Mass Production of Metal Oxide Nanoparticle Dispersion for solar control Application

Z. Shen*, W. Soh*, J. Zhang*, A. Wang*, W. Chen*, J. Yun*, D. Sher*, J. Chen**
*NanoMaterials Technology Pte Ltd, 28, Ayer Rajah Crescent #03-03, Singapore, email: zhigang.shen@nanomt.com
** Sin-China Nano Technology Center, State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing, P. R. China

ABSTRACT

Zinc oxide and antimony-doped tin oxide nanoparticle-dispersions were successfully produced by high gravity controlled precipitation method. The ZnO and ATO dispersion samples showed high transparency, high solid loading, small particle size and uniform particle size distribution. In addition, the obtained ZnO and ATO dispersions are further used for solar control coating application. The prepared coating containing ZnO and ATO nanoparticles for glass could realize blocking ultraviolet, high transparency for visible light, as well as strong absorption of infrared light. These interesting characters endow the metal oxide nanoparticle dispersion to be a promising candidate for the coating applications such as smart window, solar collector, optical devices, etc.

Keywords: metal oxide dispersion, nanoparticle, high gravity controlled precipitation, heat-ray shielding

1 INTRODUCTION

There has been a great demand to shield ultraviolet (UV) and infrared (IR) radiation (heat rays) by employing visible light transparent coating on the windows of automobiles, buildings,etc., in order to reduce the energy consumption for air conditioning and thereby decrease the emission of carbon dioxide, as well as eliminate damage to the coating of indoor furnitures and irritation to human skin [1]. Nano-particulate arrays of conductive compounds such as tin doped indium oxides (ITO), antimony doped tin oxides (ATO), and lanthanum hexaboride (LaB_6) have recently been reported as a new IR absorbing filter for solar radiation [2]. At the same time, Inorganic UV blockers, such as zinc oxide (ZnO), titanium dioxide (TiO_2), and cerium oxide (CeO_2) which are non-toxic and chemically stable under exposure to both high temperatures and UV, are more preferable to organic UV blockers in blocking UV radiation [3]. With these particle-dispersed filters, low cost solar control applications can be expected against high-cost multilayered thin film filters typically using sputtering technology. The traditional solid state reactions at high temperatures to synthesize metal oxide compounds often resulted to form agglomerated large and irregular shaped particles, therefore, the post-synthesis milling process is required to produce nanoparticles. In this paper, the nano-size particle dispersions of metal oxide compounds were directly synthesized by the unified approach, high gravity controlled precipition (HGCP) process with low cost. The obtained ZnO and ATO dispersion are further used for solar control coating application.

2 EXPERIMENTAL

In a typical experiment, metal salt solution was continuously mixed and reacted with precipitant solution in HGCP reactor to form homgeneous suspended solution, and then a certain amount of surfactant was introduced into the solution, where the concentration of surfactant in the solvent was adjusted to 20~30 wt% of formed metal oxide, and final contentration of metal salt was adjusted to 0.2-1 mol/L with molar ratio (metal salt to precipitatant) of 0.8~1.2 [4,5]. After that, the solutions were transferred into another closed reactor to age at 60-300 ^{o}C for 1-10hr. after the ageing process, the product were centrifuged, washed with water or other solvent for 4 times, and vacuum dried at 60 ^{o}C. The powder obtained could be dispersed in solvent to form high solid-loading dispersion.

The primary size and shape of the nanoparticles were observed by a transmission electron microscopy (TEM, JEOL, JEM-3010). The secondary particle size and distribution (PSD) in dispersions have been evaluated by a particle size analyzer (Horiba LB-550), which is based on the dynamic light scattering method and can measure undiluted high-contentration liquids. The phase compositions of the sample were measured with a X-ray diffractor (CuKα= 1.5406) (XRD-6000, Shimadzu, Japan). The optical response of the coatings of the using spectro-photometer (Hitach U-400), giving outputs of transmittance and reflectance profiles in the UV, Visible, and infrared range (200-3200 nm), and yielding visible light transmittance (VLT), where the coating solution was formed by mixing the ATO dispersion and ZnO dispersion with acrylic resin in water at a mass ratio of H_2O: acrylic resin: ATO: ZnO = 65:20:10:5, and painted on a quartz glass by bar coating or gravity flow method.

