Mechanochemical synthesis of ZnO nanostructured powder using different organic surfactants and their influence on the particles size and morfology

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ABSTRACT

Pure zinc oxide (ZnO) nanostructured powder was prepared by the mechanochemical method followed by a heat-treatement in a planetary ball-mill using agate vials and alumina balls. Mechanochemical processsing involves the mechanical activation of reactant mixture in a liquid phase (wet milling). We studied the influence of organic surfactants on reduction of ZnO particle size, their shape and size distribution. As a process controling agent (PCA) we used different organic compounds such as oxalic acid and oleic acid. After milling procedure intermediate compounds were calcinated in air to form ZnO powder. Powders caracterization was preformed using X-ray diffraction method (XRD) and scanning electron microscopy (SEM).

SYNTHESIS

Sample I PCA Oxalic acid ($H_2C_2O_4{\cdot}2H_2O$)

The mixture of $ZnCl_2$ powder and water solution of $H_2C_2O_4{\cdot}2H_2O$ with a molar ratio of $2[HC_2O_4]^-:Zn^{2+}$ was sealed in an agate vial with alumina balls measuring Ø 8 mm. Milling was performed in a planetary ball mill Retsch PM4, using the ball-to-powder mass ratio 10:1. Mechanochemical process was carried out for a range of times: 30 min, 1, 2 and 4 h respectively at 200 rpm applying reversal mode of milling. The as-milled powder was then isothermally treated at temperature of 450 ºC in air for 1 h.

Sample II PCA Oleic acid ($C_{18}H_{34}O_2$)

The mixture of $Zn(CH_3COO)_2{\cdot}2H_2O$ powder with 10wt% of oleic acid dissolved in ethanol was mechanochemicaly treated for various times: 4, 7 and 10h in that order at 200 rpm applying reversal mode of milling. Ball-to-powder mass ratio was 10:1. After milling procedure, samples were isothermally treated at temperature of 275 ºC in air for 30 min and washed with deionized water. Sample was left to dry over night at room temperature.

Field-emission scanning electron microscopy (FE SEM)

The FESEM measurements were performed on a SUPRA 35 VP Carl Zeiss field-emission scanning electron microscope. The samples were prepared by re-dispersing in ethanol by means of an ultrasonic bath and filtering the dispersions using polycarbonate membranes with 50-nm pore sizes. Carbon was used to prevent charging. Figs. 1 and 2 show particles morphology of the samples revealed by scanning electron microscopy. **Sample I** consists of particles with mean size of ~ 100 nm. Particles are approximately spherical in shape and agglomerated. **Sample II** consist of particles irregular in shape embedded in oleic acid matrix. Size of ZnO particles is in the 100-200 nm range.

Sample I

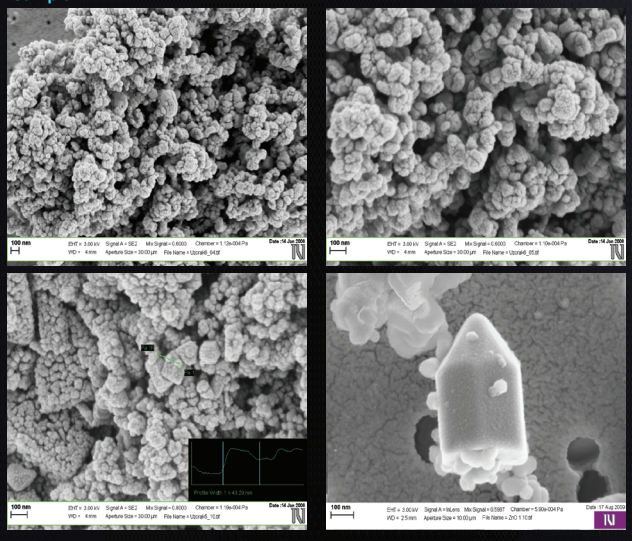

Fig. 1 FE SEM micrographs of ZnO powder (PCA oxalic acid)

Sample II

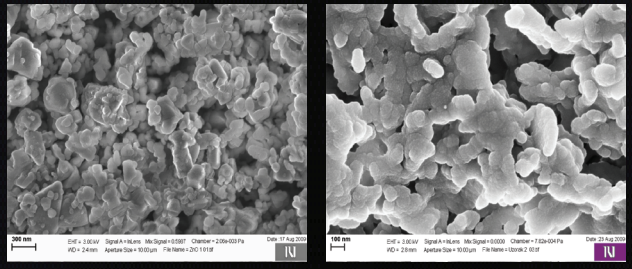

Fig. 2 FE SEM micrographs of ZnO particles implanted in oleic acid matrix

XRD

The X-ray diffraction data were collected on a Phillips PV 1050 diffractometer with Cu-$K_{\alpha 1,2}$. Measurements were done in 2θ range 10-80 ^{0} with scanning step width of 0.02 ^{0} and 2 s time per step. All of the indexed peaks in the obtained diffraction are well matched with that of bulk ZnO (JCPDS Card No. 36-1451), which confirms that the synthesized crystalline powder has a wurtzite hexagonal structure.

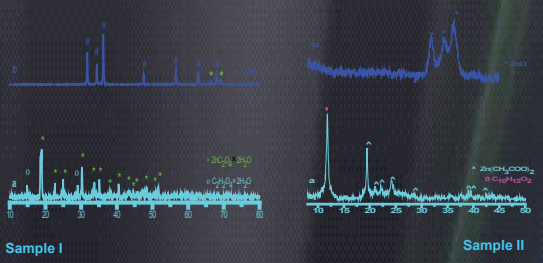

Fig. 2 XRD patterns. Sample I (a) miliid fo 4h; (b) calcinated at 450^{0}C for 1h. Sample II (a) milled for 10h; (b) calcinated at 275^{0}C for 30 min.

CONCLUSION

In summary, well crystallized, nanostructured ZnO powder can be readily obtained by mechanochemical procedure and thermal treatment. Using different sorts of process controlling agents it is possible to control the particle size and morphology. Using oxalic acid as a PCA, sample I, we obtained ZnO particles of better uniformity, spherical and less agglomerated then the particles in sample II. With oleic acid as PCA ZnO particles are not completely dispersed because of residual amount of oleic acid, where ZnO particles are embedded, and which was not entirely washed out.

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