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Preparation, Characterization and Evaluation of Nano Zinc Oxides as Pigments

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THREE samples of nano zinc oxide are prepared by using both the hydrothermal and the direct precipitation methods. The characterization of the produced samples shows that the prepared samples have different nano size. Also, it is found that there are an agreement between the calculated values of the particle size from the x-ray diffraction and the TEM measurements. On other hand, the prepared samples are tested as pigments according to the ASTM (1980 and 1981) for comparison with a commercial ZnO. The test showed that the nano sized ZnO exhibits an excellent property when used as pigments relative to the commercial sample.

Keywords: Nano zinc oxide, Hydrothermal, Precipitation and Pigment .

Zinc oxide (ZnO) powders have different applications. For example as catalysts, in paints and other construction applications [(1)] .By introducing the nano technology, zinc oxide gains a special attention. Zinc oxide nano sized powder have unique optical and electrical properties[(1-3)] ,which introduce advanced applications such as chemical and gas sensors, rubber industry to reduce vulcanization process time, cosmetic and pharmaceutical industries[(4-6)]. Thin films of nano sized ZnO are used in the more advanced applications such as transparent transistors[(7)], solar and photovoltaic devices[(8,9)], UV rays, and varistors[(10,11)].

In general, zinc oxide powder is produced by three distinct processes[(4,12)]; direct oxidizing zinc metal, or reduction of an ore to zinc metal followed by controlled re-oxidation, to a far lesser extent or precipitation of the oxide or carbonate from an aqueous solution followed by calcinations. Where Nano-sized zinc oxides are prepared by using different advanced methods such as, sol-gel method [(5,13)], thermal deposition, spray pyrolysis and modified precipitation methods.

Chang Chun Chen *et al.* used the direct precipitation method to synthesize nano-sized ZnO particles using some alternative raw materials to study their effects on the macrostructure of the product [(1)]. Chou *et al.* prepared nano-sized zinc oxide from $Zn(NO_3)_2$ solutions containing hexamethylene tetra amine. They found that the shape of the obtained particles depend on the pH of the medium of the reactions[(14)]. The micro emulsion method was also used to prepare Zno nano sized particles by Singhal *et al.* [(15)]. Komaraeni *et al.* [(16)] used micro wave

irradiation of Zn $(NO_3)_2$ solutions neutralized at pH 8-12 to prepare ZnO nanparticles. T. Tsuchida and S. Kitajima[17] applied mechano-chemical processing in the synthesis of ZnO, nanoparticles. The literature survey [1, 14-17] showed that chemical, physical and microstructure of ZnO powders are dependent on the synthesis procedure.

The aim of present work is preparation and characterization of ZnO nanosized various methods and studying the effect of temperature on the produced products. Also, this work extended to evaluate the produced materials as pigments according to the standard methods and in comparison with a commercial ZnO.

Materials and Methods

Materials

Zinc 2-ethylhexanoate, $Zn(CH_3COO)_2.2H_2O$, containing 1% of ethylene glycomonomethylether supplied by Fluka. Tetra-methylaminehydroxide, TMAH, [(CH3)4NOH, 25%, w/w aqueous solution, electronic grade, 99.99% supplied by Fluka. $Zn(NO_3)_2$ and $(NH_4)_2CO_3$ supplied from BDH. Absolute ethanol, 2-propanol and NH_4OH solution supplied by Kemika were used. All materials were used without further purification.

Preparation methods of nano zinc oxide samples

Three methods were used to prepare zinc oxide under different conditions. The first method is the hydrothermal treatment for the precurcer materials at short ageing. In this method (1.00g) zinc 2-ethylhexanoate was mixed with 90 ml of 2-propanol with continuous stirring. After stirring for 40 min a clear solution was appeared. Then, 10 ml of 25% TMAH was added to the pervious solution with vigorous stirring. After this step the solution converted to the colloidal state. The colloidal solution was aged for 12 hr, washed carefully with ethanol and bi-distilled water. Then a precipitation at room temperature was occurred. The formed precipitate was separated by using vigorous centrifuging and dried at 60◦C, followed by autoclaving at 170◦C for 12 hr (sample I).

