

Supporting materials

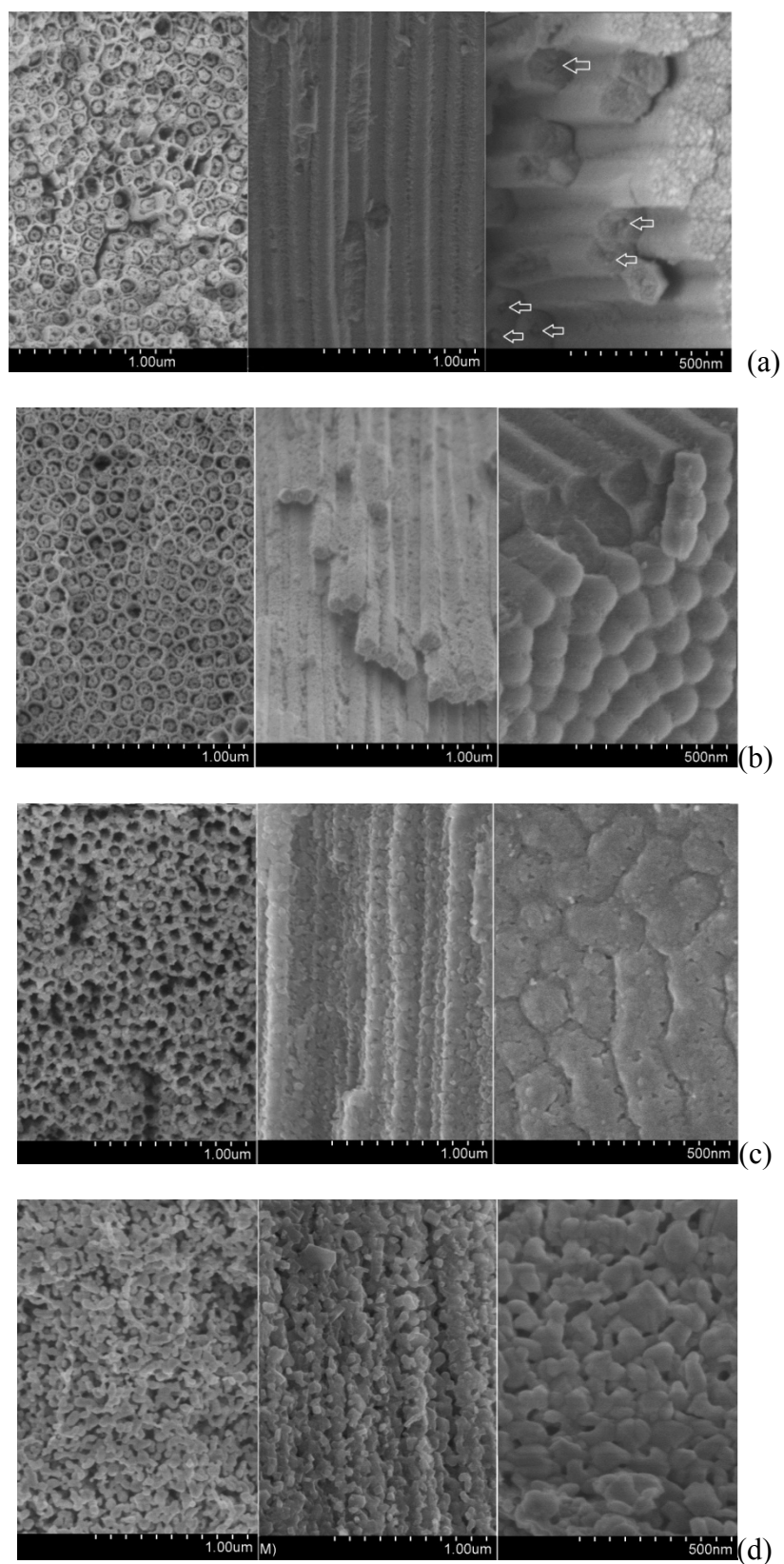


Fig. S1 SEM top, cross-sectional, and bottom images of TiO_2 nanotubes filled by Co-precursor nanorods after heat treatment at different temperatures. (a) 350°C (b) 450°C (c) 550°C (d) 700°C

The morphology of samples calcinations at 350, 450, 550, and 700°C are shown in Figure S1. The top, sectional, and bottom images in Fig.S1(a) and (b) do not exhibit dramatic changes for samples calcined at 350 and 450°C, respectively. Obvious boundaries between nanotubes and nanorods (as indicated by white arrows) from the bottom view can be observed for the sample calcined at 350°C. However, the boundaries disappear under 450°C calcination. After calcined at 550°C, the tubular structure still exists but some rods become integrated into nanotubes from the top view. The whole tube walls are converted into interconnected nanoparticles with average particles size of 50-100 nm, and gully-like features appeared on the bottom view of nanotubes. Interestingly, the nanotube structures were totally converted into porous three-dimensional granular structures as shown in Fig. S1(d). The changes can be ascribed to the formation of CoTiO_3 at high-temperature calcination of 700°C.

