



## Original Research Paper

Zinc oxide nanoparticles with surface modified by degradation of capping polymers *in situ* during microwave synthesis

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## ABSTRACT

Surface modified zinc oxide nanoparticles with variable lipophilicity were prepared by the help of microwave-assisted solvothermal synthesis from mechano-chemically prepared precursor. Sodium carbonate and zinc acetate dihydrate were used as starting materials, diethylene glycol was used as a solvent, poly(ethylene glycol) and polyvinyl alcohol were used as surface capping agents. The zinc oxide was obtained during the first three minutes of reaction and its surface was further modified with prolonged time of the reaction due to degradation of polymers used as capping and stabilising agents. Scanning Electron Microscopy was employed for powder morphology evaluation. Inorganic phase structure development was characterized by means of X-ray diffraction. Nanostructured composite materials with crystallite size below 10 nm were obtained with specific surface area varying from 35 to 86 m<sup>2</sup> g<sup>-1</sup> according to Brunauer–Emmett–Teller analysis. The progress of degradation of adsorbed polymer moieties was manifested by the powder colour change. Optical properties as well as the structure of materials were further analysed by Diffuse Reflectance Ultraviolet–visible Spectroscopy and Diffuse Reflectance Infrared Fourier Transform Spectroscopy and correlated with Thermogravimetric observations and Lipophilicity degree analysis.

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## 1. Introduction

Zinc oxide is a versatile semiconductive material with wide direct band gap (3.3 eV), and large exciton binding energy (60 meV) [1], potentially applicable in electronics [2], solar energy conversion [3], light emitting devices [4], gas-sensors [5], etc. Apart from its application in sophisticated devices, ZnO powder is also a relatively cheap chemical available in large amounts and various forms ready for applications as pigments [6], UV-protecting additive [7], antimicrobial and antifungal fillers for polymers [8,9], sun-screens and medical ointments [10,11]. The chemical properties of ZnO are utilised in chemical engineering and material processing. The largest quantity is consumed in rubber industry because ZnO is still unrivalled activator of sulphur vulcanisation [12]. On the other hand, much finer and demanding application of ZnO can be found in photocatalysis [13] and biomedicine [14,15]. Zinc oxide has most likely the most abundant forms among metal oxide materials. The properties of ZnO are strongly

dependent on its structure, morphology, aspect ratio, particle size and orientation [16–18]. Moreover, a careful reading of all above mentioned literature sources points towards the importance of surface structure and properties as the crucial factors for almost all applications of ZnO powder materials.

Surface modification of microparticles or nanoparticles is one of the most effective ways of controlling their properties for preparation of new types of smart materials with desired structure [19]. In the past decade, many scientists were focused on improving surface properties of different zinc oxide powder materials [20–22]. Some applications require bare ZnO particles with specific surface defect microstructure [23]. The easiest way how to obtain such particles usually employs calcination at optimum temperature and atmosphere [24]. On the other hand, it is often required to cover the ZnO particle surface by a functional shell and many methods have been proposed for such surface modifications of ZnO. So far, coated ceramic fillers have been successfully prepared [25,26]. Thin SiO<sub>2</sub> coatings are used to avoid photodegradation of polymer matrix when the ZnO powder is used as UV absorber in plastics [27] or in sunscreens [28]. On contrary, organic coatings usually serve as stabilising and dispersing agents that do not passivate the material function and the spectrum of surface functionalization approaches is at least as wide as for inorganic ones [29].

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Nano ZnO shows strong antibacterial activity also without the presence of light; therefore, coatings absorbing light can be applied against their easy dissolution and hydration reactions at various pH and other conditions [22].

According to our opinion, it is reasonable to couple synthesis of ZnO particles with the coating operation into one reaction step, which can be beneficial in terms of time, material and energy savings, especially if combined with the use of a rapid synthesis method.

Microwave (MW) radiation is an efficient heating method, which can significantly decrease reaction time and its advantages were already demonstrated by preparation of different materials in our previous works [30–33]. Here we adopted [34] and further developed a fast and easy method for preparation of surface modified ZnO nanoparticles with an organic shell layer in two stages. Mechanochemical preparation of a precursor from simple chemicals in the first step is followed by a MW assisted solvothermal reaction step in an open vessel reflux system used with advantage under atmospheric pressure. The MW enhanced reaction takes a few minutes only. The surface coating is developed at the expense of progressive degradation of capping and stabilizing polymers in the high boiling temperature solvent reaction mixture. The coating properties are simply dependent on the MW exposure time.

