Direct Observation of Melting Behaviors at Nanoscale Under Electron Beams and Heat to form Hollow Nanostructures

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Figures S-1, S-2 and S-3 were supplementary information to provide the electron irradiation effect of the pristine ZnO nanowire as a comparison. In Fig.S-1 (a), ZnO nanowire was not coated with Al_2O_3 shell. In Fig.S-1 (b), the ZnO nanowire will maintain the morphology at 600 °C under electron irradiation for 1 hr, proving the effect of the Al_2O_3 shell on the liquefaction and the drainage of the ZnO core.



Fig. S-1 (a) Pristine ZnO nanowire without Al_2O_3 shell coverage. (b) After electron beam irradiation over 60 min at 600 °C. If there is no Al_2O_3 shell, the ZnO core will not melt at the same observation condition.



Fig. S-2 TEM images of the single crystalline Al_2O_3 nanotubes with remained ZnO at the end of the tube (red arrow mark). (a) high magnification TEM image and (b) low magnification TEM image show the remnant ZnO at the open-end.



Fig. S-3 Al_2O_3 nanostructures with controlled thickness by atomic-layer-deposition on inner ZnO nanostructure with (a) 60, (b) 20 and (c) 25 nm in thickness. The shell of Al_2O_3 nanotubes are with different inner diameters. The diameter of the pristine ZnO nanowires is mainly in the range from 40 to 320 nm.

Three in-situ TEM videos as supplementary online material were presented to show the dynamic observation of the ZnO/Al_2O_3 core/shell nanowire heterostructures to form the Al_2O_3 nanotube at 600 °C under electron irradiation

- Supporting video-1 : The video shows that the melting behavior was occurred at the interface between ZnO core and Al₂O₃ shell. The ZnO was drained away quickly at 00:04 (red arrow mark). The spherical voids were exhibited at the core/shell nanostructure in this video. We believe that the high interfacial energy between Al₂O₃ and ZnO could be the driving force of the observed reaction.
- **Supporting video-2:** Two different stages of the ZnO melting in this video: transformation and liquefaction, followed by electron-beam-irradiation-induced drainage. In this video, it shows two different stages of the ZnO drainage at the open end of the tube. First is the melting and transforming into liquid. Second is that the drainage rate of ZnO increases under electrons irradiation.
- **Supporting video-3:** The one-way drainage of the liquidized ZnO droplet along the [0001] ZnO growth direction at high temperature was recorded in this video. We observed that the ZnO core was liquidized and disappeared along the [0001] growth direction, leaving a clear and straight single crystalline Al₂O₃ nanotubes at high temperature.