

Coating ZnO:Zn Nanoparticles with Alumina for Polymer Protection.

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ABSTRACT

Using a modified preparation large nanoparticles of ZnO and ZnO:Zn were coated (without destroying the luminescent properties of the latter), but the coating is a layer of AZO not Al₂O₃. Large nanoparticles of ZnO:Zn were coated with a layer of ZnO by using only (NH₄)HCO₃ in the absence of Al₂SO₄.

1. INTRODUCTION

The work reported herein arose from using ZnO nanoparticles to control polymer degradation. Many polymers are observed to degrade when exposed to ultraviolet light. Common polymers that are attacked include polypropylene (its tertiary carbon-hydrogen bonds are the primary focus of attack). It is believed that ultra-violet radiation induces charge transfer complexes between the polymer and oxygen leading to photolysis, producing CO and CO₂. This is called photooxidative degradation. UV radiation stabilisers such as benzophenones and hindered amine light stabilisers^{1,2} are used in plastics to reduce/prevent degradation by UV light.

Iron doped lithium aluminate nanoparticles can be used to protect polymers by downgrading the UV light into the near infra red.³⁻⁵ As an alternative approach we looked at uncoated ZnO as a UV blocking agent to protect polymers. During the early stages of this work two problems were encountered (also reported by others⁶) due to ZnO's intrinsic properties. The first is the compatibility of the ZnO nanoparticles with the polymer which can manifest with nanoparticle aggregation, but this we overcame with processing technology. The second is a more fundamental problem that arises from the band gap (3.37eV) of the ZnO, here the inherent photo-conductivity of the nanoparticles facilitates the formation of active species within or at the polymer surface that degrade the material.^{7,8} For the latter problem we decided to protect the polymers by coating the ZnO nanoparticles with a protective layer to isolate their surfaces from the polymer.

In the light of a literature report⁹ on the preparation of ZnO nanoparticles coated with a homogeneous Al₂O₃ layer, we decided to follow the method and our results are reported herein.

2. EXPERIMENTAL

ZnO nanoparticles were synthesised by Johnson Matthey (JM) using flame spray pyrolysis. The method used to coat with Al₂O₃ was based on that previously reported⁹ except that we used the method to coat ZnO nanoparticles that were preformed rather than to prepare the ZnO particles at the same time from a zinc sulphate solution. Hence we affectively join the previous experiment at the point where they re-disperse their precipitate of basic zinc carbonate (BCZ).⁹ Two samples of ZnO nanoparticles were supplied by JM, the first is referred to as sample 1 and the second as sample 4. X-ray powder diffraction (XRPD) of the samples was performed using a Bruker D8 Advance X-ray powder diffractometer fitted with a copper source and LynxEye™ silicon strip detector. The morphology and the particle size of the samples were determined using a Zeiss Supra 35 VP field emission scanning electron microscope and using a JEOL 2000FX transmission electron microscope. Photoluminescence (PL) measurements were carried out using a Bentham Instruments dual excitation and emission monochromator system.

3. RESULTS AND DISCUSSION

The XRPD data are shown in Figure 1.

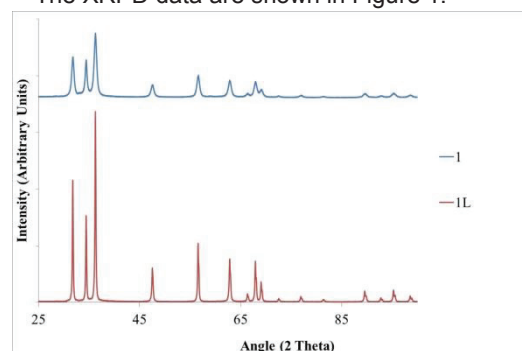


Fig. 1. XRPD patterns of ZnO nanoparticles from JM sample 1. The sample 1L is the larger nanoparticles prepared by firing sample 1.

Fitting the Figure 1 data gave the cell dimensions and ZnO crystallite sizes listed in Table 1.19.3 nm for the as received nanoparticles from JM (sample 1). The nanoparticles were annealed for 1hour in air

at 600°C where much larger nanoparticles (sample 1L) grew to a crystallite size 78.54 nm. An SEM and TEMs of the JM ZnO nanoparticles and an SEM of the annealed particles are presented in figure 2.

