

## COMMUNICATION

## Non-equilibrium transformation of titanate nanowires to nanotubes upon mechanochemical activation†

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**We report on finding the missing piece of the puzzle for interconnected titanate nanostructure reactions: converting titanate nanowires into titanate nanotubes using mechanochemical activation in a planetary ball mill. The best conversion is achieved with an individual ball impact energy of 11 mJ/hit and a cumulative milling energy of 892 J g<sup>-1</sup>.**

The field of one dimensional (1D) titanate nanostructure research has matured into an application-oriented one.<sup>1</sup> One of the driving forces behind this, is that the transformation pathways between the various titanate species during hydrothermal synthesis have been mapped and a consensus on the formation mechanism<sup>2</sup> and characterization ambiguities<sup>3</sup> has been reached. However, experimental evidence about the realization of all possible reactions in the 1D titanate nanostructure system is not yet available. The most important missing piece of the puzzle is the backwards transformation of titanate nanowires (TiONWs) into nanotubes (TiONTs).<sup>4,5</sup> Titanate nanowires represent a very stable form of sodium trititanate. In fact, they are formed by the merger of titanate nanotubes, to reduce the free energy of the system. Earlier we provided the experimental evidence for this<sup>6</sup> and Baykin *et al.* have demonstrated that the system gains approximately 20 kJ mol<sup>-1</sup> by the transformation.<sup>7</sup> The reverse reaction is not possible under the usual hydrothermal equilibrium conditions. However, it should be noted that the rearrangement of titanate nanowires into anatase nanoshuttles under hydrothermal conditions has been reported by Wang *et al.*<sup>8</sup>

Here, we report on realizing the reverse reaction (titanate nanowire to nanotube conversion) by mechanochemical activation

in a planetary ball mill. The construction of the planetary ball mill makes high ball impact energies possible.<sup>9,10</sup> Therefore, very high local temperature and pressure are experienced by the material caught between a ball and the milling drum wall for a few microseconds, and then the system is rapidly quenched as the impact energy is dissipated to the milling matrix and the drum. These conditions are suitable for non-equilibrium processing because they allow the system to be frozen into a high-energy state after impact activation.<sup>11</sup>

We performed five milling experiments on titanate nanowires. The starting H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> nanowire material was synthesized, as described earlier<sup>6</sup> and labeled "A". Samples "B"–"F" were milled for 15 min at increasing rotational speeds, so that the individual hit energy increased from 1.2 mJ/hit to 30.6 mJ/hit and the cumulative energy transferred to the system increased from 33 J g<sup>-1</sup> to 4130 J g<sup>-1</sup>.

The synthesized titanate nanowires featured a diameter of 45–90 nm and a length of 1–5 μm, and their transmission electron microscopy (TEM) appearance was identical to the well-known TiONW morphology (Fig. 1, top left). Even the lowest milling energy ("B") was enough to loosen the structure of the nanowires and break them into smaller fragments.

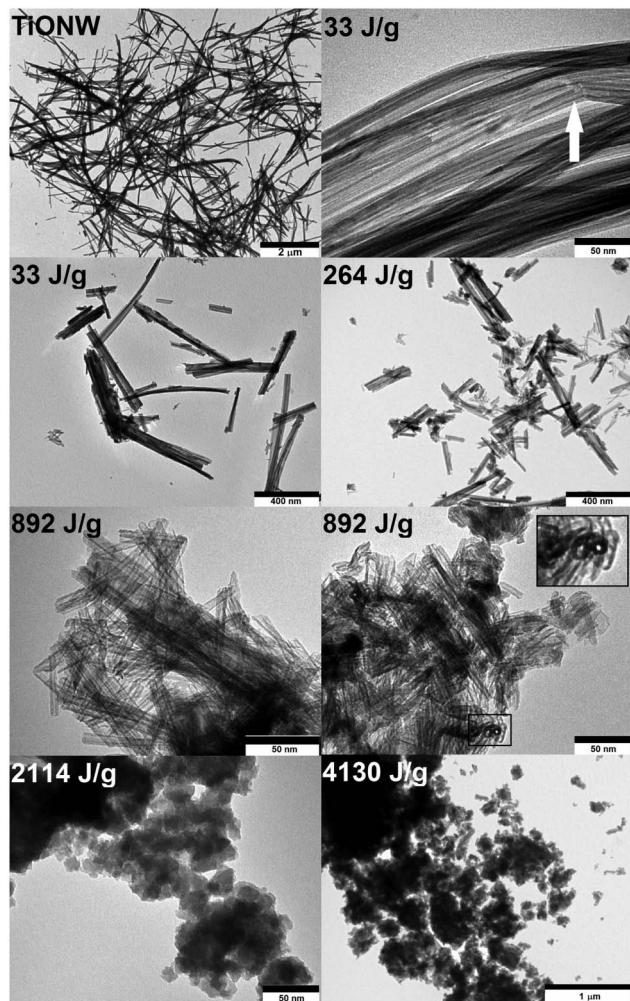
The white arrow in the top right image of Fig. 1. indicates a typical breakage point and the corresponding low resolution image depicts the resulting nanowire fragments measuring 100–680 nm in length and 18–50 nm in diameter. This means that the starting nanowires have broken into multiple pieces along their long axis, but their thickness reduction was less characteristic at this low milling energy. Increasing the cumulative milling energy to 264 J g<sup>-1</sup> resulted in shorter and thinner nanowire fragments (length 70–500 nm, diameter 18–30 nm) due to the larger number of hits. However, raising the impact energy to 11 mJ/hit and the cumulative milling energy to 892 J g<sup>-1</sup> resulted in a product of a very peculiar morphology as depicted in the third row TEM images in Fig. 1. The observed fragments are not simply even shorter pieces of the same TiONW. Rather, they appear to be very similar to literature images of titanate nanotubes. Their typical length and outer diameter measure 40–80 nm and 5–8 nm, respectively and they are open at both ends. The tubular structure is particularly