Sample II was prepared by adding 7 ml of H_2O to 100 ml of 0.2 M $Zn(CH_3COO)_2$ solution. To this solution 3 ml of concentrated NH_4OH solution was added with vigorous stirring for 30 min. The formed suspension was aged at room temperature for 72 hr. The solid precipitate was separated from the mother liquor by vigorous centrifuging. The isolated powder was washed with alcohol and bi-distilled water several times and dried at 60◦C. Further treatment was carried by autoclaving at 160◦C for 72 hr.

For the sample (III) the direct precipitation method was followed. In this method, firstly $Zn(NO_3)_2$ and $(NH_4)_2CO_3$ were prepared as a stock materials having 1.5 and 2.25 mol/L concentration, respectively. The second step, $Zn(NO_3)_2$ solutions were slowly dropped into the $(NH_4)_2CO_3$solutions with the

vigorously stirring. The product of the reaction between the two start solutions were separated by filtration and washed with bi-distilled water and ethanol, respectively. The produced powder was dried at 80 ◦C followed by calcination at 550 ◦C for 2 hr.

Characterization of zinc oxide samples

The dried produced samples were characterized by using X-ray diffraction. The morphology was examined using transmission electron microscope TEM. The X-ray diffraction, was performed by Philips diffractometer, (type P.W. 1390) using Ni-filtered Cu Kα radiation (λ = 1.5405 Å). The X-ray tube was operated at 36 kV and 16 mA. The diffraction angle 2θ was scanned at a rate of 2^{o} min^{-1}. For the TEM measurements, the tested samples were prepared by dispersing distilled water followed by ultrasonic vibration for half an hour. Then, a drop of the dispersed sample was placed onto a copper grid coated with a layer of amorphous carbon. A Jeol Transmission Electron Microscope, Jel 1230, RV 120 KV was used.

Evaluation of zinc oxide samples as pigments

The main measurements for evaluation of the produced samples as pigments were carried out according to the ASTM D (1980) and ASTM D (1981). In this evaluation, the specefic gravity, oil adsorption, hiding power, performance to heat and chemical resistance (acid and alkali resistances) were performed for the samples.

Results and Discussion

Characterization of zinc oxide samples

Figure 1 represents the X-ray diffraction spectra of the four samples of ZnO, named (a) commercial zinc oxide, (b) zinc oxide prepared by hydrothermal method with a short aging time (sample I), (c) zinc oxide prepared by hydrothermal method with a long aging time (sample II), (d) zinc oxide prepared by direct precipitation method (sample III). The x-ray patterns for all charts are nearly identical in the values of 2Θ except for the commercial sample which have some inconsiderable peaks.

