Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information for the manuscript „*Non-equilibrium transformation of titanate nanowires to nanotubes upon mechanochemical activation*" by G. Kozma et al.

Synthesis

Titanate nanowires were synthesized by the hydrothermal method at 130 °C in 10 M NaOH solution from anatase in a rotating autoclave as described earlier[1]. The reaction product was washed to pH 7 and dried at 80 °C in air. The obtained nanowires were exposed to mechanical energy transfer in a Fritsch Pulverisette 6 type planetary ball mill. For each sample 2.0 g TiONW were placed into a 80 mL silicon-nitride milling drum together with 10 pieces of 10 mm diameter silicon-nitrid balls. The mill was run for 15 minutes at various rotational speeds (from 100 rpm to 500 rpm) to obtain a total of 6 samples (the starting material "A" and 5 milled products). These were labeled in alphabetical order according to the increasing amount of energy transferred to the nanowires.

	B	C	D	E	F
Disk speed (rpm)	100	200	300	400	500
ΔE_b (mJ/hit)	1.2	4.9	11.0	19.6	30.6
E_{cum} (J/g)	33	264	892	2114	4130

Table 1. Individual ball impact energy (ΔE_b) and cumulative milling energy (E_{cum}) transferred to the titanate nanowires at various planetary ball mill rotational speeds

Characterization

TEM analysis was performed with a FEI Tecnai G^2 20 X-TWIN electron microscope with a point resolution of 0.26 nm operating at 200 kV. Samples were drop casted from ethanol suspension and dried onto holey carbon copper grids of 300 mesh at room temperature. XRD profiles were measured on a Rigaku Miniflex II powder X-ray diffractometer using a Cu Kα radiation source (λ = 0.15418 nm) at a scanning rate of 4°/min in the 2θ range of 5° – 80°. The specific surface area of the samples was calculated by the 5 point BET method from N_2 adsorption isotherms recorded at 77 K on a Quantachrome NOVA 3000e instrument. Samples were degassed for 1.5 hour at 150 °C before measurement.

Milling energy calculation

Equation 1. was used to calculate the impact energy ΔE_b transferred to the system by each individual ball hit[2-4].

$$\Delta E_b = \frac{1}{2}\varphi_b K_a \left(\rho_b \times \frac{\pi d_b^3}{6}\right) W_p^2 \left(\left(\frac{W_v}{W_p}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2 \left(1 - 2\frac{W_v}{W_p}\right) - 2R_p \left(\frac{W_v}{W_p}\right)\left(\frac{D_v - d_b}{2}\right) - \left(\frac{W_v}{W_p}\right)^2 \left(\frac{D_v - d_b}{2}\right)^2 \right) \qquad \text{Eq. 1.}$$

Here ϕ_b is the obstruction coefficient, K_a is a constant of the mill, ρ_b is the density of the balls, W_p and R_p are the rotational speed and the radius of the planetary ball mill disk, respectively, D_v and d_b are the diameters of the milling drum and the balls, respectively and W_v is the rotational speed of the milling drum. The specific cumulative energy (E_{cum}) received by 1 g of TiONWs during the experiment can be calculated according to equation 2 from the impact energy ΔE_b, the frequency of impacts (ν_t), the milling time (t) and the amount of titanate nanowires in the drum (m_p).

$$E_{cum} = (\Delta E_b \cdot \upsilon_t \cdot t)/m_p \qquad \text{Eq. 2.}$$

References for the Supporting Information

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