A Real Time Observation of Phase Transition of Anatase TiO₂ Nanotubes into Rutile Particles by in situ Joule Heating Inside a Transmission Electron Microscope


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It has been demonstrated that some properties of TiO₂ are very sensitive to its structure. Since the anatase phase is chemically and optically active, it is suitable for catalysts and supports [1]. Usually, the anatase phase can be transformed into rutile via post-annealing [2], because anatase is thermodynamically unstable. This anatase-to-rutile phase transition, which is dependent upon annealing temperature, induces the variation of the optical properties in TiO₂ films [3]. Therefore, the post–annealing should be a controlled process in order to make desirable properties of a TiO₂ film for various applications. In view of this, we have taken a new approach to synthesize rutile nanoparticles. Here, we report the phase transition of anatase TiO₂ nanotubes into nano-meter size rutile particles via in situ Joule heating inside a high resolution transmission electron microscope (HRTEM). The Joule heating experiment was carried out by using a special scanning tunneling microscopy holder from “Nanofactory Instruments” in a JEM 4000FX TEM, operated at 200kV. When the TiO₂ nanotube was in contact with the STM tip, the Joule heating experiment was conducted by applying a constant bias voltage. Fig. 1a shows a TiO₂ nanotube contacted on both ends and free standing in high vacuum (10⁻⁶ Torr), inside the TEM. Under 10V bias, the current, \( I \), starts to increase gradually with time, \( t \), and reaches a maximum value of 12 \( \mu \)A in a period of 180 sec, as shown by the \( I \) vs \( t \) plot (Fig. 2). Fig. 1(b) shows the image of the TiO₂ nanotube undergoing the heating at constant bias voltage of 10V for 180 sec. On increasing the bias voltage to 20V, it was observed that the current increased drastically to a maximum value of 20 \( \mu \)A in a time period of 130 sec and then started to decrease gradually with the further breaking of the nanotube, while at the same time the nanometer diameter titania underwent a solid state reaction and grew into a bigger crystal of 20-25 nm (as shown in the image of Fig. 1c). On increasing the bias heating voltage to 30V, the current increased slightly from 13.75 \( \mu \)A to 15 \( \mu \)A in a time period of 30 sec. Due to this increase in current at this stage, some of the rutile particles formed agglomerates of around 100-200 nm and finally the nanotube structure collapsed. In conclusion, we have shown for the first time, the anatase nanotube dissociation and their phase transformation to rutile in real time. The anatase nanotubes under Joule heating dissociate to small particles (~10-20 nm) of anatase at low bias voltage (≤10V). At an intermediate bias range, between 10V and 20V, the anatase nanoparticles transformed to rutile.