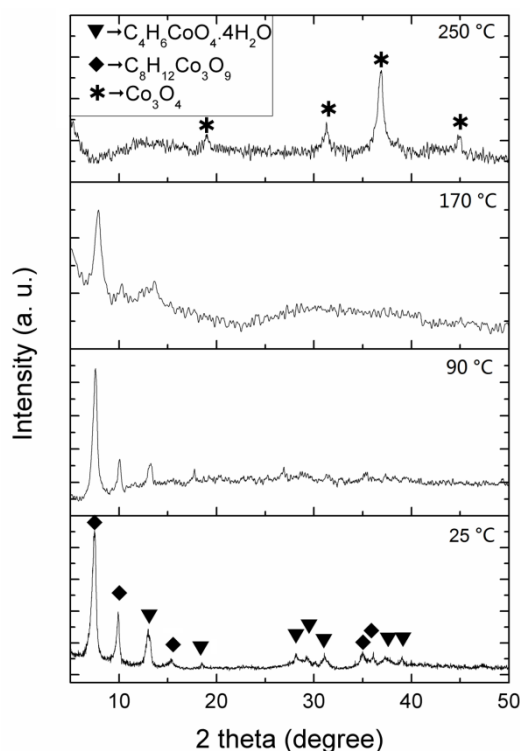


Fig. S2 XRD patterns for as formed Co precursor calcined at 90, 170, 250°C

Fig. S2 gives the XRD pattern of the cobalt-containing solid precursors that was calcined at 90, 170, and 250°C. The diffraction peaks of the as-formed precursor (25°C) could be indexed perfectly to cobalt oxide acetate $\text{C}_8\text{H}_{12}\text{Co}_3\text{O}_9$ (JCPDS card No. 22-0595) and cobalt acetate hydrate $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ (JCPDS card No. 25-0372) without any obvious impurity peaks. The XRD patterns of the hydrothermal product show that typical peaks of the two products weaken at 90°C annealing and gradually disappear after calcination at 170°C, which is more apparent when 2θ is greater

than 20°. When the calcination is above 250°C, all peaks of the XRD pattern correlate well with the standard data (Co₃O₄, JCPDS card No. 42-1467), which indicates that the pure cubic phase Co₃O₄ is synthesized here.

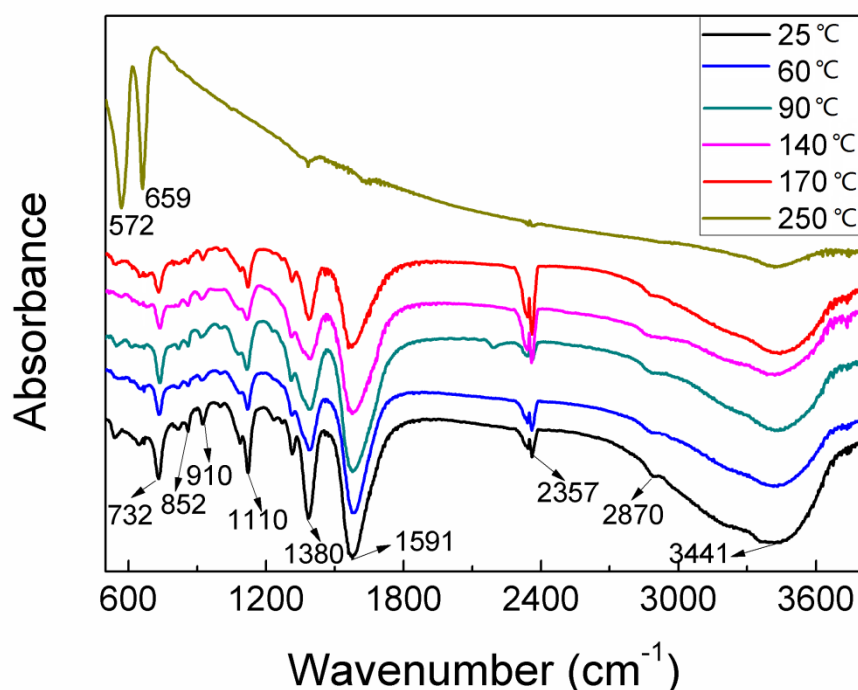


Fig. S3 FT-IR spectra of as formed Co precursor calcined at 60, 90, 140, 170, 250 °C

