

Supporting Information

Zinc dioxide nanoparticulates: a hydrogen peroxide source at moderate pH

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Available literature data on alkaline earth and d¹⁰ transition metal peroxides.

The available data for the alkaline earth and d¹⁰ transition metal peroxides and the calculate dissolution constants based on equation (1) are summarized in table S1:

Table S1: Thermodynamic data of metal peroxides.

	H_f (kJ/mol)	G_f (kJ/mol)	K_{eq}[*]
BeO₂	-594.1±62.7 ¹⁷	NA	NA
MgO₂	-622.6±4.2 ¹⁵ -623.0 ¹⁶	-569 ¹⁵	2.8*10³
CaO₂	-654.4±4.2 ¹⁵ -659.0 ¹⁶	-602.5 ¹⁵	8.1*10¹⁴
SrO₂	-641.0±16.7 ¹⁵ -642.7 ¹⁶	-590.8 ¹⁵	9.8*10¹⁷
BaO₂	-637.6±25.1 ¹⁵ -629.7 ¹⁶	-585.8 ¹⁵	1.2*10¹⁹
ZnO₂	-347.3±62.7 ¹⁷	NA	NA
CdO₂	-251.0±62.7 ¹⁷	NA	NA
HgO₂	-58.6±62.7 ¹⁷	NA	NA

NA = not available.

* Calculated from Gibbs free energy values of the metal ions and H₂O_{2, (aq)}³⁴

Synthesis protocols

Synthesis of zinc peroxide nanoparticles. 0.462g of zinc acetate dihydrate (Sigma, Israel) was dissolved in 12 mL of concentrated NH_4OH solution (Analytical grade, Biolab, Israel). 100 mL of 30% hydrogen peroxide solution (Biolab, Israel) were added slowly to the first solution with gentle stirring to obtain zinc peroxide precipitate. The stirred suspension was left for 10 minutes. The precipitate was separated by centrifugation at 5000 rpm for 5 min, and then washed twice with ethanol and once with diethyl ether and dried under vacuum for 0.5 hr.

Synthesis of Magnesium peroxide, MgO_2 . 0.6g of magnesium sulfate 7-hydrate (J.T. Baker) were dissolved in 20 mL of 30% hydrogen peroxide solution. 2 mL of concentrated NH_4OH solution were added to obtain about 70% magnesium peroxide precipitate. The precipitate was separated by centrifugation at 5000 rpm for 5 min, and then washed twice with ethanol and once with diethyl ether and dried under vacuum for 0.5 hr.

Analytical Instruments

TG and DSC studies were performed on Thermobalance, TG50 and differential scanning calorimeter, DSC 822 (Mettler, Toledo) in the range 25–300 °C under nitrogen flow at a heating rate of 2 °C min⁻¹.

High Resolution Transmission Electron Microscope (HRTEM) imaging was conducted using a JEM-2100F (Japan). HRTEM imaging was performed at 200 kV. A

drop of the suspension of the sample in ethanol was deposited onto 400 mesh copper grids covered with a lacey carbon net.

Raman spectra were measured on an In Via Raman microscope (Renishaw, New Mills). An argon laser was used as an excitation source, with excitation wavelength of 514 nm.

Scanning Transmission Electron Microscope (STEM) imaging was performed at 10 kV using the FEI Magellan TM 400 L (Eindhoven, Holland). The specimen was prepared by deposition of a drop of the ethanol suspension of the sample onto a 400 mesh copper grid coated with carbon film.

XRD measurements were performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm, Göbel Mirror parallel-beam optics, 2° Soller slits and 0.2 mm receiving slit. XRD patterns from 5° to 75° 2 θ were recorded at room temperature using CuK α radiation ($\lambda=1.5418$ Å) under the following measurement conditions: Tube voltage of 40 kV, tube current of 40 mA, step scan mode with a step size of 0.02° 2 θ and counting time of 1 s/step. XRD patterns were processed using Diffrac Plus software.

Dynamic light scattering (DLS) tests were performed on a Nano-ZS Zetasizer (Malvern, UK). The sample was prepared by dispersing the ZnO₂ NP (0.02 wt%) in deionized water. The sample was sonicated for 15 minutes before the measurement.

Brief

Zinc peroxide nanoparticles are a convenient solid source of hydrogen peroxide. The solid contains more than 25 wt% peroxide, which is retained down to pH 6, some two pH units lower than the alkali earth peroxides.