

Short communication

# Synthesis of stabilized nanoparticles of zinc peroxide

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## Abstract

Stabilized nanoparticles of zinc peroxide were formed by a novel and simple technique. The technique is based on oxidation–hydrolysis–precipitation procedure, using zinc acetate as a precursor. The oxidizer was hydrogen peroxide and water was used for hydrolysis and as a preparation medium. The surface modifier was polyethylene glycol 200 (PEG200). ZnO<sub>2</sub> was identified and studied by a variety of characterization techniques, including DLS, XRD, DSC, and TEM. Quite stable nanoparticles of ZnO were also obtained from the peroxide powder by heat treatment. The transition temperature, 233 °C, was determined by DSC.

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**Keywords:** Zinc peroxide; Stabilized nanoparticles; PEG; Zinc oxide

## 1. Introduction

Zinc peroxide is mostly used in the rubber industry [1–5], and for high-tech plastic processing [6,7] it may function as an oxidant and oxygen donor in compositions or mixtures containing explosive materials and pyrotechnical mixtures [8]. Zinc peroxide can also be useful in the cosmetic [1,9] and pharmaceutical industries and for therapeutic applications [9–12].

Zinc peroxide preparation is well known. It is mostly produced by adding one of the following: ZnO [13,14]; Zn(OH)<sub>2</sub> [14,15]; ZnEt<sub>2</sub> [16]; Zn(NO<sub>3</sub>)<sub>2</sub> [13,17]; ZnCl<sub>2</sub> [18] or ZnCO<sub>3</sub> [14], to a solution of hydrogen peroxide, sometimes with an additional source of energy such as light. Nanoparticles of zinc peroxide can additionally be used as precursor for preparation of ZnO nanoparticles [19,20]. Preparation of stabilized nanoparticles of zinc peroxide has been reported [21], using zinc oxide as precursor and phosphate acid or salt derivatives as stabilizers.

In a previous work in our lab [22], nano-sized titanium dioxide (TiO<sub>2</sub>) has been stabilized successfully. In this study we have employed this stabilization technique to prepare zinc peroxide nanoparticles. For this purpose, zinc acetate [Zn(CH<sub>3</sub>COO)<sub>2</sub>] has been used as precursor and polyethylene glycol 200 (PEG200) as a surface modifier. To examine the efficiency of the surface modifier as nanoparticle stabilizer, the ZnO<sub>2</sub> has

been produced in two different mediums: without PEG200 (ZnO<sub>2</sub>–WOPEG) and with PEG200 (ZnO<sub>2</sub>–WPEG).

## 2. Experimental

### 2.1. Materials

Zinc acetate dehydrate, Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (Fluka, 99.5%); 30% hydrogen peroxide aqueous solution, H<sub>2</sub>O<sub>2</sub> (Carlo Erba); PEG 200, H(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH (Fluka); and sodium hydroxide, NaOH (Ridel deHaen, 99%) were used in their commercial forms.

### 2.2. Preparation of ZnO<sub>2</sub> nanoparticle solution

Three grams of zinc acetate dehydrate was dissolved in 30 mL distilled water and 15 mL of 30% H<sub>2</sub>O<sub>2</sub>. One hundred and twenty milliliter of PEG 200 was added to the stirring mixture. The preparation procedure was carried out in a continuously stirred opened glass beakers, V=0.25 L, at room temperature. The stirrer velocity was kept constant for all the experiments. After 2 h of stirring, a clear and colorless to yellowish solution has been received.

### 2.3. Preparation of ZnO<sub>2</sub> nanoparticle powder

In order to precipitate the product, NaOH solution (pH 13) was added to form a basic medium. This was done until a pH

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Table 1  
Possible stabilizers (sizes in nm by volume)

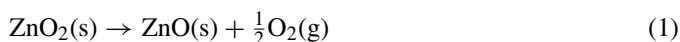
	Ethylene glycol	Di(ethylene glycol)-methyl ether	PEG200	PEG1000	PEG4000	ZnO <sub>2</sub> WOPEG
D50	Not stable	48	19	Not stable	Not stable	193
D90	Not stable	75	29	Not stable	Not stable	269

value of 11.5 was achieved. Upon the addition of the NaOH, the mixture was changed to a white color suspension.

