Acta Montanistica Slovaca Ročník 18 (2013), číslo 2, 119-124

Study of de-aggregation of mechanochemically synthesized ZnSe nanoparticles by re-milling in the presence of $ZnCl_2$ solution

Marcela Achimovičová[1], *Zdenka Bujňáková*, *Martin Fabián* and *Anna Zorkovská*

Conventional mechanochemical synthesis of zinc selenide, ZnSe nanoparticles was performed in a planetary ball mill by high-energy milling of zinc (Zn) and selenium (Se) powders. Mechanochemically synthesized ZnSe was subsequently re-milled in circulation mill in $ZnCl_2$ solution in order to study de-aggregation, physical-chemical and optical properties of ZnSe nanoparticles. The mechanochemically synthesized and re-milled samples were characterized by X-ray diffraction analysis (XRD) that confirmed the presence of cubic and hexagonal ZnSe phases. Size of crystallites calculated from XRD patterns has decreased from 50 to 19 nm for cubic ZnSe phase and from 145 to 2.5 nm for hexagonal ZnSe phase after re-milling for 110 min in $ZnCl_2$ solution. Size, phase composition, morphology, and crystallinity of ZnSe nanoparticles were studied by transmission electron microscopy (TEM) and selected area electron diffraction (SAED). UV-Vis optical spectroscopy has provided an evidence of blue shift of the re-milled nanocrystalline ZnSe particles from the direct band gap of 2.67 eV characteristic of bulk ZnSe crystals. Colloidal stability of ZnSe nanoparticles dispersions was studied by ζ–potential measurements.

Key words: *Zinc selenide, Mechanochemical synthesis, Re-milling, Nanoparticles*

Introduction

Zinc selenide, ZnSe that belongs to group of II-VI binary semiconductors has appeared as perspective material for optoelectronic applications in light-emitting diodes, blue laser diodes, photo-detectors and full colour displays (Zhang et al., 2009; Kumar and Singh, 2009; Cao et al., 2011), tunable mid-IR laser sources (Fedorov et al., 2007) high speed optical devices, photovoltaic and laser screens (Archana et al., 2009). Nowadays, the preparation of ZnSe is usually focused on the synthesis of ZnSe nanoparticles from single molecular precursors with intrinsic optical and luminescent properties, respectively. All main ZnSe preparation routes require high or elevated temperatures for initiating and/or progress of the reactions for example pyrolysis of the organometallic precursors (Peng et al., 1997; Murray et al., 1993) and toxic H_2Se method (Wang and Herron, 1991; Jones, 1997). Later Li and co-workers (1999) have developed the solvothermal elemental reaction method of II-VI semiconductors nanocrystals preparation, and Wang and co-authors (1999) have used the low-temperature aqueous method of ZnSe preparation. Ball milling technique or so-called mechanochemical synthesis was also used for preparation of ZnSe (de Lima et al., 1999; Baltazar-Rodrigues et al., 2009; Gotor et al., 2013). This method has several advantages. Mechanochemical synthesis is simple, dry, time-convenient, one-step process under environmentally friendly and essentially waste-free conditions, which could be interesting for a subsequent semiconductor technology (Baláž et al., 2013). One disadvantage is only agglomeration of particles during milling or mechanochemical synthesis. In order to prevent the particles against agglomeration a presence of various liquids as water, polyvinylpyrrolidone, dodecane, cyclohexane, polymeric surfactants, and alcohols were used during milling (Williams and Phelan, 1985; Tangsathittalchi, 2002; Guérard, 2008; Yu et al., 2011, Bhattacharya et al., 2004; Haas et al., 2001; Baláž et al., 1988). In general, for electrostatic stabilization of colloidal particles the salts with monovalent (Cs, Rb, K, Na, Li) or divalent cations (Ba, Sr, Ca, Mg) are used. Different phases have different charge affinities, so that an electrical double layer forms at any interface and then electrostatic stabilization of colloids is based on the mutual repulsion of electrical charges of individual particles. $ZnCl_2$ is also the salt with the divalent cations and can be used for electrostatic stabilization of particles during milling.

