SYNTHESIS OF ZnO NANOPOWDER WITH VARIOUS MICROSTRUCTURES VIA DIFFERENT CHEMICAL PROCESSING

(Farklı Kimyasal Prosesler ile Çeşitli Mikroyapılarda ZnO Nanotoz Sentezlenmesi)

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ABSTRACT- In the present research work, the wet chemical, solvothermal, sol gel methods for synthesis of ZnO nanopowder with different microstructures has been carried out. The results obtained from XRD, BET and Particle size analyzer and SEM show that the nanopowders are single crystals and have nanowires, nanorods and flowerlike microstructures with a narrow size distribution. Wet chemical processing can be an attractive method for industrial production of the micro powders, but solvothermal processing is easy and cheap method to prepare nano powders which can be used in industrial range. The photoluminescence characterization of the nanostructures exhibited a UV irradiation and a visible emission band centered at green region which can be adjust with processing routes.

Keywords: Zinc Oxide, Chemical Processing, Nano Powders, Microstructure, Optical Properties.

INTRODUCTION

The ZnO is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, first aid tapes, etc.

This semiconductor has several favorable properties: good transparency, high electron mobility, wide bandgap, strong room-temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid

crystal displays and in energy-saving or heat-protecting windows, and electronic applications of ZnO as thin-film transistors and light-emitting diodes are forthcoming as of 2009.

Zinc oxide (ZnO) is a wide band gap semiconductor, having high excision binding energy of 60 meV. It has attracted intensive research efforts for its unique properties which make it a good candidate for many applications [1-4]. The nanostructure materials show a high surface/volume ratio, which critically affects the electronic and optical properties [2].

Zinc oxide (ZnO) is one of very important II–VI semiconductors, exhibiting many interesting properties including near-UV emission, transparent conductivity, and piezoelectricity. transparent conducting electrodes of solar cells, flat panel displays, surface acoustic devices, UV lasers and chemical and biological sensors. Because of their specific morphologies and structures such as nanorods, nanotubes, nanorings, nanowires, pencil-like, whisker, tetrapods, needles and flower-like [5-9]

ZnO is desirable for photocatalysis and photo electrolysis due to its inertness, stability, and low cost. It is also self regenerating and recyclable. Absorption in this range can be improved by dye sensitization, doping, particle size modification, and surface modification [10-13]. In this paper, we report the synthesis and characterization of ZnO nano powders with different Process parameters by a zinc acetate precursor. The photocatalytical properties of as prepared ZnO microstructures have also been investigated and obvious dependence of catalytic properties on morphologies and sizes of final products has been found.

EXPERIMENTAL PROCEDURE

All the materials were of analytical grade and were purchased from Merck, Germany. In a typical procedure, a mixture of 15 ml ethanol (C2H5OH)/water and 0-10 vol.% of triethanolamine (TEA, C6H15NO3) was prepared. Zinc acetate dehydrate [Zn(CH3COO)2·2H2O] crystals were added to the initial solution under vigorous agitation .When the zinc acetate crystals were dissolved completely, 15 ml sodium hydroxide (NaOH) solutions were added to

the solution to increase the pH of the mixture to about 11. The resultant solution was then transferred into an autogenous Teflon-lined stainless steel autoclave which was sealed and maintained at 100-150 °C for 15 h. After the reaction was completed the autoclave was cooled down to room temperature naturally. Other samples were prepared by ultra sonicating in the Sonicator (Misonix Inc., 1000V, 20 KHz) for 15 minutes. To remove unavoidable impurities, the obtained white precipitates were filtered and washed with deionized water for several times and eventually dried at 55 °C in an oven. The obtained powders were characterized with scanning electron microscopy (SEM, Philips XL30), Brunauer–Emmett–Teller (BET) technique (Micromeretics Gemini 2375, USA), X-ray diffraction analysis (XRD, Philips X'Pert diffractometer).

In order to test the photocatalytic behavior of the synthesized powders, photo decoloration of AR27 in water has been chosen as a test reaction. A solution containing known concentration of dye (300 mg.L-1) and semiconductor powders (0.1 mol.L-1) was prepared, and then 50 ml of the suspension was transferred to a 500 ml Pyrex reactor. Then, the lamp was switched on to initiate the reaction. During reaction, agitation was maintained and the temperature and pH fixed. The suspension was sampled after an appropriate time until 90 min. The concentration of dye was determined by a spectrophotometer (521 nm intensity). The irradiation source was a mercury lamp (UV-C, 254 nm, Philips, Germany).

RESULTS AND DISCUSSION

The XRD patterns from the ZnO nanostructure agreed well with the typical wurtzite hexagonal structure of the lattice constant of a = 3.248°A and c = 5.206°A with hexagonal symmetry which belongs to the P63mc (No. 186) space group. The peaks were indexed according to the JCPDS No. 36- 1451. Utilizing Scherrer formula ($d = k\lambda/B \cos \theta$, where d represents the average crystallite size of the particles, λ the wavelength of Cu Kα, 1.54056 °A, B the full width at half maximum (FWHM) intensity of the peak in radian, θ(1 0 1) is Bragg's diffraction angle and k is a constant usually equal to ~0.9), the average crystallite size of the particles was calculated and showed in Table 1.