3 RESULTS AND DISCUSSION

The ZnO dispersions with different solid loading are illustrated in figure 1a. It can be seen that even the solid loading as high as 50 wt%, the ZnO dispersion is still transparent. It is found that the dispersion produced by HGCP process is still stable even after 1 year of storage.

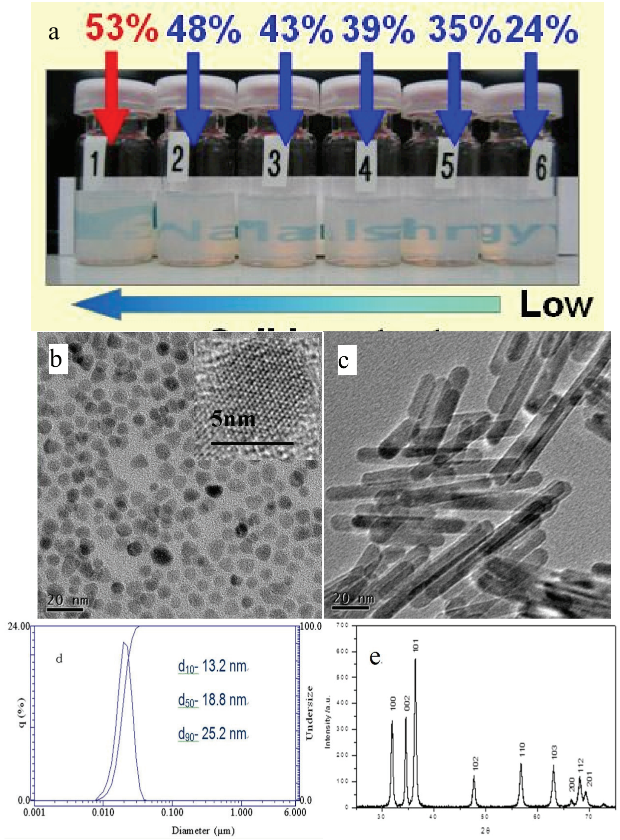

Figure 1. The analysis results for the ZnO nanparticles and the dispersion produced by HGCP process: (a) The dispersion photo of different solid loading, (b) TEM, (c) XRD, and (d) PSD.

Figure 1b is HRTEM image for exemplary ZnO nano-particles obtained by HGCP process followed by in-situ modifcation during ageing process. It can be seen from Figure 1b that the zinc oxide nanoparticles obtained are substantially monodispersed. The particle morphology was found to be near-spherical or prismy. The primary particle size is about 6 nm. The size range is from 5 to 8 nm. Discrete specks of darker shades (ZnO nanoparticles) can be clearly observed with little or no overlapping between the darker shades, indicating that there is little or no aggregation of the particles. Moreover, it is observed that the zinc oxide nanoparticles are approximately the same size, which is indicative of a narrow size distribution of nanoparticles present in the monodispersion.

The particle shape of ZnO is short rod and the particle size is about 5~8 nm in the short dimension and 30-100 nm in the long dimension, if the ZnO particles produced by HGCP process without in-situ modification step, which is shown in figure 1c.

The mean secondary particle size and particle size distribution of the ZnO nanoparticles was investigated using dynamic light scattering (DLS) particle size analyzer LB-500 characterization. Figure 1d depicts the results obtained from the DLS characterization. From Figure 1d, it can be observed that ZnO nanoparticles with an average secondary particle size of 18.8 nm and size range of between 10 nm and 27 nm were obtained. The steepness ratio (d_{90}/d_{10}) of the particles is 1.9. Narrow peak width in the DLS graph also suggests that the ZnO nanoparticles are close to being monodispersed and have a narrow particle size distribution.