Experimental

Mechanochemical synthesis of ZnSe was performed by high-energy milling of zinc (97 %, ITES, Slovakia) and selenium powders (99.5 %, Aldrich, Germany) in a planetary ball mill Pulverisette 6 (Fritsch, Germany) according to the reaction:

[1] *Mgr. Marcela Achimovičová, PhD., Mgr. Zdenka Bujňáková, RNDr. Martin Fabián, PhD., RNDr. Anna Zorkovská, PhD.*, Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovakia, tel.: +421-55-7922606, achimovic@saske.sk, bujnakova@saske.sk, fabianm@saske.sk, zorkovska@saske.sk

$$Zn + Se \rightarrow ZnSe \quad (1)$$

The reaction is thermodynamically possible because of negative value of enthalpy change ΔH^0_{298} =-159 kJ mol^{-1}. The following conditions were used for mechanochemical synthesis: loading of the mill – 50 balls of 10 mm diameter, material of milling chamber and balls – tungsten carbide, volume of milling chamber – 250 ml, mass of Zn – 2.26 g, mass of Se – 2.74 g, milling atmosphere – Ar, rotational speed of the mill planet carrier – 300 min^{-1} (5 Hz), milling time – 20 min.

Re-milling of mechanochemically synthesized ZnSe was performed in a circulation mill MiniCer (Netzsch, Germany) under following conditions: loading of the mill – 85 % balls of 0.6 mm diameter, material of milling chamber and balls – yttrium stabilized ZrO_2, volume of suspension – 300 ml, mass of sample – 2 g, milling atmosphere – 0.15 g.L^{-1} (10^{-3} M) $ZnCl_2$ solution, revolutions of the milling shaft – 3000 min^{-1} (50 Hz), milling time – 30, 60, 110 min.

X-ray diffraction measurements (XRD) were carried out using a D8 Advance diffractometer (Bruker, Germany) equipped with a θ/θ goniometer, CuK_α radiation (40 kV, 40 mA), a secondary graphite monochromator, and a scintillation detector. The diffraction data were collected over an angular range 20°<2θ<100° with steps 0.025° and a counting time of 5 s.step^{-1}. The commercial Bruker processing tools have been used for the data treatment. Diffrac ^{plus} Eva and the ICDD PDF 2 database have been used for the phase identification and the Diffrac ^{plus} Topas software has been utilized for the Rietveld analysis.

Transmission electron microscopy (TEM) analysis was performed on a microscope Jeol JEM-2100 F. Prior to TEM investigation the powders were crushed in mortar, dispersed in ethanol and fixed on copper supported carbon films.

Nanophox Particle size distribution was measured by a photon cross correlation spectroscopy using a Nanophox particle size analyser (Sympatec, Germany). The values x_{50} represent particle mean diameter.

UV-Vis optical absorption spectra were taken using a Helios Gamma spectrophotometer (Thermo, Great Britain) in the range of 200-800 nm. Prior to UV-Vis measurements, samples were dispersed in absolute ethanol.

The surface charge of mechanochemically synthesized ZnSe particles and ZnSe nanoparticles after subsequent remilling in $ZnCl_2$ solution was determined by the laser-Doppler electrophoretic light scattering Zetasizer Nano-Z (Malvern, Great Britain) using a 4 mW He-Ne laser (λ=632.8 nm). ζ-potential can be converted from measured electrophoretic mobility using the Smoluchowski´s equation:

$$\zeta = \frac{\eta U_E}{\varepsilon} \quad (2)$$

where ζ is the zeta-potential, ε is the dielectric permittivity of the solution (equal to $\varepsilon_0\varepsilon_r$, ε_0 is the permitivity of the vacuum and ε_r the relative permitivity of solution), U_E is the electrophoretic mobility of the dispersed particles and η is the viscosity of the dispersed phase. The ζ-potentials were calculated from the electrophoretic mobility using eq. (2), wherein the thickness of the electrical double layer is assumed to be smaller in comparison to the dispersed particle size. The Smoluchowski equation (without any other correction) as an approximation was used. 1 g of sample was dispersed in 1L of deionized water for the measurements. Then the each dispersion was subjected to sonification for 15 min. The pH of dispersions was 5.76. For each sample 3 measurements were averaged to determine the corresponding ζ-potential.