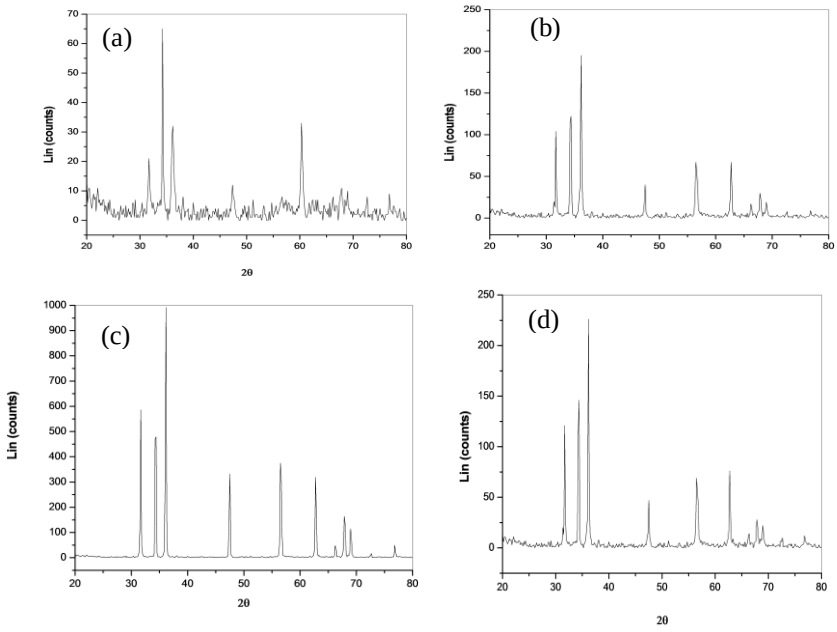

Fig. 1. X-ray diffraction patterns of (a) commercial ZnO, (b)ZnO prepared by hydrothermal method with a short aging time, (c) ZnO prepared by hydrothermal method with a long aging time and(d) ZnO prepared by direct precipitation method.

The X-ray patterns indicate that the formation of hexagonal wurtzite phase of zinc oxide is in agreement with the results obtained by Mir *et al*. and Ghoul *et al*. [18, 19]. Also, it is noticed that for all samples the peaks appear at 2Θ= 31.8; 34.5; 36.3; 47.7; 56.5; 62.7; 67.8 and 69 with a negligible value. The appearance of these peaks can be attributed to (100), (002), (101), (102), (110), (103), (112), (201) plans of zinc oxide, respectively as pointed out by Peng *et al.* and Krithiga *et al.* [20, 21]. Also, it is observed that sharpens of these peaks is well defined and narrow, showing that an asymmetry in the crystalline shapes was formed. The average particle size of the four samples was calculated using Scherer's Equation [22] (Table) 1:

$$D = 0.9\,\lambda / B\cos\Theta_B$$

where D is the crystallite size, λ the x-ray wavelength (1.5418), Θ_B is the maximum of the bragg diffraction peak, and B is the line width half maximum (in radians).

The results indicate that the three prepared samples have nano-particle size ranging from 18 to 37 nm while for the commercial sample the particle size is high (equal to 331 nm) relatively to the prepared samples. The observed results are in a

good agreement with the result obtained by El mir *et al.* [23], Omri *et al.*[24] and Amrut *et al.* [25] and close to ZnO reported in JCPDS card (No. 36-1451).

TABLE 1. Particle size of the samples .

No.	Sample prepared methods	Size estimated by Scherer method	Size estimated by TEM photography
1	Commercial zinc oxide	331	185-402
2	Method I (Hydrothermal with short ageing and autoclaving time)	37	26-52
3	Method II (Hydrothermal with long ageing and autoclaving time)	29	24-38
4	Method III (Direct precipitation)	18	8-27

Figure 2 represents TEM photograph of the prepared and the commercial samples. The commercial sample (a) shows a randomly shaped participates without defined structure. The particle size appeared to be from 185 – 402 nm. For the sample prepared by the hydrothermal with short ageing and autoclaving time (b), the distribution of participates shows some coagulated particles and randomly distributed, while the other particles start to coagulate (26-52 nm). For the sample prepared by the hydrothermal with long ageing and autoclaving time (c) it is clearly observed, that some crystals plates start to be formed with defined edge. It is observed that most of plates take a defined hexagonal shapes but with non homogeneity in size 24-38 nm. For the sample prepared by direct precipitation method (d) an improvement in the crystallinty and well defined structure appears with size (8-27 nm).