Table 1: Name, process condition and Crystalline size (Scherrer equation) and Specific surface area (BET).

Name	Process	Solvent	Surfactant	Crystalline size (nm) (FWHM)	Specific surface area (m^2/g) BET
UW0	ultrasonic	water	0	27	44.43
UW1	ultrasonic	water	10% TEA	24	51.50
UE0	ultrasonic	ethanol	0	52	78.88
UE1	ultrasonic	ethanol	10% TEA	60	121.05
SW0	solvothermal	water	0	70	75.70
SW1	solvothermal	water	10% TEA	88	88.12
SU0	solvothermal	ethanol	0	41	71.46
SU1	solvothermal	ethanol	10% TEA	50	63.39
CE1	Chem. con.	ethanol	10% TEA	>100	32.50

The results indicate that Sonicated samples have smaller crystalline size and samples which results from ethanol have been broaded the peak width at half maximum (FWHM) but the grain sizes of samples with or without surfactant agent TEA [14] are not changed. The sonicating process is fast and powders [15] have no time to crystalline growth [14], but solvothermal process is time consuming and diffusion and reaction in high temperature and pressure cause bigger crystalline size [16]. The high pressure, polarization condition, OH radicals of ethanol and deionized water could affect on the size and microstructure of powders [8, 16].

Table 1 shows the specific surface area of samples which is related to powders size and agglomeration of powders. The effect of three parameters is observed, the surfactant agent [14] and process [15,16]. The sample with TEA/ ethanol and sonicated has higher surface area than others. Sonicating could de agglomerate soft wet chemical synthesized powders, and TEA and solvent could control surface charges. This charge influences on the agglomeration, morphology, and the synthesis mechanism.

The SEM images of the specimens are depicted in Fig. 1. The images clearly show the presence of powders on the entire surface. The powders have different morphology. A careful observation of the micrographs shows that the samples with TEA and ultrasonic process have small crystalline size. These powders size and surface area are agreed with

BET results. The EDS spectra of the specimens showed the presence of Zn and O only, indicating that the powders are of chemically pure ZnO. The morphology of solvothermal powders are different from ultra sonic powders, it implies that the process is a powerful parameters to control microstructure.

The time of ultrasonic activating process was relatively short; therefore the growth mechanism of the synthesized powders seems to be completely different from the solvothermal reported growth mechanisms of zinc oxide nanostructures [6, 8, 12, 15]. The ultrasonic irradiation played a critical role in the rapid formation of ZnO powders. During the activation, the reacting phenomenon was occurred by the interaction of the dipole molecules with the high frequency. Polar molecules such as H_2O and ethanol have high dipole moments that make them appropriate solvents for sonar-assisted reactions.

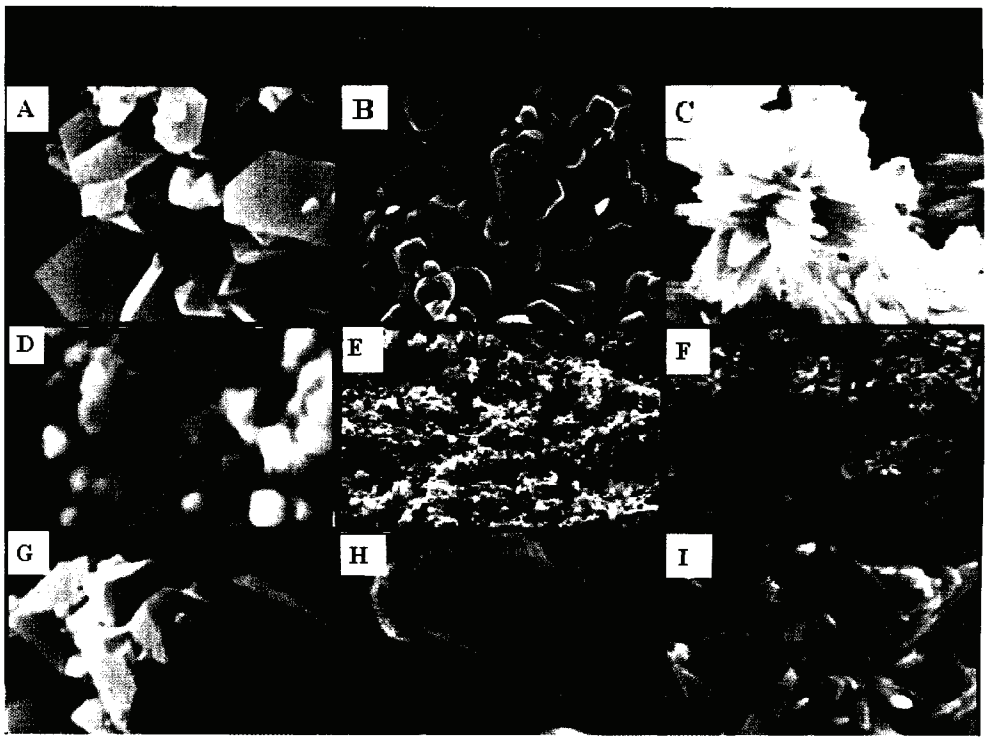

Figure 1. SEM images of ZnO nano powders (a, b, c, d, e, f, g, h, I : nanostructure in 5000 magnifications related to SW1, SU0, UW1, SU1, EU0, EU1, SW0, CE1, UW0 respectively).