Results and discussion

The XRD patterns of mechanochemically synthesized ZnSe and re-milled ZnSe in the presence of $ZnCl_2$ solution are plotted in Figure 1. The results confirm that mechanochemically synthesized ZnSe contain 73 % of cubic (Stilleite, ICDD PDF 37-1463) and 16 % hexagonal (ICDD PDF 80-0008) ZnSe modifications (Tab. 1). Subsequent wet re-milling for 110 min brought about decreasing of the cubic phase and increasing of the hexagonal phase in ZnSe and the size of cubic and hexagonal crystallites has also markedly decreased. The agglomerates of ZnSe typically produced by dry milling were broken into the particles having the crystallites of 19 and 2.5 nm diameter after re-milling in $ZnCl_2$ solution. The amount of unreacted Zn has decreased to zero with re-milling in $ZnCl_2$ solution as well.

Tab. 1. Time of milling, t_M, the content of synthesized cubic ZnSe phase, C-phase, the content of synthesized hexagonal ZnSe phase, H-phase, cubic crystallite size, d_C, hexagonal crystallite size, d_H, and the contents of unreacted Zn and Se for mechanochemically synthesized ZnSe in planetary ball mill (PM) and for ZnSe re-milled in circulation mill (PM/CM).

Sample	**t_M** [min]	**C-phase** [%]	**d_C** [nm]	**H-phase** [%]	**d_H** [nm]	**unreacted Zn** [%]	**unreacted Se** [%]
PM	20	73	50	16	145	6	5.5
PM/CM	20/110	61	19	31	2.5	0	8

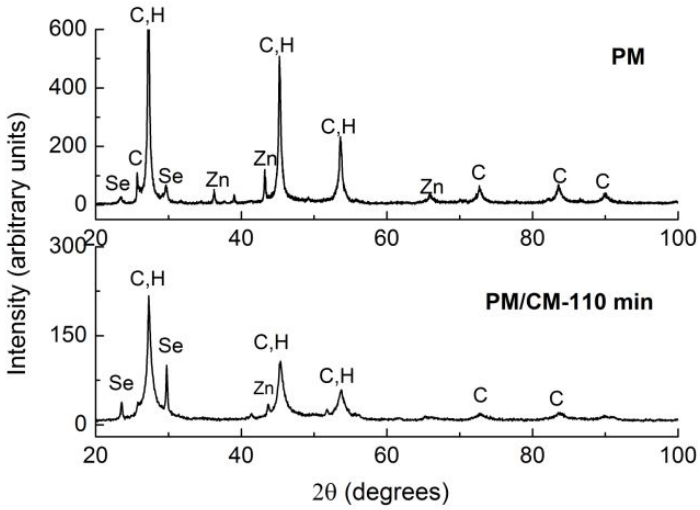

Fig. 1. X-ray diffraction patterns of mechanochemically synthesized ZnSe (PM) in planetary ball mill and re-milled ZnSe (PM/CM) in circulation mill for 110 min. C-cubic ZnSe, H-hexagonal ZnSe.

TEM analysis of mechanochemically synthesized ZnSe after 20 min of milling (sample PM, Tab. 1) has revealed that the sample contains two types of ZnSe grains: nanosized particles and larger up to about 1 μm large particles (Fig. 2a). Selected area electron diffraction (SAED) analysis has shown the nanosized particles have mostly cubic ZnSe modification, whereas the larger ZnSe particles mainly have comprised hexagonal modification of ZnSe. The favourable effect of wet re-milling on refinement of particles is clearly seen in Fig. 2b. Although in both cases the prepared particles were found in agglomerated state, those treated by wet re-milling (Fig. 2b) are characterized by smaller size (<50 nm) and have more homogenous distribution. The selected area electron diffraction pattern (SAED, Fig. 2b-inset) reflects the nanoscale character of prepared ZnSe sample.