## 2. Materials and methods

### 2.1. Synthesis methodology

Sodium carbonate anhydrous, p.a., (purity 99%, Penta, Czech Republic), zinc acetate dihydrate, p.a., (purity 99%, Penta, Czech Republic), diethylene glycol, p.a., (purity 99%, Penta, Czech Republic), polyethylene glycol 400, p.a., (Fluka, Germany), poly(vinyl alcohol) Mowiol 8-88, (Mw ~ 67,000, Sigma Aldrich) were used as starting chemicals. Precursor (sample denoted as S0) was prepared by grinding of 11 g  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  with 20 ml of 10 wt% solution of poly(vinyl alcohol) (PVA) in diethylene glycol (DEG) for 5 min in a vibration mill (VM 4, Czech Republic), followed by addition of 5.3 g of  $\text{Na}_2\text{CO}_3$  and grinding continued for about 20 min. Obtained pasty mixture was washed by demineralised water and ethanol to remove possible by-product or rests of original soluble chemicals. The white powder dispersion was collected by a suction filtration and obtained filtration cake was left to dry freely. Synthesis of final products started by a mixing of 1.5 g of precursor with 80 ml of DEG and 10 ml of polyethylene glycol (PEG) in a boiling flask. The mixture was stirred vigorously with a magnetic stirrer and then sonicated in ultrasound bath (Elma S 80, Ultrasonic) for 15 min to achieve better dispersion of the precursor in the liquid medium. Possible metal chips originating from milling drum and bodies were removed by a magnet. Six individual mixtures were prepared and then exposed to microwave (MW) irradiation in open vessel system for different reaction times from 1.5 to 5 min. Microwave reaction was performed in a modified domestic microwave oven (CRW-TECH, frequency 2.45 GHz, maximum power 1150 W, unknown land of origin) equipped with an external condenser. All mixtures were heated at maximum heating power. The suspensions were left to cool to the laboratory temperature after MW exposure. Precipitates were collected by suction filtration, washed with demineralised water followed by ethanol and finally dried in air up to the constant weight. In this way, six different final products were obtained numbered according to their order from shortest to longest reaction time, i.e. from S1 to S6 (S1-1.5 min; S2-2 min; S3-2.5 min; S4-3 min; S5-4 min; S6-5 min).

### 2.2. Measurements and analysis

Microscopic images of samples were taken by the use of scanning electron microscope Tescan Vega LMU (Tescan, Czech Republic).

The phase structure of powders was characterized by powder X-ray diffraction (XRD) using X'Pert PRO X-ray diffractometer (PANalytical, The Netherlands) with  $\text{Cu K}\alpha$  radiation of  $\lambda = 0.1540598$  nm. The size of ZnO crystallites was considered to be nearly identical with the size of diffracting area  $d_{\text{diff}}$  which is easily accessible via Scherrer's formula using  $\Delta(2\theta)$  which is full-width at half-maximum (FWHM) of XRD patterns. The particle shape and other factors were neglected to simplify the procedure and the calculation followed the well-known formula [35]:

$$d_{\text{diff}} = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where the constant 0.9 is the shape factor,  $\lambda$  is the wavelength of the X-ray source,  $\beta$  is the FWHM in radians. The actual value of  $\beta$  was obtained by deconvolution of instrumental broadening effects using Warren correction method. The  $\theta$  is the Bragg angle, i.e. the half of the  $2\theta$  position of the selected diffraction line.

The TA Q 500 apparatus (TA Instruments, US) was used for thermogravimetric analysis (TGA). This analysis was performed at the constant heating rate of 10 °C/min under stable air flow. The amount of each sample was approximately 15 mg.

The study of UV–vis absorption of the powder samples was performed with the aid of the UV–vis spectrometer AvaSpec 2048-2 (Avantes, The Netherlands) with the light source type AvaLight-DHS-DUV. Integrating sphere ( $\text{BaSO}_4$  coated) and white tile  $\text{BaSO}_4$  reflectance standard were used for relative diffuse reflectance (DR-UV–vis) spectrometry. The relative reflectance was recorded for wavelengths in the range 265–800 nm due to relatively small sensitivity of the detector in NIR on one side and reflectance limit of the sphere coating material in UV on other side of spectral range.

FTIR spectrometer Nicolet 6700 (Thermo Scientific, US) was used for collection of infrared DRIFT spectra, utilizing 32 scans and resolution  $4 \text{ cm}^{-1}$  setup. The spectra are presented in Kubelka–Munk units.

The specific surface area was obtained via the multipoint Brunauer–Emmett–Teller analysis of nitrogen adsorption/desorption isotherms at 77 K recorded by Belsorp-mini II (BEL Japan, Inc.) apparatus. Samples were outgassed for 3 h at 115 °C prior to the measurements.

The lipophilic degree (LD) of nanoparticles is usually characterized by examination of dispersibility of defined amount of nanoparticles in water with the addition of organic solvent (methanol). Hence, the LD is expressed actually in vol% units. The original method [19,36] is relatively material demanding as each test of single liquid concentration consumes 0.5 g of sample. Therefore, we adopted the LD concept but modified the procedure in accordance with the framework of theoretical and practical analysis of wetting and dewetting of powders [37]. A series of stock water–methanol mixtures was prepared ranging from pure distilled water up to pure methanol graded in 5 vol% steps. The lipophilic degree was estimated as the concentration of the water–methanol mixture which readily wetted the tested powder. In more detail, the procedure was as follows: A small amount of powder (approx. 0.5 g) was spread into a uniformly thick layer on a glass substrate and tested by droplets of 5  $\mu\text{L}$  of testing liquids. The measurement was several times repeated for each sample in ascending as well as in descending order of used concentrations to find precisely the transition between wetting and dewetting behaviour.

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