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TEM Characterization of ZnO Nanoparticles Obtained by Mechanosynthesis

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ZnO is a wide-band-gap semiconductor (3.4 eV), which has attracted considerable attention during the last two decades due to its potential applications in optics and optoelectronics. ZnO has been used for short-wavelength laser devices and light-emitting diodes [1], and more recently, researchers have reported its possible application in solar cells [2],[3],[4]. ZnO has been used as a diluted magnetic semiconductor, when doped with transition metals and even pure nanostructured ZnO has been found to present magnetic behavior [5].
Using commercial ZnO powders as a starting point, particle size was reduced by mechanical milling in a high energy shaker SPEX mill. The apparatus and milling media are made of hardened steel and the milling ball to powder weight ratio was set to 5:1
Thin specimens suitable for electron microscopy were prepared by placing clean, dry crushed powders onto commercial holey carbon coated copper grids. Morphology and particle size was determined in a JEOL-2200FS HR-FE-TEM, equipped with an in-column energy filter (Ω-filter), with a spatial resolution of about 0.16 nm.
Furthermore, Electron Energy Loss Spectroscopy (EELS) was used to monitor changes in electronic structure of ZnO as particle size decreases. The energy resolution of the EELS spectra was determined by measuring the full width at half-maximum (FWHM) of the zero loss peak, which was typically close to 1.0 eV when the TEM was operated at 200 kV. EELS spectra were Fourier-Log deconvoluted to obtain the single scattering distributions S(E) and the real and imaginary parts of the dielectric function were obtained, after removing surface loss effects, by Kramers-Kronig Analysis.

Figs. 1-3 show TEM micrographs of ZnO particles after 0, 10 and 15 hrs. milling times, respectively. Fig. 4 shows the Kramers-Kronig derived imaginary part of the dielectric function, ε_2, from EELS spectra, for three particle sizes studied (200, 100, 20 nm), and corresponding to 0, 10 and 15 hr milling times, respectively. Spectra were shifted up for clarity. In all three spectra, five well defined peaks can be identified, labeled as A, B, C, D and E. Energy peak position A cannot be stated accurately, due to the uncertainties introduced by the zero-loss peak removal. Peak B is found at 8.8 eV and does not seem to shift as particle size is changed. Featured peak C shifts monotonically to lower energy as particle size decreases: 12.6, 12.4 and 12.1 eV for 200, 100 and 20 nm, respectively. Featured peak D appears as a shoulder whose actual energy position cannot be stated unambiguously because of energy resolution limitations. Peak E remains constant at 31.3 eV for 200 and 100 nm particle size, but decreases to 29.7 eV for 20 nm particles.

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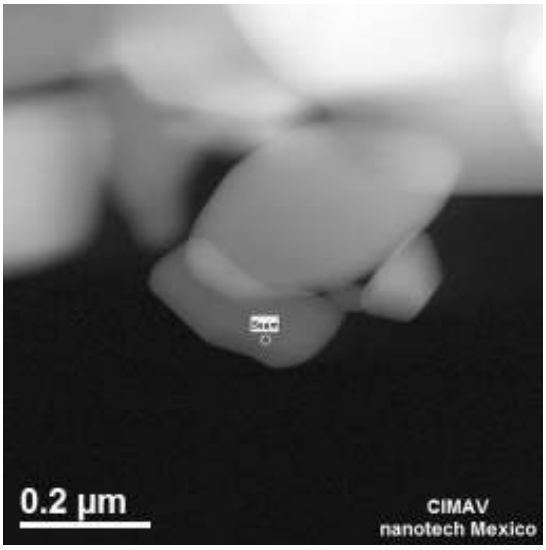

Figure 1. TEM micrograph of commercial ZnO

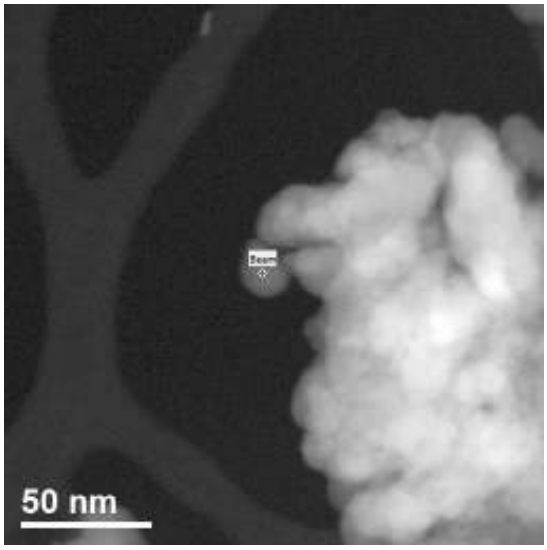

Figure 2. TEM micrograph of ZnO after 10 hrs. milling

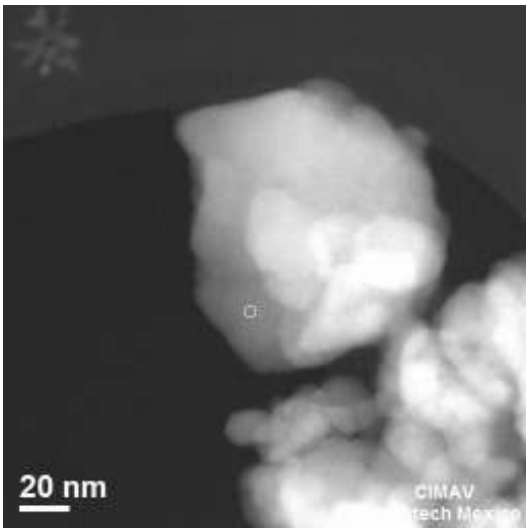

Figure 3. TEM micrograph of ZnO after 15 hrs. milling

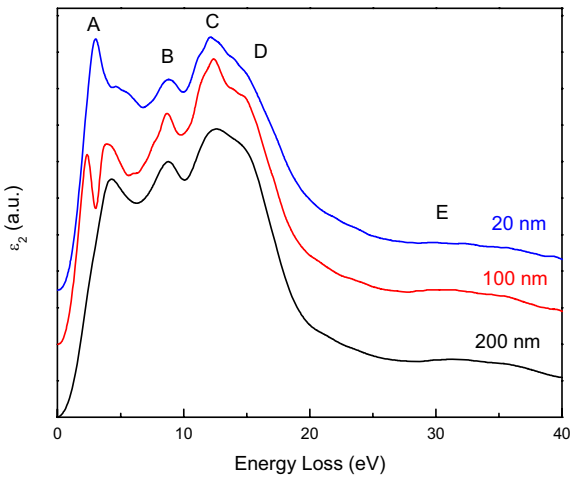

Figure 4. Kramers-Kronig derived imaginary part of the dielectric function vs. particle size

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