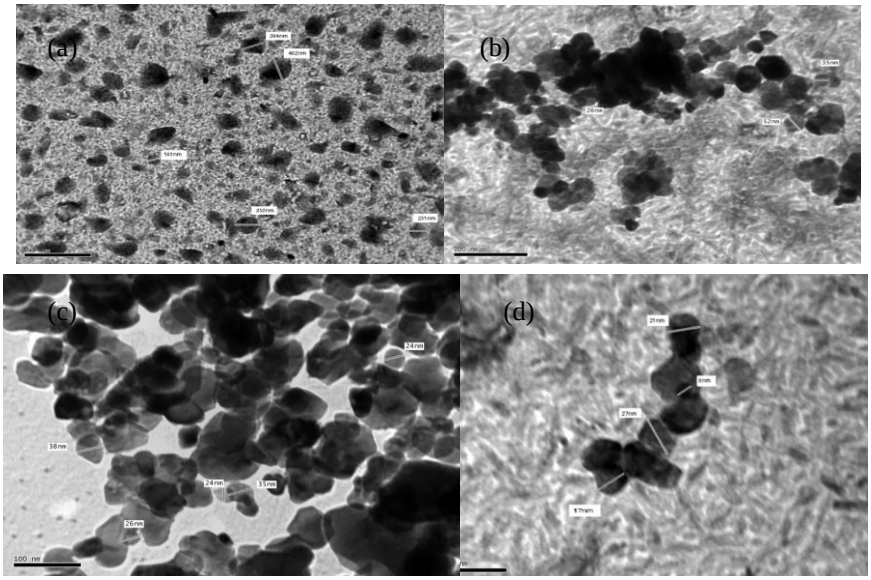

Fig. 2. TEM of (a) commercial ZnO (350 nm), (b), (c) and (d) Nano ZnO (54 nm, 35 nm and 20 nm) .

Figure 3 represents the histogram of the particle size of the four samples under consideration.

Both the measurements of the particle size by scherer's equation or the TEM show that the prepared samples have nano-particle size.

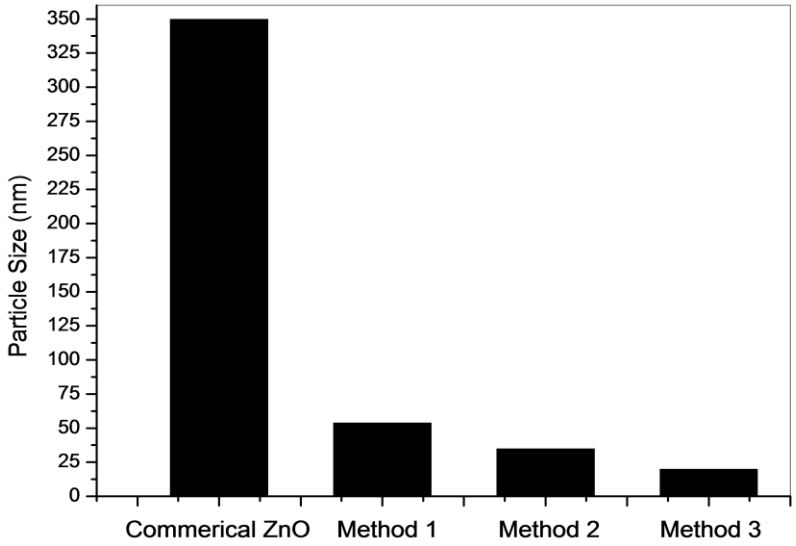

Fig. 3 . The particle size using different prepared methods .

Results of the tested samples as pigments

Some measurements were carried out to evaluate the prepared ZnO as pigments in comparison with the commercial ZnO. The specific gravity of all samples was shown in Fig. 4 a, from the curve it is clear that the commercial sample has higher specific gravity, while the sample (III) has lower specific gravity value. On the other hand, it is clear that specific gravity of all samples is ranging from 5.57 to 5.82. These values indicate that all samples are suitable to be used as pigment, where no settling occurred.

The results of oil adsorption for all samples were shown in Fig. 4 b, the results also, indicate that the more suitable samples for using as pigment is sample (III) according to ASTM applied methods.