Table 1. Phases present and crystallite sizes within ZnO nanoparticles and their products.

Sample and sample number ()	Phase present in XRPD data and lattice parameters	Crystal Size (nm)
JM ZnO (1)	ZnO, $a = 3.2525(1)\text{\AA}$, $c = 5.2141(2)\text{\AA}$	19.32(5)
JM ZnO fired in air at 600°C for 1h (1L)	ZnO, $a = 3.2519(1)\text{\AA}$, $c = 5.2104(2)\text{\AA}$	78.54(25)
ZnO:Zn (2)	ZnO:Zn, $a = 3.2514(1)\text{\AA}$, $c = 5.2080(1)\text{\AA}$	175.83(95)
ZnO:Zn (3A)	ZnO:Zn, $a = 3.2515(1)\text{\AA}$, $c = 5.2084(1)\text{\AA}$ 54.42(41)% of this material is present	212.9(31)
	$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, $a = 13.7200(52)\text{\AA}$, $b = 6.3628(25)\text{\AA}$, $c = 5.3742(21)\text{\AA}$, $\beta = 97.730(38)^\circ$ 45.59(41)% of this material is present	8.79(14)
ZnO:Zn coated with ZnO (3B)	ZnO, $a = 3.2515(1)\text{\AA}$, $c = 5.2085(1)\text{\AA}$	126.65(25)
JM ZnO (4)	ZnO, $a = 3.2523(1)\text{\AA}$, $c = 5.2111(1)\text{\AA}$	21.03(6)
ZnO:Zn (5)	ZnO:Zn, $a = 3.2521(2)\text{\AA}$, $c = 5.2096(4)\text{\AA}$	172.55(93)
ZnO:Zn/Al ₂ O ₃ (6A)	ZnO:Zn, $a = 3.2519(2)\text{\AA}$, $c = 5.2095(5)\text{\AA}$	167.28(91)
ZnO:Zn/Al ₂ O ₃ (6B)	ZnO, $a = 3.2529(1)\text{\AA}$, $c = 5.2111(1)\text{\AA}$	126.65(25)

It was decided to produce larger nanoparticles of ZnO:Zn rather than ZnO as the former is a well-known phosphor and in addition to having UV screening potential it can down convert UV light into visible light. To form such nanoparticles a second sample of ZnO nanoparticles (sample 4) was fired at 800°C for 45 minutes in a reducing atmosphere. This gave larger ZnO:Zn nanoparticles (sample 5) with an average crystallite size of 172.6nm (see Figure 3 XRPD data). Nanocrystals from the ZnO:Zn sample (sample 5) were coated⁹ and the precipitated material (sample 6A) was calcined at 600°C for 1 hour to form sample 6B. The XRPD data for samples 5, 6A and 6B are much sharper (more like bulk ZnO:Zn) than those of sample 4 as

expected for much larger nanoparticles.

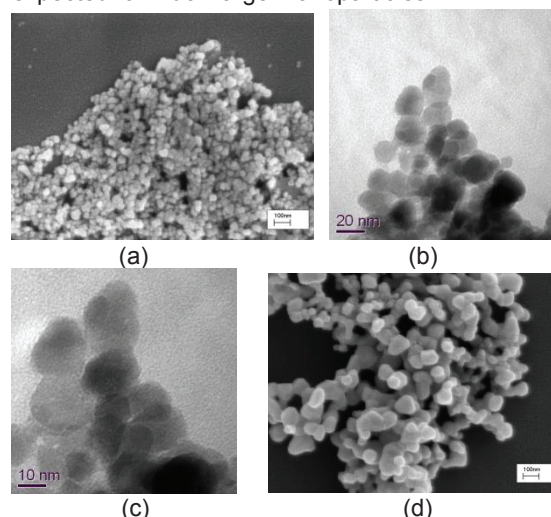


Fig. 2. SEM (a) and TEMs (b) & (c) micrographs of nanoparticle crystals of ZnO as supplied by JM sample (1). SEM (d) is of sample 1L.