The white precipitate was separated by centrifuge and after the centrifugation process the powder was washed three times by NaOH solution. Finally, two additional washes by distilled water were done until final pH of 8.4 for the residue water was reached. The resultant precipitate was dried at 80 °C for 2 h in an evacuated oven.

#### 2.4. Preparation of ZnO nanoparticle powder

Dried ZnO<sub>2</sub> powder was heated at 300 °C for 10 h in an evacuated oven. The powder is decomposed by the following reaction:



The decomposition temperature is sufficiently low, and hence the resulting ZnO primary particles remain nanometric, although the ZnO powders are agglomerated.

#### 2.5. Characterization techniques

Particle size of the ZnO<sub>2</sub> nanoparticle solution was measured in water suspensions by dynamic light scattering (DLS), using a Zeta PALS, Brookhaven Instruments Corporation, equipped with 35 mW,  $\lambda = 660$  nm solid state laser and an avalanche diode detector.

ZnO<sub>2</sub> nanoparticle powders, with PEG (ZnO<sub>2</sub>-WPEG) and without PEG (ZnO<sub>2</sub>-WOPEG), were characterized by three methods: transmission electron microscopy (TEM) observations were performed using a Philips CM120 working at 120 kV. X-ray diffraction (XRD) patterns were obtained on a Philips X'pert powder diffractometer, Cu K $\alpha$ , with step size of  $\Delta 2\theta = 0.05^\circ$ . Differential scanning calorimetry (DSC) analyses were performed using a TA Q10.

ZnO nanoparticle powder with PEG (ZnO-WPEG) and without PEG (ZnO-WOPEG), were characterized by the same three methods that are described above and in addition by TGA using a TGA/DTA, 92-16.18, Setaram. DLS measurements on ZnO powders that were re-dispersed in water were also performed.

Table 2  
particle sizes (nm, by volume) obtained with different ratios of H<sub>2</sub>O/PEG200

	0% PEG	3% PEG	10% PEG	20% PEG	30% PEG	50% PEG	80% PEG
D50	193	23	32	13	31	22	19
D90	269	38	44	19	63	33	29

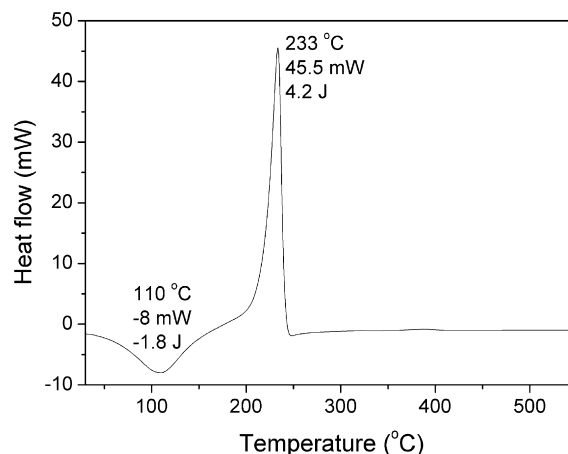


Fig. 1. DSC curves for ZnO<sub>2</sub>-WPEG 15.27 mg sample.

### 3. Results and discussion

#### 3.1. Characterization of the ZnO<sub>2</sub> nanoparticle solution

The ZnO<sub>2</sub> nanoparticle solutions of Section 2.2 were examined by DLS. The results show a significant difference between the two mixtures, namely with PEG200 (WPEG) and without

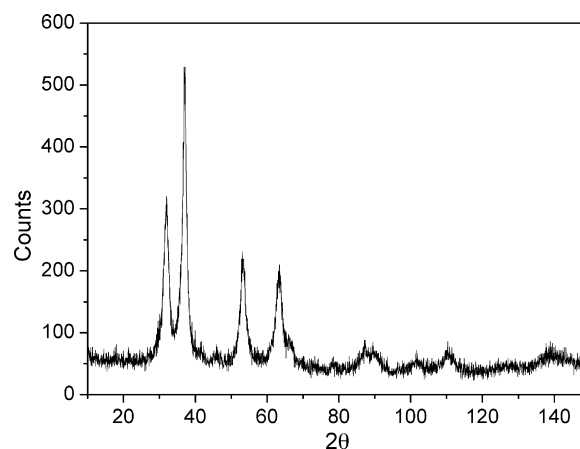


Fig. 2. XRD of ZnO<sub>2</sub>-WPEG.

