In order to investigate the effect of particle size and morphology on the optical properties of ZnO, a series of ZnO powders were synthesized by low-temperature hydrothermal processing using zinc acetate dihydrate and sodium hydroxide as the starting materials, and polyvinylpyrrolidone as the stabilizing agent. The particle size and morphology were tailored by adjusting the reactant molar ratios ([Zn^{2+}]/[OH^-]) from 1:1 to 1:5. The optical properties of the ZnO powders as well as their dependence on the particle size and morphology were investigated by Ramon and UV-Vis diffuse reflectance spectroscopy (DRS).

Experimental

In the series of experiments, the reaction temperature and time were kept constant, while the [Zn^{2+}]/[OH^-] molar ratio in the starting solution was changed in order to tailor the particle size and shape. Namely, the [Zn^{2+}]/[OH^-] molar ratio was varied from 1:1, 1:2, 1:3, 1:3.5, 1:4 to 1:5, resulting in the pH values of the reaction solution: 9, 10, 11, 12 and 13, respectively. The starting materials, zinc acetate dihydrate (Zn(CH_3COO)_2·2H_2O), sodium hydroxide (NaOH) and polyvinylpyrrolidone (PVP, (C_6H_9NO)_n) as a stabilizing agent, were used without any additional treatment. (0.01 mol) of zinc acetate dihydrate and PVP, an adequate amount of the aqueous solution of NaOH was added dropwise, resulting in a white precipitate. The as-prepared suspension was thermally treated in 2 l Parr stainless steel stirred reactor under non-equilibrium conditions up to 120 °C at a constant heating rate of 2 °C/min, under constant stirring of 400 rpm. The reaction time was 72 h.

Results and discussion

The XRD patterns of the prepared ZnO powders are presented in Fig. 1. All of the diffraction peaks in the recorded XRD patterns are in agreement with those of hexagonal wurtzite ZnO without peaks related to impurities or ZnO in other crystal phases. The unit cell parameters, crystallite size (D) in crystallographic directions [100], [010] and [002], and the crystallinity degree of the ZnO powders are calculated and listed in Table 1.

The morphologies of the synthesized ZnO powders are shown in Fig. 2. ZnO powders, synthesized at pH 8, consists of micro-rods. The hydrothermal processing performed at pH 9 led to changes in the particle shape from cracked micro-rods to non-ideal hexagonal prisms; the edges of the hexagonal prisms were non-ordered, while the pyramids at their ends were partly formed. At pH 10, the particles with regular geometrical shape corresponding to the hexagonal structure and uniform size distribution were prepared (Fig. 2, ZnO10). Powder ZnO11, consists of ellipsoidal particles. When the pH value was tuned to 12, powder with spherical particles which tend to group in clusters of around 200 nm in diameter was synthesized, ZnO12. Finally, ZnO13 powder, synthesized at pH 13 consists of spherical nano-sized particles with average diameters of ~50 nm.

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The optical properties of the ZnO powders were determined by the extrapolation of the linear part of the absorption function (F(E))2, presented in Fig. 7. A slight red-shift of 0.06 eV which occurs in the absorption edge, meaning that micro-rods absorb a larger amount of visible light, can be explained by a longer optical path for light transport through the micro-rods (ZnO8, ZnO9) than through sub-micron or nano-particles (ZnO12, ZnO13).

The direct band gap energies (Eg) of the ZnO powders were determined by the extrapolation of the linear part of the absorption function (F(E))2, presented in Fig. 7. A slight red-shift of 0.06 eV which occurs in the absorption edge, meaning that micro-rods absorb a larger amount of visible light, can be explained by a longer optical path for light transport through the micro-rods (ZnO8, ZnO9) than through sub-micron or nano-particles (ZnO12, ZnO13), resulting in a greater absorption capacity.