g. The dispersants used included tris(2-butoxyethyl) phosphate (OP_3, 95%; TCI, Tokyo, Japan) and two types of polymeric polyethylenimines (PEIs) with molecular weights of 1800 g/mol (L-PEI, 99%; Alfa Aesar, USA) and 10,000 g/mol (H-PEI, 99%; Alfa Aesar, USA). The polar organic solvent dimethylacetamide (DMAC, 99%; J.T. Baker, USA) was used as the dispersion medium.

The electrokinetics of GZO nanopowder was analyzed using the electroacoustic method (ZetaProbe, Colloidal Dynamics Inc., North Attleborough, MA, USA). For the zeta-potential measurements, GZO suspensions in DMAC with a solid content of 0.5 wt% were prepared with the addition of 5 wt% of different dispersants. The suspensions were mixed and deagglomerated by a ball mill (MUBM236, Yeong-Shin, Taiwan) at 300 rpm with the addition of 50% mill charge of 5-mm yttria-stabilized zirconia media for 24 h at room temperature. In the adsorption experiments, the suspensions were prepared with a solid content of 20 wt% (based on the weight of solvent) in the presence of various concentrations of dispersants (based on the weight of GZO powder). The powder suspensions were deagglomerated by ball milling for 24 h and centrifuged at 5500 rpm to separate GZO nanopowder from the supernatant. The separated nanopowder was dried in an oven at 80 °C, and the amount of dispersant adsorbed onto the nanopowder was determined by thermogravimetric analysis (Q50, TA Instruments Ltd., Crawley, UK). The rheology of GZO suspensions with a solid content of 20 wt% and with OP_3, L-PEI, and H-PEI added at various concentrations was analyzed by using a concentric cylinder rheometer (AR1000, TA Instruments Ltd., UK). In addition, the thixotropic behavior was analyzed based on the suspensions with solid contents of 10–40 wt% in the presence of 10 wt% of L-PEI or H-PEI. Cone-plate geometry fixtures with a diameter of 20 mm and cone angle of 1° were chosen for the steady-shear rotation tests. All the rheological curves were fitted using the software (V 5.2.26, Rheology Advantage™, UK) attached to the rheometer. The reliability of the equation was evaluated by the coefficient of determination (R^2). The R^2 obtained from the fittings of all samples are within 0.95–1.0.

3. Results and discussion

For the dispersion of nanopowders, the investigated dispersant candidates are generally small molecules or polymers with low molecular weights because of their reasonable size compared to the small nanoparticles. Three dispersants—OP_3 and two types of PEI—were chosen, and their dispersion efficiencies for GZO nanopowder in the polar organic solvent—DMAC were explored. The chemical structures of the investigated dispersants are shown in Fig. 1. OP_3 is a small molecular surfactant with a phosphate group, and L-PEI and H-PEI are both polyethylenimines (PEIs) with molecular weights of 1800 g/mol and 10,000 g/mol, respectively. The solubility parameters (δ) of the dispersants and solvent are 23.5 $MPa^{1/2}$ for PEI [26], 20.5 $MPa^{1/2}$ for OP_3 [27], and 22.7 $MPa^{1/2}$ for DMAC [28]. The δ values of OP_3 and PEI are very close to that of DMAC, indicating that DMAC is good solvent for dissolving OP_3 and PEI. On the other hand, the logarithm of acid dissociation constant (pKa) of the suspension components was also
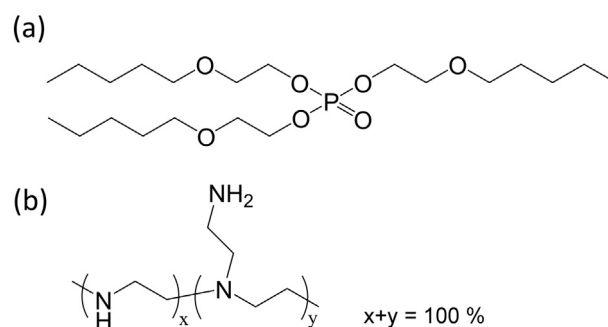

Fig. 1. Chemical structures of (a) tris(2-butoxyethyl) phosphate (OP_3) and (b) polyethylenimine (PEI).

compared. Although the pKa of GZO has not been reported in the literature, the content of Ga in GZO is extremely low and Ga exhibits a higher cationic potential than does Zn, as a consequence of its smaller ionic radius and higher charge valence [29], we assumed that GZO should be more acidic than ZnO and the pKa of GZO is slightly lower than that of ZnO. The pKa of ZnO has been reported to be 9.3 [30]. From the electrokinetic measurements, it is found that GZO exhibits a negative zeta potential at −1.5 mV in DMAC. This indicates that DMAC should be like an alkaline medium for the dispersion of GZO, although the exact pKa is not clear due to its very different reports in the literature, ranging from −0.5 to 30 [31–33]. Since DMAC is a high polar solvent, the dispersed GZO is possible to carry charge via the ionization mechanism based on the electron affinity differences between itself and the dispersion medium, parallel to the case occurred in an aqueous suspension [34]. When H-PEI or L-PEI was added, the GZO powder changed to exhibit a positive charge in DMAC. The pKa of PEI has been reported to be ~11 [35,36]. The possibility for the varied zeta potential of GZO is that both PEIs are positively charged and have adsorbed on GZO. The low positive value of zeta (ζ) potentials due to the addition of PEI may be caused by two reasons. One is that PEI does not have a good dissociation in DMAC; the other is the adsorbed amount of PEI on GZO is low. And the combined reason is also probable. The dispersant OP_3 has a reported pKa ranged from −3 to −9 [37], lower than any possible pKa value reported for DMAC. Therefore, OP_3 would preferentially dissociate to carry a negative charge in DMAC. As shown in Table 1, the resulting zeta potential of GZO with the addition of OP_3 is −4.0 mV, just evidencing the specific adsorption of OP_3 onto GZO.

The adsorption isotherms of OP_3, L-PEI, and H-PEI on GZO nanopowder are compared in Fig. 2(a). Their significant adsorptions correspond well to the behaviors predicted on the basis of the zeta-potential measurements. The adsorption amounts of the three dispersants increased with increasing dispersant concentration and finally reached saturation, demonstrating typical chemisorption behavior [38]. The adsorption saturations for OP_3, L-PEI, and H-PEI were approximately 20, 74, and 112 mg/g GZO, respectively. We further analyzed the exact adsorption behavior of the dispersants using the Langmuir monolayer adsorption equation (Eq. (1)) [39]:

$$\frac{C_e}{A_s} = \frac{C_e}{C_m} + \frac{K}{C_m}, \tag{1}$$

Table 1
Zeta potentials (ζ) and adsorption layer thicknesses (t) of GZO nanopowders in DMAC upon the addition of various dispersants.

Dispersant	ζ (mV)	t (nm)
None	−1.5	–
OP_3	−4.0	3.1
L-PEI	9.3	3.1
H-PEI	15.0	5.1