PEG200 (WOPEG).

ZnO<sub>2</sub>-WPEG : $D(50) = 19$  nm and  $D(90) = 29$  nm

ZnO<sub>2</sub>-WOPEG : $D(50) = 193$  nm and  $D(90) = 269$  nm

This demonstrates that the PEG200 is important for obtaining nanoparticles, probably due to steric stabilization that the PEG200 provides [22]. Different possible stabilizers have been tried in a preliminary study. This includes ethylene glycol, Di(ethylene glycol)-methyl ether, PEG200, PEG1000 and PEG4000. The best results were obtained with the PEG200 and hence we chose it. See Table 1.

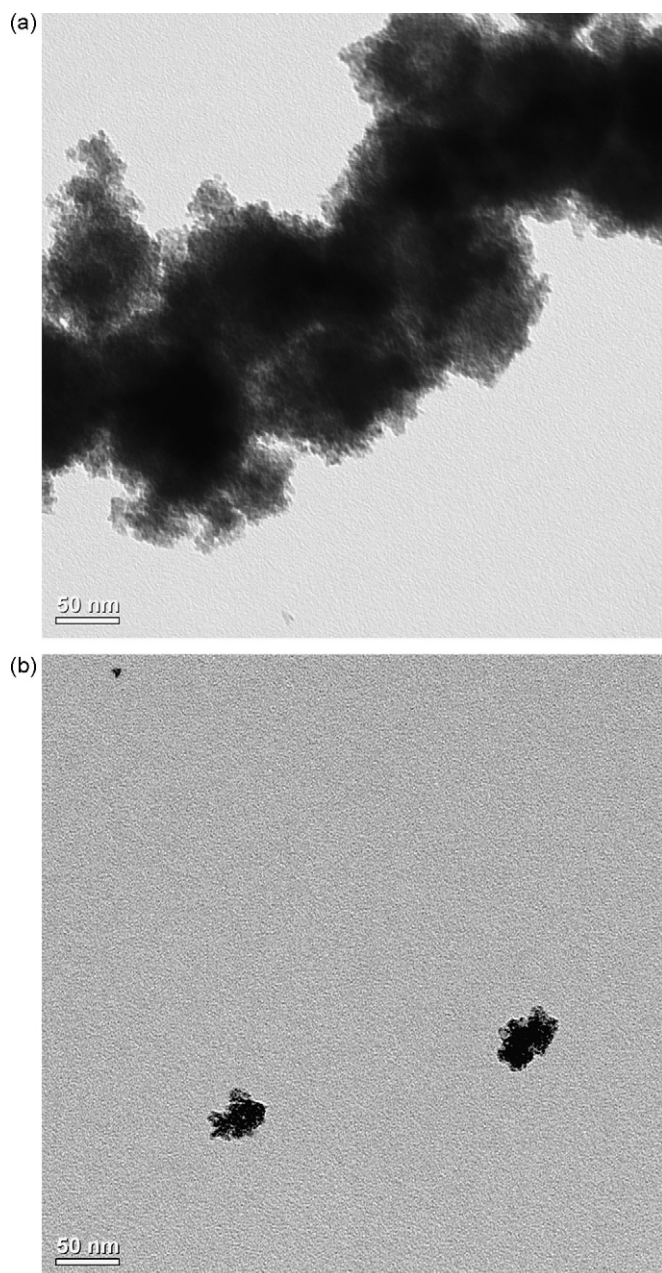


Fig. 3. TEM micrographs of as precipitated (a) ZnO<sub>2</sub>-WOPEG and (b) ZnO<sub>2</sub>-WPEG. The bars are 50 nm.