Ultrasonic powders are tuned so that water molecules absorb energy causing molecular motion and heating. The movement and polarization of ions under the field of the sonic chamber may result in transient, and localized the reaction system, facilitating the growth and formation of ZnO powders [15]. The usage of a basic condition and an

alcoholic environment are two crucial keys in ensuring the formation of the growth unit of zinc hydroxides and a controlled release of the units from the solution [11]. As seen in our SEM, ethanol or water was utilized as the solvent and the reactions were performed in these solutions, zinc hydroxide species could be easily formed, stabilized by TEA as a surfactant and served as growth units for the formation of ZnO nuclei and epitaxial (or normal growth without TEA) growth of ZnO nuclei into nanostructures. ZnO is usually obtained from water solutions via the formation of an intermediate compound and then its dissolution to form ZnO nuclei. The growth of ZnO through the above mechanism is a prolonged and slow process and results in formation of perfect and large crystals as seen in solvothermal method [16] (Fig. 1). However, with the help of ultrasonic activating, the ZnO nuclei formed rapidly through the decomposition of hydroxides and therefore very small crystals can be obtained through such rapid precipitation.

As it is known, ZnO have hexagonal closest packing (HCP) unit cells and growth rate on the surfaces of that is different, consequently, as the radiation time goes on, ZnO wires grow along <0001> directions on the surface of nuclei and therefore, the outside end planes of these wires are Zn terminated (0001) surfaces. But these 1D rods [5] need suitable surfactant and process conditions.

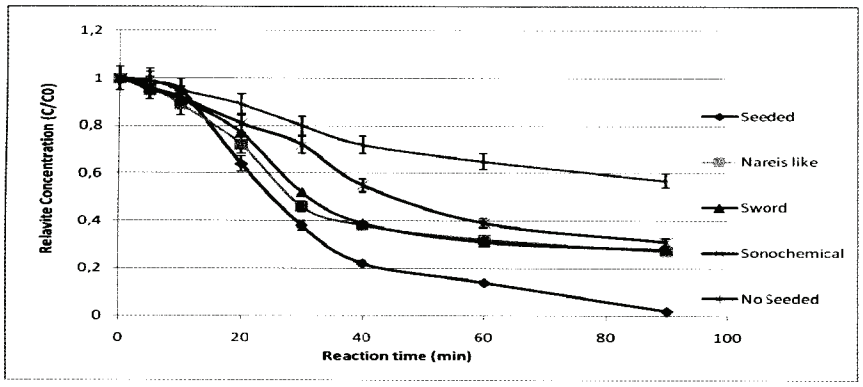

Figure 2. Degradation of AR 27 in various semiconductors (Seeded "SU0", Narcislike "UW1", Sword "EU1", Sonochemical "UE0", No seeded "UW0").

Fig.2 shows the effect of single particles on photodegradiation of AR 27. It can be seen from the graph that the order of photocatalytic activity of powders for AR27. Previously papers on AOP claim that the photocatalytic efficiency of ZnO depends on its phases, and crystallite size. This variability has been attributed to difference in the rate of

recombination, adsorptive affinity, or band gap between the phases. The un pure phase implies a lower mobility of charge-carriers than pure and electron hole pairs recombined without contributing in reaction. The wurtzite has a large band gap (3.2 eV) and it is more active in UV irradiation than Vis. The Fermi level of produced in impurities and crystal dislocation is damaged in un pure preparation methods with unsuitable washing and TEA effects. The surface of powder is the most effective structural parameter of catalyst, because photocatalysis is an interfacial reaction. Thus, a higher specific surface area induces a higher number of accessible active sites. It has other effects on the e-/ h+ recombination time, band gap energy, penetration of light, consequently, photocatalyst reactivity [17]. The powder has smaller crystallite size, more surface area (according to BET results) and better activity.

CONCLUSION

It was shown that the methods (Wet chemical, Microwave assisted, sonochemical, and seeded processes), pH, TEA and precursors have efficiently effects on physical properties like: crystalline size, specific surface area, morphology, phase formation and impurities.

These nano powders with various physical properties have different P.L. and photocatalytic activity.

Changing the parameters could be a suitable way to control and optimize the nano powders in many applications (photocatalytic activity).

ZnO nanoparticles with average diameter of about 10-100 nm were prepared by different chemical processes.

Using TiO_2 as a core of ZnO nano powders could be a suitable way to increase the photocatalytic activity of ZnO nano powders.

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