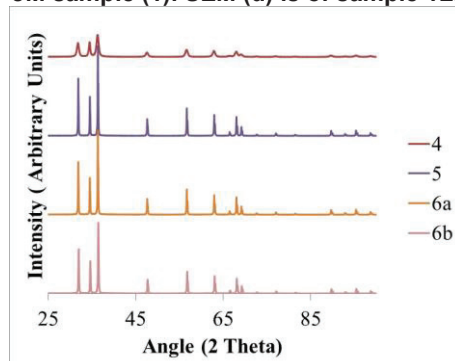


Fig. 3. XRPD patterns of 4, 5, 6A and 6B

Figure 4 presents both a TEM micrograph of crystals of ZnO:Zn (sample 5) (prepared from the JM sample 4 nanophosphor by firing for 45 minutes at 800°C in a reducing atmosphere) and their photoluminescent emission spectrum.

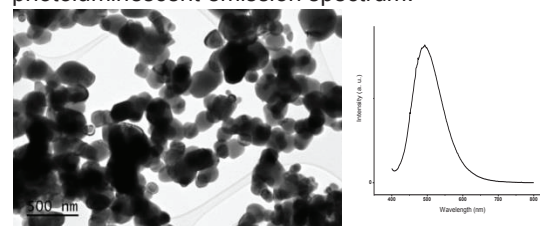


Fig. 4. (Left) TEM micrograph of the nanometre sized crystals of ZnO:Zn (sample 5); (Right) Their photoluminescent emission spectrum (excited at 350 nm).

Figure 5 presents crystals of ZnO:Zn first fired from sample 4 then coated⁹ (sample 6A). These crystals have an average crystallite size of 167.6nm (see figure 3). In Figure 5(a) the fired crystals are shown with a large amount of much smaller crystals. In Figures 5(b) and 5(c) some of the larger crystals in (a) are shown at higher magnification and there is some evidence of a coating on the larger crystals. It appears that these larger ZnO:Zn

nanoparticles did not fully dissolve/react with the NH_4HCO_3 solution (1.25 M) and the 50 ml of $\text{Al}_2(\text{SO}_4)_3$ solution (0.03 M) in the time the reaction took place, rather they only partially dissolve and when filtered they can be seen to coexist with smaller material; that is the precipitate of the Zn^{2+} and Al^{3+} materials that formed from the surface of the ZnO crystals that did dissolve.

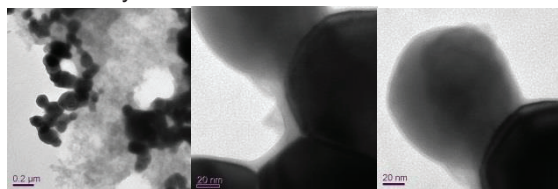


Fig. 5. TEM micrographs of the crystals of ZnO:Zn (sample 6A). (a) The fired crystals are shown with many much smaller crystals. In (b) and (c) some of the larger crystals in (a) are shown at higher magnification and there is some evidence of a coating on them.

Figure 6 presents the TEM micrographs of the crystals of ZnO:Zn shown in figure 5 after being fired at 600°C (sample 6B). In Figure 6(a) the fired crystals are shown with a large amount of much smaller crystals. In Figures 6(b) and 6(c) some of the larger crystals in 6(a) are shown at higher magnification. In 6(b) and 6(c) there is evidence of a coating on the larger crystals. This shows that the method⁹ does appear to work for larger nanoparticles where there is not enough acid to dissolve the larger particles. However the coating is not pure Al_2O_3 but is a ZnO layer doped with Al^{3+} .

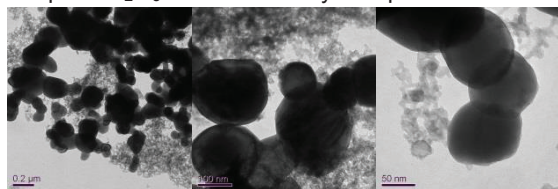


Fig. 6. TEM micrographs of the crystals of ZnO:Zn (sample 6B). (a) The fired crystals are shown with a large amount of much smaller crystals. In (b) and (c) some of the larger crystals are shown at higher magnification, these show some evidence of being coated.