To thoroughly support the conclusion of Fig S2, the FT-IR of all the samples calcined at 60, 90, 140, 170, and 250°C are shown in Fig. S3. The FT-IR spectra demonstrate no modification in peaks in accordance with the calcinations temperature except 250 °C. Fig. S3 reveals absorption band characteristics for epoxide groups at 731 cm⁻¹ (C-C in epoxide), 910 and 852 cm⁻¹ (C-O-C in epoxide)^[34]. The bands at 1110 cm⁻¹ were from the C-C framework vibration in the main chain of the C₈H₁₂Co₃O₉ and C₄H₆CoO₄·4H₂O. The band occurring near 1380 cm⁻¹ corresponds to symmetry deformation vibration of δ_{sym}(CH₃). The initial interaction produced surface acetate species, characterized by broad band centered at 1580 cm⁻¹, which represents the asymmetric stretching ν_{asym}(COO) for carboxyl ion^[35]. The band at 2357 cm⁻¹ was attributed to the absorption of CO₂^[36], and the band at 3441 cm⁻¹ was due to antisymmetric stretching vibrations in the carboxylate of H₂O, while the the absorption peak situated around 2881 cm⁻¹ is ascribed to -CH₂ stretching vibration^[37]. Furthermore, it can be observed that two strong absorption bands occur at 563 and 672 cm⁻¹ in the 250°C calcined sample, which were assigned to ν(Co-O) modes. The former peak is attributed to the M-O in which M is Co³⁺ and is octahedrally coordinated, while the latter band can be assigned to the stretching vibration mode of

M–O in which M is Co^{2+} and is tetrahedrally coordinated ^[38,39]. The two bands indicate the $\text{C}_8\text{H}_{12}\text{Co}_3\text{O}_9$ and $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ can be transformed to the Co_3O_4 structure after 250°C heat treatment (the structural formula of the two precursors can be seen in Figure S4, Supporting Information). The formation process ascertained for Co_3O_4 is in good agreement with the XRD results.

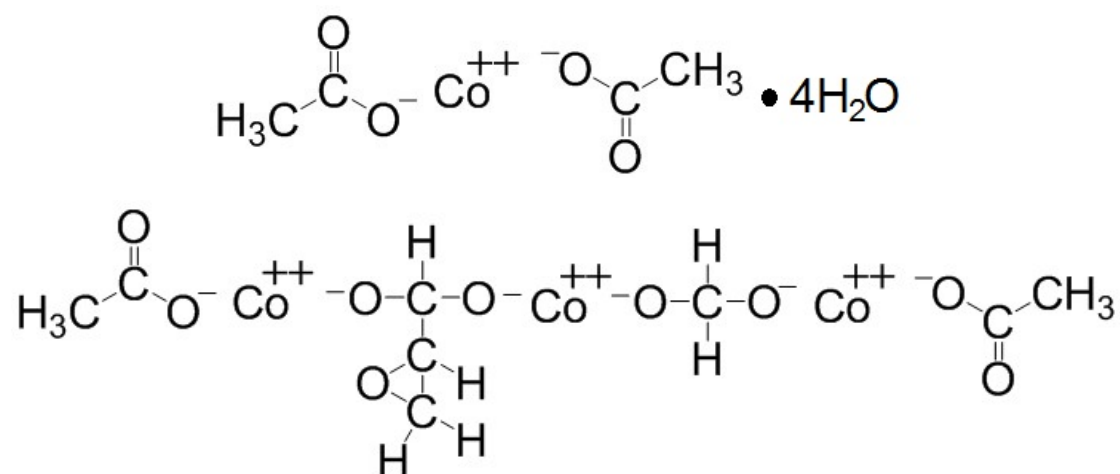


Fig. S4 The structural formula for cobalt acetate hydrate $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ and cobalt oxide acetate $\text{C}_8\text{H}_{12}\text{Co}_3\text{O}_9$