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## Supplementary information



Figure: STEM-HAADF image of the micropillar, from the tomography tilt series

## Electron tomography processing and segmentation

The electron tomography tilt series was processed using FEI Inspect 3D for alignment, tilt axis identification and 3D reconstruction. The following processing has been carried out with minimal human input to minimise operator bias; this is made possible by the combination of good signal-to-noise acquisition in the detectors (and therefore the pristine STEM images) and the specimen geometry: thanks to the cylindrical shape, the images acquired at high tilt angles still preserve good signal and contribute to a clean 3D reconstruction. The "rolling ball" method integrated in ImageJ was used to subtract the background. Segmentation was carried out by global thresholding; the value has been chosen as the one maximising the surface area of the TiO<sub>2</sub> network. It has been verified that such value determines a threshold that includes TiO<sub>2</sub> features while avoiding polymer regions and artefacts from the tomographic reconstruction. The voids within the TiO<sub>2</sub> network are assumed to be filled with HTM polymer. Although the contrast given by the polymer is not sufficient for clear identification in the interior volume of the tomogram, EDX (Energy Dispersed X-ray) analysis confirmed its presence within the structure.