The photoluminescent spectrum of sample 6B is presented in Figure 7. The luminescent properties of 6B were not diminished by the coating process. The unit cells, phase present and crystallite sizes found by fitting the XRPD data shown in figure 7 for samples 4, 5, 6A and 6B are presented in Table 1. As the particle size increases from sample 4 to sample 5 the cell size decreases in volume. As expected the cell sizes of samples 5 and 6A are the same (within experimental error) though the crystallite size of the latter is smaller consistent with the latter's surface reacting with the solution as described above. On firing sample 6A to form 6B the unit cell is seen to be the same. There was no

evidence of carbonate phases in the XRPD data of sample 6A though small crystals were observed in the TEM and SEM micrographs in figures 4 and 5, we believe that this is because the larger ZnO:Zn nanoparticles remaining after the reaction in solution dominate the XRPD data.

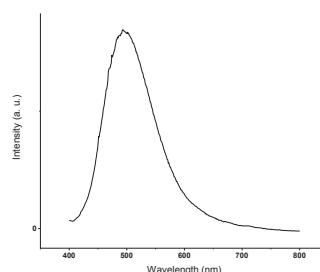


Fig. 7. Photoluminescence emission spectrum of ZnO:Zn (sample 6B) nanometre sized crystals (excited at 350nm) after being coated in AZO.

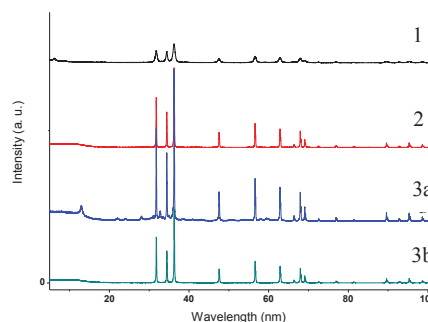


Fig. 8. XRPD patterns of 1, 2, 3A and 3B

Having shown it was possible to coat larger nanoparticles, it was decided to explore what would happen if no $\text{Al}_2(\text{SO}_4)_3$ was used in the preparation. This yielded sample 2 which was further treated with 10 ml $(\text{NH}_4\text{HCO}_3)$ solution (1.25 M)). The slurry was filtered to obtain precipitates, which were washed and dried at 80°C overnight; this sample is referred to as sample 3A. The final product was obtained by calcining the precipitates at 600°C for 1 hour (sample 3B). The XRPD data for these larger ZnO:Zn crystals are presented in Figure 8. Again as in figure 3 the larger nanoparticles in this case samples 2, 3A and 3B are much sharper than those of sample 1. In addition the XRPD data for 3A in Figure 8 shows evidence for BCZ which arises from the ZnO:Zn nanoparticle's surfaces dissolving into the solution.

On firing sample 3A the BCZ is converted back to ZnO so no evidence for BCZ is found in the XRPD data for sample 3B. Figure 9 presents TEM micrographs of sample 3A. The crystals have smaller pointed crystals growing from their surfaces.

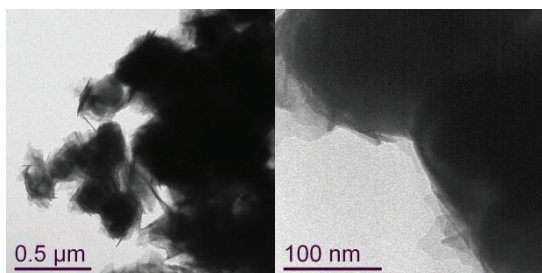


Fig. 9. TEM micrographs of crystals of ZnO:Zn (sample 3A). These crystals clearly show smaller pointed crystals growing from their surfaces.

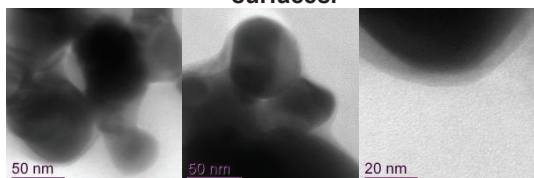


Fig. 10. TEM micrographs of crystals of ZnO:Zn (sample 3B), The crystals are clearly coated.