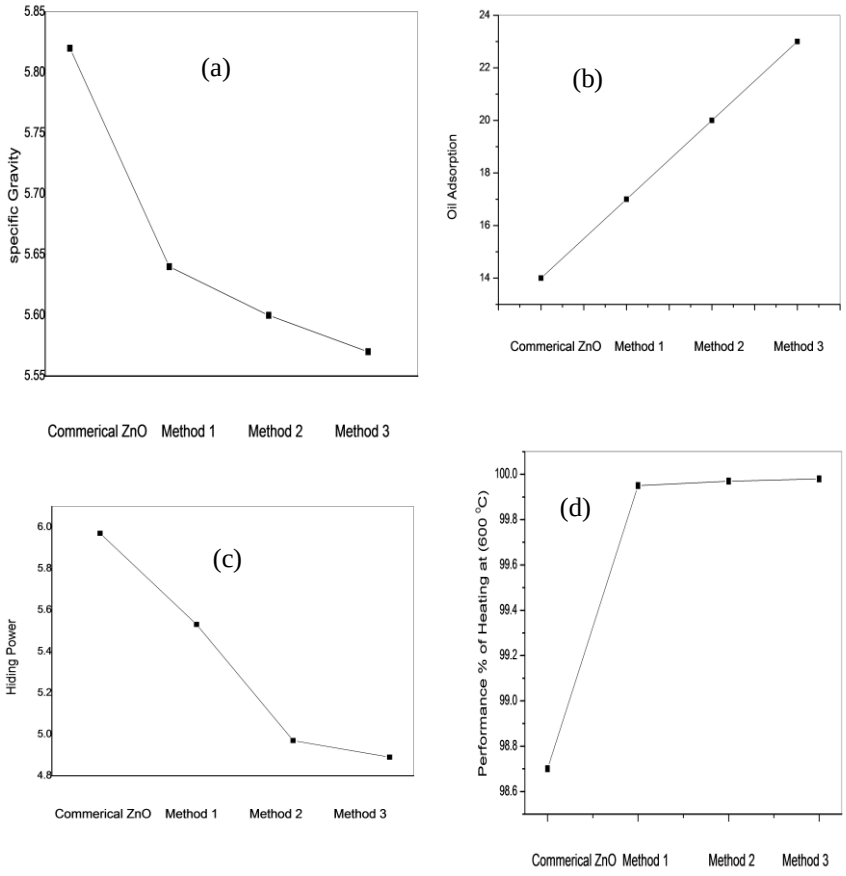

Fig. 4. Specific gravity, oil adsorption, hiding powerand heating at 600 ^{0}C tests for commercial ZnO and Nano ZnO as a pigment.

Also, hiding power and heating performance of all samples were shown in Fig. 4 c and empasise the same results.

In general, the agreement between measured values and those mentioned in the ASTM shows that as the particle size of the prepared samples decreases the efficiency of painting performances increases due to dispersion of ZnO through the substrate.

Also, the chemical resistance (acid and alkali resistances) was shown in Fig. 5 for all samples. The obtained results favored the use of ZnO nano oxides for paints with excellent results .