We have later tried different ratios of H<sub>2</sub>O/PEG200. Reasonable results were obtained with less PEG200, and definitely this should be explored in more details later on. Since we have done most of our characterization measurements on the 80%PEG, we present it here. The particle sizes (by volume) obtained with different ratios are presented in Table 2.

### 3.2. Characterization of the nanoparticle powders

The DSC results, Fig. 1, reveal two peaks, an endothermic one (at 110 °C) for water and perhaps also the PEG release and an exothermic one (at 233 °C) for oxygen release, according to Eq. (1). The temperature of the oxygen release (233 °C), is in accord with the value from the literature [9] (>150 °C) and may serve as an update to it. The fact that the exothermic peak is related to Eq. (1) was verified by XRD, as described below.

XRD analysis was done on ZnO<sub>2</sub>-WOPEG and ZnO<sub>2</sub>-WPEG powders in order to identify the material. A representative result is shown in Fig. 2, for ZnO<sub>2</sub>-WPEG, and a similar result was received for the other sample as well. The four dominant peaks:  $2\theta = 32.0, 37.1, 53.4, 63.4^\circ$  match to the XRD JCPDS of ZnO<sub>2</sub> (card number 13-0311) [17].

TEM observations of the precipitated ZnO<sub>2</sub>-WOPEG and ZnO<sub>2</sub>-WPEG, demonstrate a slight difference between the agglomeration shapes as shown in Fig. 3. ZnO<sub>2</sub>-WOPEG resulted in quite dense agglomerates, whereas ZnO<sub>2</sub>-WPEG created typically as smaller agglomerates.

ZnO characterization (with and without PEG200) was also done, in order to verify the presence of ZnO and to check the consequences of stabilization of the ZnO<sub>2</sub> on the resulting ZnO powders. The XRD representative result in Fig. 4 is for ZnO-WOPEG, and a similar result was received for the other sample as well. The seven dominant peaks:  $2\theta = 32.2^\circ, 34.8^\circ, 36.4^\circ, 48.2^\circ, 57.0^\circ, 63.2^\circ, 68.3^\circ$  match to the XRD JCPDS of ZnO (card number 36-1451) [23].

TEM observations of the precipitated ZnO-WOPEG and ZnO-WPEG, demonstrate a significant difference between the two samples as shown in Fig. 5. This is despite the fact that the PEG is released during the heat treatment of the ZnO preparation.

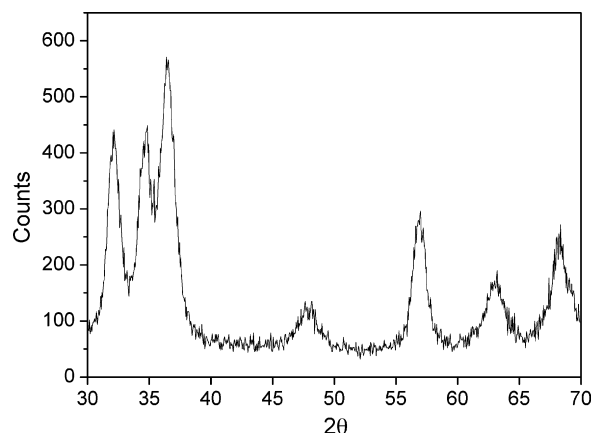


Fig. 4. XRD of ZnO-WOPEG.