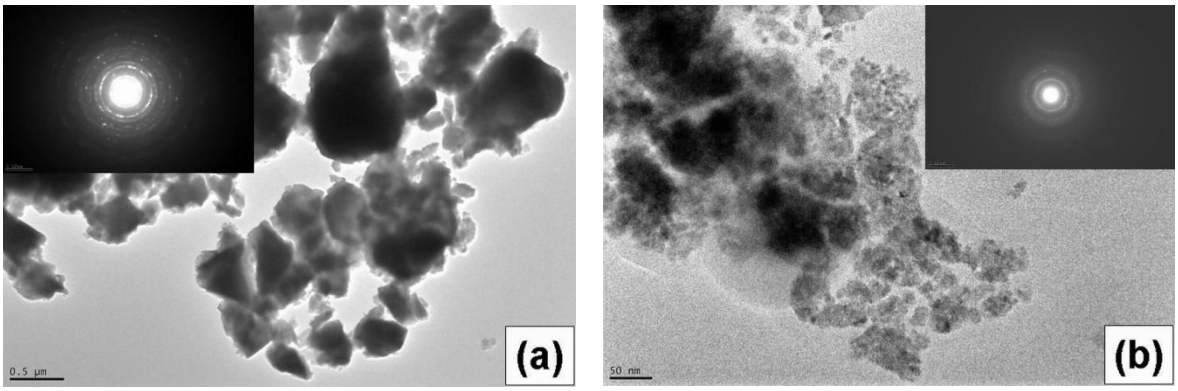

Fig. 2. (a) TEM image of the ZnSe mechanochemically synthesized after 20 min of milling (sample PM), (b) TEM image of the ZnSe mechanochemically synthesized after 110 min of wet re-milling in $ZnCl_2$ (sample PM/CM).

Figure 3 shows the particles of PM and PM/CM-30 min ZnSe samples have non-monomodal (polydispersive) density distribution. With increasing time of re-milling or circulation milling ZnSe particles assign monomodal density distribution and particle mean diameter values, x_{50} are decreasing (Tab. 2). Comparing PM-sample and sample re-milled in circulation mill in the presence of $ZnCl_2$ for 110 min particle mean diameter has decreased 4.3 times.

Tab. 2. The values of particle mean diameter and ζ-potential values for mechanochemically synthesized ZnSe in planetary ball mill (PM) and for ZnSe re-milled in circulation mill (PM/CM).

Sample: re-milling time [min]	**PM**	**PM/CM:30**	**PM/CM:60**	**PM/CM:110**
Particle mean diameter, x_{50} [nm]	912	866	226	210
ζ-potential [mV]	-44.58	-2.41	+4.22	+3.69

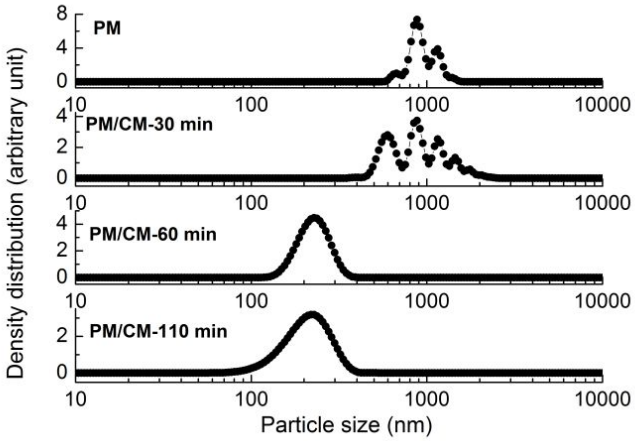

Fig.3. Density distribution curves of the mechanochemically synthesized ZnSe particles in planetary ball mill (PM) and ZnSe particles re-milled in circulation mill with $ZnCl_2$ (PM/CM).

UV-Vis optical absorption spectra for mechanochemically synthesized ZnSe in planetary ball mill and for ZnSe re-milled in circulation mill with $ZnCl_2$ solution are given in Figure 4 and they confirmed that samples re-milled with $ZnCl_2$ for 30 and 110 min contain nanoparticles. Their spectra assigned the blue shift from direct band gap energy of 2.67 eV characteristic for bulk ZnSe crystals (Wang and Du, 2006). The spectra illustrate the extended small absorption edges at about 252 nm and 260 nm that correspond to 4.93 and 4.77 eV. The spectrum of mechanochemically synthesized ZnSe in planetary ball mill has shown no absorption edge, and therefore, no blue shift from the direct band gap energy of bulk ZnSe crystals. This has evidenced, that particles mechanochemically synthesized in planetary ball mill are strongly aggregated.