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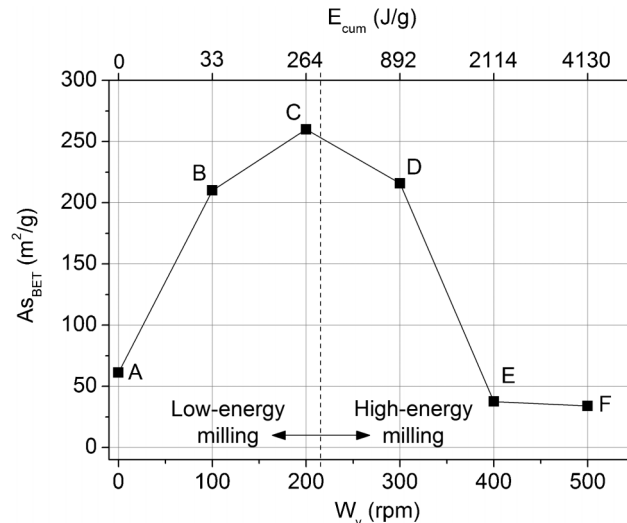
† Electronic supplementary information (ESI) available: Details of the experimental procedures and milling energy calculation method. See DOI: 10.1039/c3ra40863a



**Fig. 1** Characteristic TEM images of the starting titanate nanowires (top left) and milling products obtained at various cumulative milling energies. The inset in the 892 J g<sup>-1</sup> (right hand side) image provides a magnified view of the tubular cross-section of the milling product.

well visible in the magnified image of a circular cross-section object crossing the focal plane of the TEM instrument, shown in the inset (Fig. 1, third row, right image). The tubular nanoobjects are replaced by agglomerates of isotropic nanoparticles of 12–20 nm in diameter at cumulative energies above 2 kJ g<sup>-1</sup> (Fig. 1, bottom row).

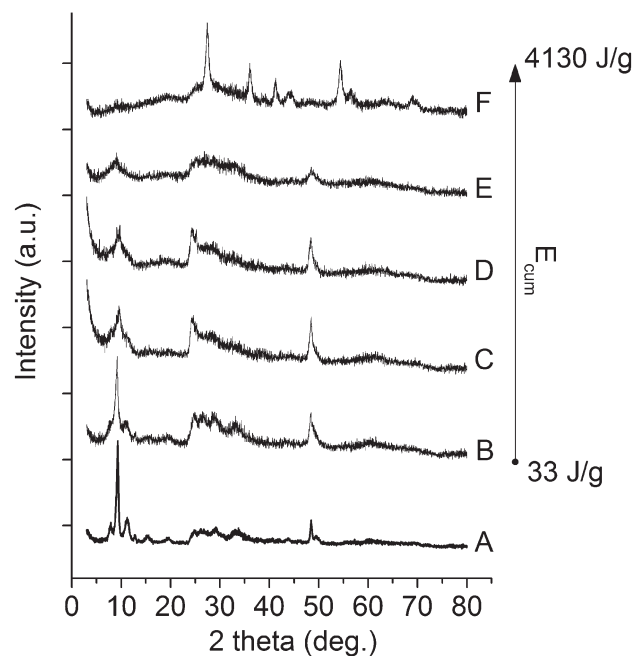
The specific surface area measurements depicted in Fig. 2 allow more insight into the conversion process. The starting nanowires (“A”) are characterized by an  $A_{S_{BET}} = 57 \text{ m}^2 \text{ g}^{-1}$  value, which agrees well with literature reports on TiONWs.  $A_{S_{BET}}$  increases to above  $200 \text{ m}^2 \text{ g}^{-1}$  for all samples milled with a cumulative energy below  $1 \text{ kJ g}^{-1}$  because delamination of the titanate sheets from the large TiONW body makes previously hidden sheet faces available for nitrogen adsorption. The largest specific surface area ( $260 \text{ m}^2 \text{ g}^{-1}$ ) belongs to the 264 J g<sup>-1</sup> sample, which consists of the thinnest stripes. Samples “B” and “D” have smaller specific surface areas because the fragments of the 33 J g<sup>-1</sup> sample are somewhat thicker, due to the lower milling energy,