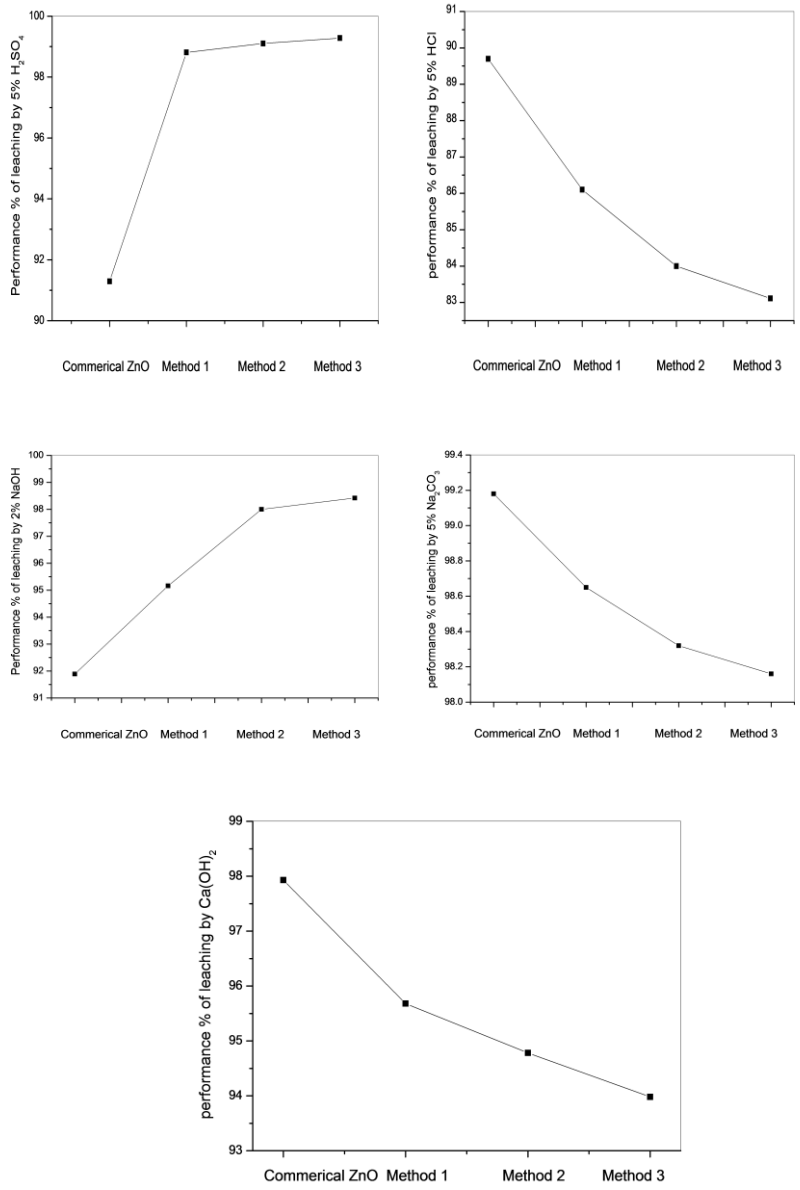

Fig. 5. Results of performance % of leaching by 5% H_2SO_4, 5% HCl, 2% NaOH, 5% Na_2CO_3 and 5%$Ca(OH)_2$ tests for commercial ZnO and nano ZnO as a pigment.

Conclusion

From the analysis of the obtained data for the prepared samples of zinc oxides by hydrothermal and direct precipitation methods, it may be conclud that:

1- All prepared samples have nano-sized particle size.
2- The prepared samples can be used successflly as pigments, where they exhibit an excellent values according to ASTM .
3- As the particle size decreases the efficiency and the quality of paints increase, due to the disperssion of the small particale size of the pigment (ZnO).

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تحضير و توصيف و تقييم اكاسيد الزنك النانومترى كمخضبات

عدلى عبدالله حنا ، وليد عبد الحليم عبد الغفار محمد و هدى رفعت جلال
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تم تحضير ثلاث عينات من اوكسيد الزنك النانومترى باستخدام الطريقة الحرارية والترسيب المباشر مع تغير المواد الداخله فى التحضير و ظروف المعالجة وتم توصيف العينات الناتجه باستخدام طيف حيود الاشعة السينية و الميكروسكوب الالكترونى النافذ ودلت النتائج على ان العينات الثلاثة المحضرة تقع فى حجم النانومترى و تم اختبار العينات المحضرة كمخضبات طبقا للمواصفات القياسية العالمية و مقارنتها باوكسيد الزنك التجارى المستخدم فى الاسواق.

دلت قياسات الكثافة – مقاومه الاحماض و الكيماويات – التأثر بدرجه الحراره وغيرها أفضليه العينات المحضرة عن العينه التجارية المستخدمه و أعزى ذلك إلى صغر حجم الحبيبات مما يؤهلها للانتشار.