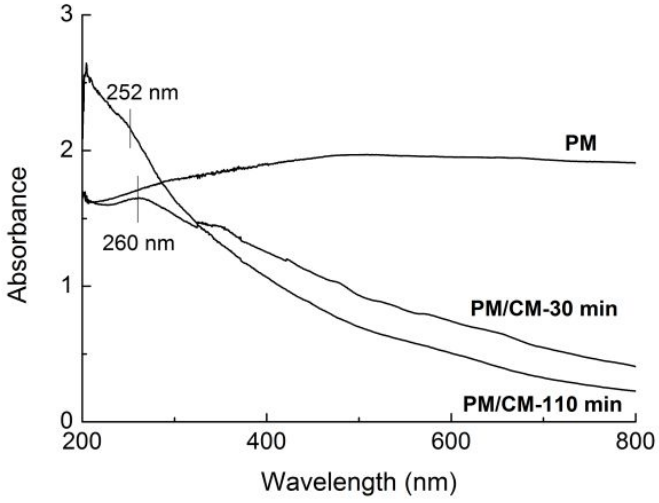

Fig.4. UV-Vis optical absorption spectra for mechanochemically synthesized ZnSe in planetary ball mill (PM) and for ZnSe re-milled in circulation mill (PM/CM).

Generally, ζ-potential indicates the degree of repulsion between adjacent, similarly charged particles in the dispersion. A value of 30 mV (negative or positive) can be taken a general dividing line separating low-charged surfaces from highly-charged surfaces (Zetasizer Nano Series User Manual 2004). In our case ζ-potential of mechanochemically synthesized ZnSe particles and ZnSe particles re-milled with $ZnCl_2$ solution has changed from -44.58 to +3.69 mV. That means the divalent Zn^{2+} cations were adsorbed at the negatively charged mechanochemically synthesized ZnSe surface with increasing time of circulation milling (Tab. 2). The negative surface charge of ZnSe particles has decreased and changed to positive values in consequence of circulation milling in presence of $ZnCl_2$ solution. Probably attractive forces still prevail between the surfaces of ZnSe particles in 10^{-3} M $ZnCl_2$ solution at pH 5.76.

Conclusions

Comparative study of structural and physical properties of mechanochemically synthesized ZnSe and subsequently re-milled ZnSe in $ZnCl_2$ solution was performed. XRD analysis has confirmed that ZnSe contains cubic and hexagonal phases and after re-milling of mechanically synthesized ZnSe in $ZnCl_2$ solution in circulation mill the cubic crystallite size has decreased 2.6-times and the hexagonal crystallite size has decreased 58-times. TEM analysis has also demonstrated the favourable effect of wet re-milling on the refinement of ZnSe nanoparticles under 50 nm and their homogenity. ZnSe particles have assigned monomodal density distribution with increasing time of re-milling and particle mean diameter value, x_{50} has decreased 4.3-times after 110 min of re-milling. UV-Vis optical absorption spectra of remilled ZnSe have assigned the blue shift from direct band gap energy of 2.67 eV characteristic for bulk ZnSe crystals. In consequence of re-milling in solution of Zn^{2+} cations ζ-potential of ZnSe has changed from -44.58 to +3.69 mV. However, total de-aggregation and stabilization of ZnSe nanoparticles has not been achieved.

***Acknowledgement**: The present work was supported by the Slovak Grant Agency VEGA (project 2/0043/11), the Slovak Research and Development Agency APVV-0189-10, and Centre of Excellence of Advanced Materials with Nano- and Submicron-Structure (NANOCEXMAT-26220120019 and 26220120035) that is supported by the Operational Program "Research and Development" financed through European Regional Development Fund.*

References

Archana, J., Navaneethan, M., Ponnusamy, S., Hayakawa, Y., Muthamizhchelvan, C.: Optical, structural and surface morphological studies of bean-like triethylamine capped zinc selenide nanostructures. *Materials Letters 63, 1931-1934.*

Baláž, P., Mockovčiaková, A., Boldižárová, E., Ficeriová, J.: Physical and chemical changes of sulphides during intensive grinding in organic liquids. *Powder technology 98, 74-78, 1988.*

Baláž, P., Achimovičová, M., Baláž, M., Billik, P., Cherkezova-Zheleva, Z., Criado, J.M., Delogu, F., Dutková, E., Gaffet, E., Gotor, F.J., Kumar, R., Mitov, I., Rojac, T., Senna, M., Streletskii, A., Wieczorek-Ciurowa, K.: Hallmarks of mechanochemistry: from nanoparticles to technology. *Chemical Society Review, Advance Article, DOI: 10.1039/C3CS35468G, 2013.*.