**Fig. 2** Specific surface area of the milled titanate nanowires as a function of the rotational speed of the planetary ball mill.

whereas the 892 J g<sup>-1</sup> sample consists of rolled-up nanotubes where a part of the sheet surface is unavailable for nitrogen adsorption. The specific surface area of the isotropic nanoparticles obtained by milling above 2 kJ g<sup>-1</sup> is less than  $50 \text{ m}^2 \text{ g}^{-1}$ , because these samples are nonporous and their nitrogen adsorption capacity is determined by the open surface of the nanoparticle agglomerates.

The crystalline phase transformations of the materials were characterized by powder X-ray diffractometry (XRD) as depicted in Fig. 3. The synthesized TiONWs (“A”), milled nanowire fragments



**Fig. 3** XRD of the starting titanate nanowires (“A”) and products obtained by increasing the milling energy.

(“B” and “C”) and nanotubes (“D”) all exhibit characteristic peaks at  $9.6^\circ$ ,  $26.3^\circ$  and  $49.6^\circ$ , which are frequently used in the literature to identify titanate nanowires. Therefore, we now conclude that the original titanate nanowires were transformed into titanate nanotubes in the planetary ball mill when the cumulative milling energy was  $892 \text{ J g}^{-1}$ . Sample “E” consists of isotropic nanoparticles of a titanate crystal structure, according to the XRD, but a loss of reflection intensity and peak broadening indicate that a partial amorphization process took place. Sample “F” is characterized by XRD peaks at  $27.5^\circ$ ,  $36.2^\circ$ ,  $41.3^\circ$  and  $54.3^\circ$ , which are clear indicators of a rutile crystal structure.

The following interpretation explains these findings; a high energy mechanical impact can transfer enough energy to a titanate nanowire to delaminate smaller nanotube precursor sheets from it. Similar delamination processes were observed for titanate nanowires in solution under acidic conditions,<sup>12</sup> but neither have identified any nanotube products, nor were ever reported for mechanical agitation, until now. Here, the system is automatically quenched, microseconds after each impact in the planetary ball mill and therefore, the delaminated nanotube precursor sheets cannot reassemble into a titanate nanowire, even though that would be thermodynamically favourable. Therefore, they roll up into short titanate nanotubes instead, as suggested earlier for hydrothermal synthesis conditions of titanate<sup>13,14</sup> and halloysite nanotubes,<sup>15</sup> as well as for intercalated kaolinite nanoscrolls.<sup>16</sup> The delamination process can be initiated by ball impact energies as low as  $1.2 \text{ mJ/hit}$ , but the characteristic process at low energies is nanowire fragmentation along the long axis. Energies around  $1 \text{ kJ g}^{-1}$  are sufficient to create individual titanate sheets which are able to roll up into nanotubes, whereas cumulative energies above  $2 \text{ kJ g}^{-1}$  create a situation where the sufficiently large number of hits on the formed titanate nanotubes furthers their transformation. The nanotubes are ground into small, isotropic nanoparticles, then subsequent hits assist the recrystallization of these particles into the rutile phase, confirming the findings of Plodinec *et al.*<sup>17</sup>

Summarizing, the main importance of the reported work is that it provides the first experimental evidence for the transformation of titanate nanowires into titanate nanotubes. We have shown that this transformation is possible in the highly non-equilibrium conditions of a mechanochemical reactor and that careful energy control must be maintained, so that the transformation can be stopped at the titanate nanotube stage, which is an intermediate

phase *en route* to the mechanically initiated transformation of titanate nanowires into isotropic rutile nanoparticles.

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