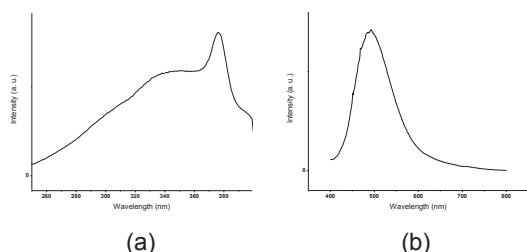


Fig. 11. Photoluminescence (a) excitation and (b) emission spectra of the ZnO:Zn (sample 3B) nanometre sized crystals after being coated in ZnO. The excitation spectrum was monitored at 492 nm and the emission spectrum was obtained using 350 nm excitation.

On firing sample 3A to 600°C for 1 hour sample 3B was produced (TEM micrographs are presented in Figure 10). It is apparent that the crystals are coated with a less dense material which must be a non-crystallized form of ZnO. Sample 3B also shows good photoluminescence properties (Figure 11). Once again it is demonstrated that these coating procedures do not disturb the photoluminescent properties of the crystal areas that do not dissolve.

The unit cells, phase present and crystallite sizes found by fitting the XRPD data (Figure 8) for samples 1, 2, 3A and 3B are presented in Table 1. It is clear that as the particle size increases from sample 1 to sample 2 the cell size decreases in volume in agreement with the findings from Table 2 for samples 4 and 5. As expected the cell sizes of samples 2 and 3A are the same within experimental error, however the crystallite size of the ZnO:Zn particles are larger in the latter sample. Firing sample 3A to form 3B shows no change in the unit cell size, however the crystallite size is smaller than sample 2 as expected. There was no evidence of carbonate phases in the XRPD data of sample 6A though small crystals were observed in the TEM and SEM micrographs in Figures 4 and 5, we

believe that this is because the larger ZnO:Zn remaining after the reaction in solution dominate the XRPD data.

4. CONCLUSIONS

A number of findings have been reported herein that are useful for preparing coated nanoparticles. These are that it is possible to coat large nanoparticles of ZnO and ZnO:Zn using the method but the coating is a layer of AZO not an Al₂O₃ layer, and that it is also possible to coat large nanoparticles of ZnO:Zn with a layer of ZnO by using only (NH₄)HCO₃. It has also been shown that these coatings can be applied to the large ZnO:Zn nanoparticles without destroying their luminescent properties. These coated particles did not degrade polystyrene while protecting it.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- 1) P. Gijssman, G. Meijers, and G. Vitarelli, *Polymer Degradation and Stability*, **65**, 433-441 (1999).
- 2) P. Gijssman, J. Hennekens, and D. Tummers, *Polymer Degradation and Stability*, **39**, 225-233 (1993).
- 3) J. Silver, R. Withnall, R. Li, A. Lipman, P. J. Marsh, G. R. Fern, K. Tarverdi, P. Bishop and B. Thiebaut, *Proc. IDW*, 1409-1412 (2011).
- 4) R. Withnall, J. Silver, R. Stone, R. Li, A. Lipman, K. Tarverdi, B. Thiebaut, P. Bishop, S. Subbiah, D. Johnson and P. Reip, *Proc. of the 3rd Intern. Conf. on Nanopolymers, Düsseldorf*, 13-14 September, pp 1-6 (2011).
- 5) J. Silver, R. Withnall, G. R. Fern, Rui Li1, A. Lipman, C. Catherall, A. Salimian, P. G. Harris, K. Tarverdi1, P. Bishop, B. Thiebaut, P. W. Reip and S. Subbiah, *Proc. of the 5th Intern. Conf. on Optical, Optoelectronic and Photonic Materials and Applications, Nara, Japan*, 3-7 June, p 44 (2012).
- 6) Z. Chi, Z. Zhang, F. Wang and G. Wang, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **340**, (2009) 161-169.
- 7) Z. Y. Huang, T. Barber, G. Mills and M. B. Morris, *J. Phys. Chem.* **98** (1994) 12746-12752
- 8) Y. Yamamoto, N. Imai, R. Mashima, R. Konaka, M. Inoue and W. C. Dunlap, *Methods Enzymol.*, **319**, (2000) 29-37.
- 9) F. Yuan, H. Peng, Y. Yin, Y. Chunlei and H. Ryu. *Materials Science and Engineering B*, **12** (2003) 55-60.