Figure 1e shows the XRD pattern of the nanosized ZnO particles prepared by HGCP process. It can be seen from figure 1d that the crystal structure was almost exclusively related to a hexagonal wurtzite crystalline system (JCPDS 36-1451).

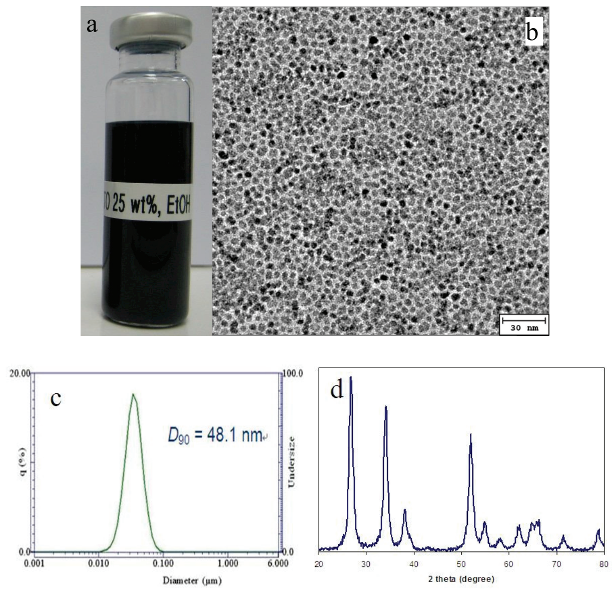

Figure 2. The analysis results for the ATO nanoparticles and the dispersion (a) the photo for 25 wt% ATO dispersion, (b)TEM, (c) PSD, and(d) XRD.

The ATO dispersion with 25 wt% solid content are illustrated in figure 2a. It can be seen that the ATO could be dispersed well in ethanol. Figure 2b is TEM image for exemplary ATO nanoparticles obtained by HGCP process followed by ageing at 290 ˚C in closed vessel. During the ageing process, suitable surfactant will added in to modify the ATO nanoparticles. It can be seen from Figure 2b that the ATO particles obtained are substantially monodispersed. The particle shape was found to be near-spherical. The primary particle size is about 7 nm. The size range is from 5-9 nm. Figure 2c depicts the results obtained from the DLS characterization. From Figure 2c, it can be observed that ATO nanoparticles with an average secondary particle size of 26.7 nm and size range of between 10 nm and 57 nm were obtained. Narrow peak width in the DLS graph also suggests that the ATO nanoparticles are close to being monodispersed and have a narrow particle size distribution. Figure 2d shows the XRD pattern of the nanosized ATO particles prepared by HGCP process. It can be seen from figure 2d that the diffraction peak positions agree well with the reflactions of cassiterite SnO_2 (JCPDS file number 21-1250), meanwhile no other peaks ascribed to antimony compounds are detected.

Similarly, the dispersion of ZnO and ATO in different solvents (H_2O, EtOH, BtAc, MEK, Toluene, Hexane) could be selectively prepared by HGCP process when the suitable surfactant was chosen during the modifcation step [4,5]. The process involved achieving instantaneous molecular mixing for metal salts and precipitant reactants, which favors to form homogenious nucleation, particles growth environment. At the same time, the HGCP process is easy to scale up. The process had been scaled-up and a pilot plant with a production scale of more than 100 tons metal oxide dispersion per year was built and commercial production plant is in planning stage.