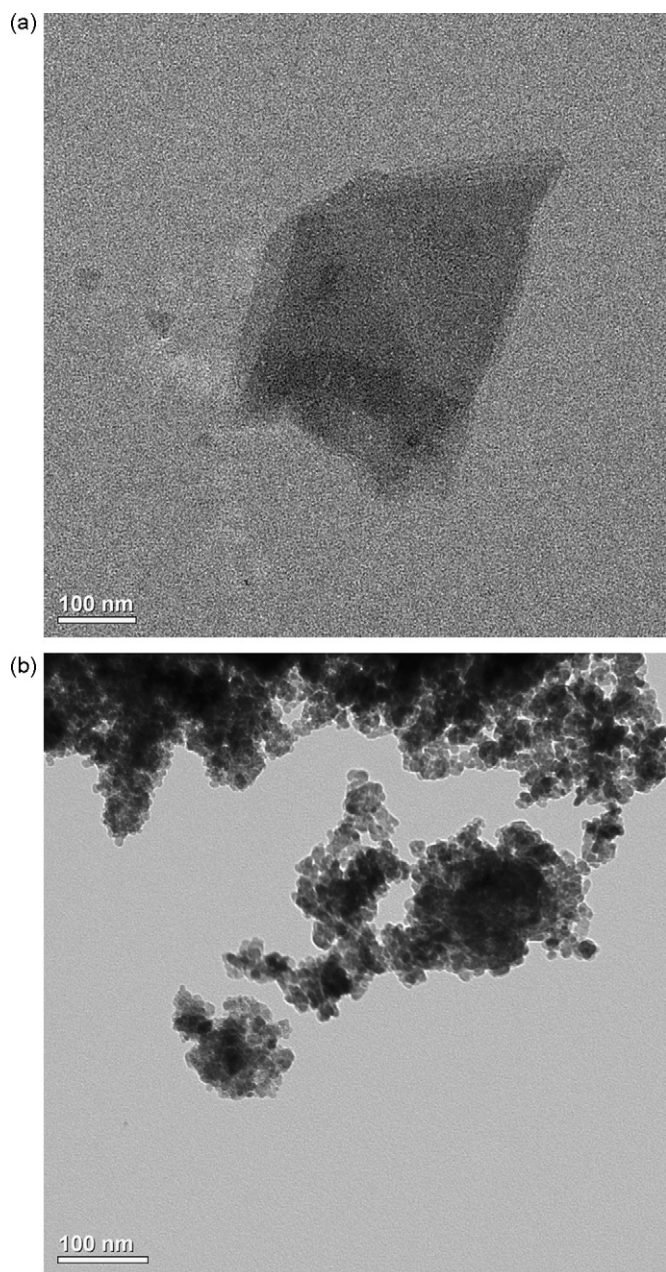


Fig. 5. TEM image of (a) ZnO–WOPEG and (b) ZnO–WPEG annealed for 10 h at 300 °C. The bars are 100 nm.

ZnO–WOPEG contains agglomerates, which are packed into a relatively dense phase, whereas ZnO–WPEG consists of nanoparticles, which are arranged as a highly porous, sponge-like phase. Another TEM image of agglomerated zinc oxide nano-crystallites ZnO–WPEG with a diameter of  $\sim 10$  nm at higher magnification is shown in Fig. 6. DLS measurements that were done in order to quantify the agglomerate size show similar sizes, 500 nm for the ZnO–WPEG and 550 nm for the ZnO–WOPEG samples. These measurements were done using the BIC Zeta-PALS machine on powder samples that were ultra-sonicated in water at low pH value. Combining the TEM observations and the DLS measurements, we can conclude that the ZnO powders are comprised of agglomerates that are of