Baltazar-Rodrigues, J., de Lima, J.C., Campos, C.E.M., Grandi, T.A.: Temperature effect on mechanically alloyed nanometric ZnSe powder. *Powder Technology 189, 70-73, 2009.*

Bhattacharya, P., Bellon, P., Averback, R.S., Hales, S.J.: Nanocrystalline TiAl powders synthesized by high-energy ball milling: effects of milling parameters on yield and contamination. *Journal of Alloys and Compounds 368, 187–196, 2004.*

Cao, H., Xiao, Y., Zhang, S.: The synthesis and photocatalytic activity of ZnSe microspheres. *Nanotechnology 22, 015604 (8pp), 2011.*

de Lima, J.C., dos Santos, V.H.F., Grandi, T.A.: Structural study of the Zn-Se system by ball milling technique. *Nanostructured Materials 11, 51-57, 1999.*

Fedorov, V.V, Gallian, A., Moskalev, I., Mirov, S.B.: En route to electrically pumped boadly tunable middle infrared lasers based on transition metal doped II-VI semiconductors. *Journal of Luminescence 125, 184-195, 2007.*

Gotor, F.J., Achimovicova, M., Real, C., Balaz, P.: Influence of the milling parameters on the mechanical work intensity in planetary mills. *Powder Technology 233, 1–7, 2013.*

Guérard, D.: Ball milling in the presence of a fluid: results and perspectives. *Reviews on Advanced Materials Science 18, 225-230, 2008.*

Haas, S., Hässlin, H.W., Schlatter, Ch.: Influence of polymeric surfactants on pesticidal suspension concentrates: dispersing ability, milling efficiency and stabilization power. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects 183–185, 785–793, 2001.*

Jones, A.C.: Development in metalorganic precursors for semiconductor growth from the vapour phase. *Chemical Society Reviews 26, 101-110, 1997.*

Kumar, K., Singh, J.: Wurtzite ZnSe quantum dots: Synthesis, characterization and PL properties. *Journal of Optoelectronic und Biomedical Materils 1, 59-69, 2009.*

Li, Y.D., Ding, Y., Qian, Y.T., Zhang, Y., Yang, L.: A solvothermal elemental reaction to produce nanocrystalline ZnSe. *Inorganic Chemistry 37, 2844-2845, 1998.*

Murray, C.B., Norris, D.J., Bawendi, M.G.: Synthesis and characterization of nearly monodisperse CdE (E=sulfur, selenium, tellurium) semiconductor nanocrystallites. *Journal of the American Chemical Society 115, 8706-8715, 1993.*

Peng, X., Wilson, T.E., Alivisatos, A.P., Schultz, P.G.: Synthesis and isolation of a homodimer of cadmium selenide nanocrystals. *Angewandte Chemie: International Edition in English 36, 145-147, 1997.*

Tangsathitkulchai, C.: Acceleration of particle breakage rates in wet batch ball milling. *Powder Technology 124, 67-75, 2002.*

Wang, C., Zhang, W.X., Qian, X.F., Zhang, X.M., Xie, Y., Qian, Y.T.: An aqueous approach to ZnSe and CdSe semiconductor nanocrystals. *Materials Chemistry and Physics 60, 99-102, 1999.*

Wang, H., Du, F.: Hydrothermal synthesis of ZnSe hollow microspheres. *Crystal Research and Technology 41, 323-327, 2006.*

Wang, Y., Herron, N.: Nanometer-sized semiconductor clusters: materials synthesis, quantum size effects and photophysical properties. *Journal of Physical Chemistry 95, 525-532, 1991.*

Williams, S.R., and Phelan, J.M.: Process development at Woodlawn Mines. In: Zunkel, A.D., Boorman, R.S., Morris, A.E. and Wesely, R.J. eds., *Complex sulphides processing of ores, concentrates and by-products, The AIME, Pensylvania, 293-304, 1985.*

Yu, K., Ma, Ch.M., Teng, Ch, Huang, Y., Yuen, S., Liao, S., Lee, S., Chang, Ch.: Preparation and microwave absorbency of Fe/epoxy and FeNi3/epoxy composites. *Journal of Alloys and Compounds 509, 8427– 8432, 2011.*

Zetasizer Nano Series User Manual, Malvern Instruments Ltd., *Man 0317, Issue 1.1., Feb. 2004*.

Zhang, L., Yang, H., Xie, X., Zhang, F., Li, L.: Preparation and photocatalytic activity of hollow ZnSe microspheres via Ostwald ripening. *Journal of Alloys and Compounds 473, 65–70, 2009.*