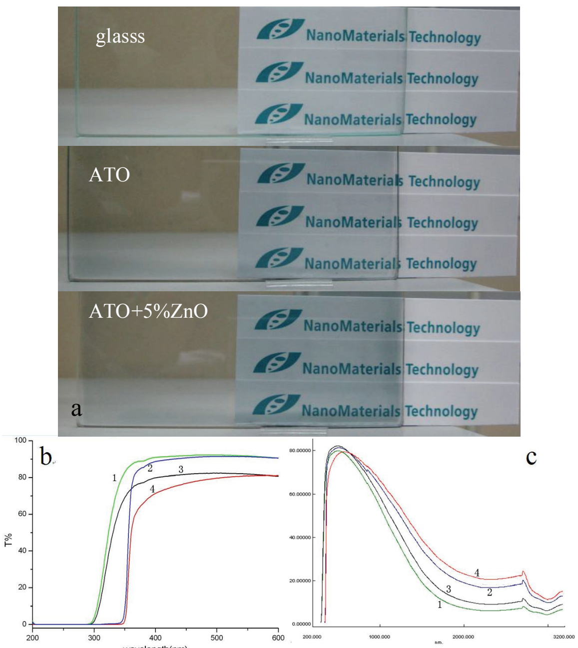

Figure 3. (a) ATO W/O ZnO coating on glass, (b)UV-Vis spectra and (c) UV-Vis-IR absorption spectrum, 1: ATO coated glass by draw down bar method, 2: ATO and ZnO coated glass by gravity flow method, 3: ATO coated glass by gravity flow method, 4: ATO and ZnO coated glass by draw down bar method

Additional studies have shown that other metal oxide nanoparticles and dispersions, such TiO_2, CeO_2 and iron oxide, can also be selectively synthesized by applying similar HGCP process followed by modification step. Thus, the present approach could be a general approach for the synthesis of other metal oxide nanoparticles and dispersions in commercial scale. It anticipated that these nano materials will find important applications in various fields. Further detailed studies on these new kinds of nano materials are in progress [4,5].

Figure 3 presents the application results of ZnO and ATO nanoparticles applied in coating on glass. The optical properties of the pure glass, the glass coated with ATO, and the glass coated with ATO and ZnO are shown in figure 3a-c, respectively. The thickness of the obtained coating was about 40 μm. It seems that no obvious difference of transprancy for ATO, ATO and ZnO coated glasses from pure glass (Figure 3a) and the glasses are all transparent. The tansmittance spectra of the pure glass, the resin within ATO nanoparticles coated glass, and the resin within ATO and ZnO nanoparticles coated glass are shown in figure 3b-c. It can be seen that the ATO coated glass shows high visible light transperency and IR shielding performance. Whatever the draw down bar coating method or gravity flow coating method, the ATO coated glass could cut off about 75% IR. It can also be seen from the figure 3b-c, a clear UV cut-off around 350 nm could be observed for the ZnO coated glass. Compared with the optical properties of the coating glass by draw down bar method, the UV light transmittance of the coating glass by the gravity flow method was lower, while the visible light transmittance was higher. It is found that highly transparent coating with ATO and ZnO loaded could cut off the UV radiation up to 97%, block 75% IR, and allow at least 85% of visible light to pass through during 10% ATO and 5 % ZnO in the matrix of resin. The method presented here can be easily adopted in industrial production to make UV and IR shielding transparent glasses, coating films or containers to protect from IR iradiation and UV damage for long lifetime.

4 CONCLUSION

In conclusion, we have developed a HGCP process to produce uniform ZnO and ATO nanoparticles and dispersions on a large scale. The various ZnO and ATO dispersions in different solvents have been investigated. This new strategy has been applied to prepare other metal oxide nanoparticles and dispersions. A wider range of application using this method is under investigation. The obtained ZnO and ATO dispersions are further used in solar control coating application. The prepared coating containing ZnO and ATO nanoparticles for glass could realize cut-off most UV, high transparency for visible light, as well as strong absorption of infrared light. It is expected HGCP method have potential to become a technology of the future to produce nanoparticle dispersions in mass scale. The nanoparticle dispersions may open new opportunities for further investigation of the novel optical, electric, and catalytic properties of these materials.

REFERENCES

[1] S. Schelm G. B. Smith, Appl. Phys. Lett. 82, 4346, 2003
[2] H. Takeda, H. Kuno, K. Adachi, J. Am. Ceram. Soc., 91, 2897-2902, 2008
[3] A. Becheri, M. Durr et.al. J. Nanopart. Res. 10:679–689, 2008
[4] Z. Shen, J. Zhang, et. al." Prcess for making nano-sized and microsized precipitate particless" US 7985388 B2.
[5] Z. Shen, M.Ng, et. al. "a process of making metal chalcogenide particles" WO 2009/067088 A2.