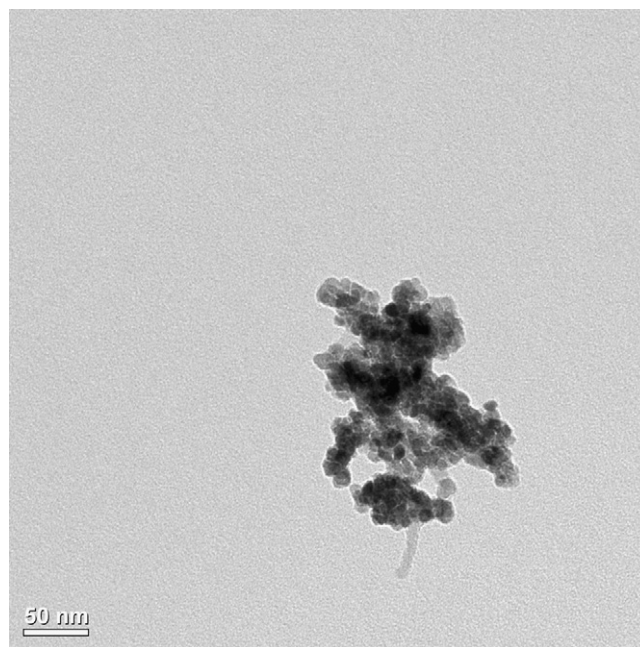


Fig. 6. TEM images of ZnO–WPEG. The bars are 50 nm.

quite similar size, but are different in their morphology and their primary particle size.

TG analysis was done in order to check whether the PEG200 is left on the ZnO–WPEG surface after the calcination treatment. For this, a sample of 70.87 mg ZnO–WOPEG and a sample of 73.65 mg ZnO–WPEG were analyzed in a TG/DTA machine from room temperature to 700 °C. The TGA results are shown in Fig. 7. The weight loss up to  $\sim 175$  °C is mainly due to water release, as verified by the DTA. Above  $\sim 430$  °C the DTA indicates that the gas released contains carbon. The initial release of mainly water is not equal for the two samples, probably due to different surface area. Hence a third curve that shifts the ZnO–WOPEG results down to start at the same point at 300 °C as the ZnO–WPEG sample, is also presented. It can be seen that the mass losses for both samples are minor and very similar,  $\sim 1$  wt%. This is quite negligible as compared to the weight

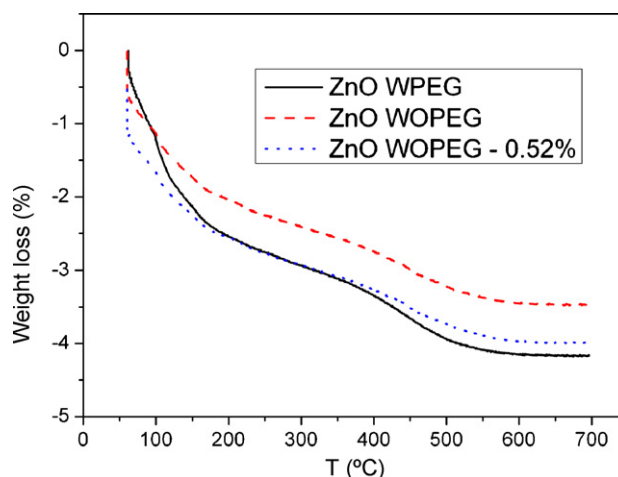


Fig. 7. TGA results of calcined ZnO–WPEG and WOPEG.

loss that we have measured for the ZnO<sub>2</sub> WPEG samples during the first calcination stage. Those were 34 wt% total (including the oxygen loss, Eq. (1)) for the WPEG and 24 wt% total for the WOPEG. These results correspond to weight losses due to water and PEG of about 20 and 10 wt% for the WPEG and WOPEG, respectively. We can conclude that there is no significant amount of PEG left after the calcination process, and the extra carbon that is released above 300 °C is in comparable amount to the carbon that is adsorbed from the atmosphere on the reference WOPEG material. The small differences, could arise from differences in surface area and perhaps also due to imprinting effects.

#### 4. Conclusions

Stabilized nanoparticles of zinc peroxide and zinc oxide were formed by an improved and simple technique. The process is spontaneous and no additional equipment or energy source is required. The zinc peroxide preparation method is based on oxidation–hydrolysis–precipitation procedure, with polyethylene glycol 200 as a surface modifier. The temperature of reduction of zinc peroxide to zinc oxide was found to be 233 °C by DSC. Pure, stabilized nanoparticles of zinc peroxide and zinc oxide remained in the nano-scale during all stages. In particular, zinc oxide powder that was made of stabilized nanozinc peroxide (with PEG200) remained as small agglomerates constructed of ~10 nm primary particles. This is despite the fact that the PEG200 was burnt out during the ZnO preparation.

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