

Electronic Supplementary Information

N-doped lepidocrocite nanotubular arrays: hydrothermal synthesis from anodic titanate nanotubes and the enhanced visible light photoresponse

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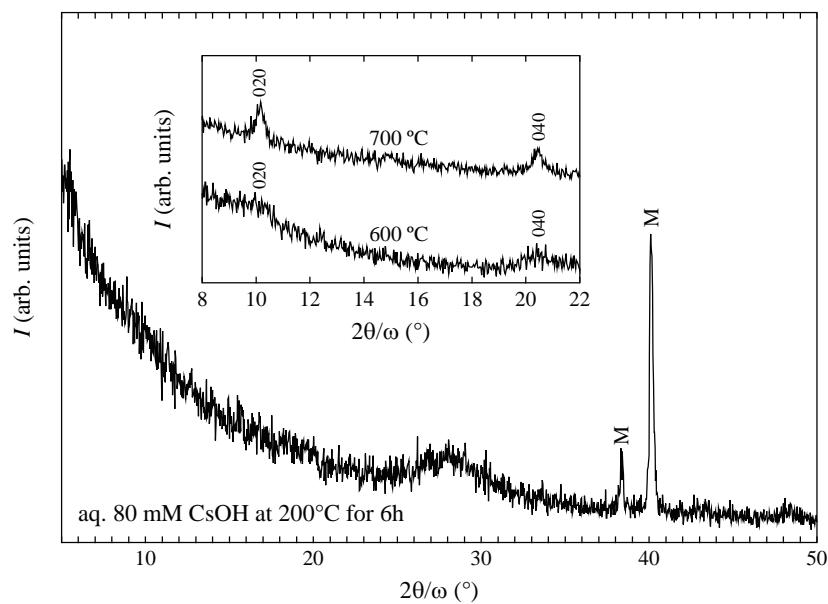


Figure S1. The X-ray diffraction patterns for the sample prepared by hydrothermal treatment in aq. 80 mM CsOH solution at 200 °C for 6 h. The M represents Ti metal. The original material (ATN) was still amorphous without any crystallized oxide phase after the hydrothermal treatment. The inset shows the annealed samples at 600 °C and 700 °C for 2 h. The broad peaks for Cs-lepidocrocite appeared at 600 °C, and the crystal growth proceeded up to 700 °C.

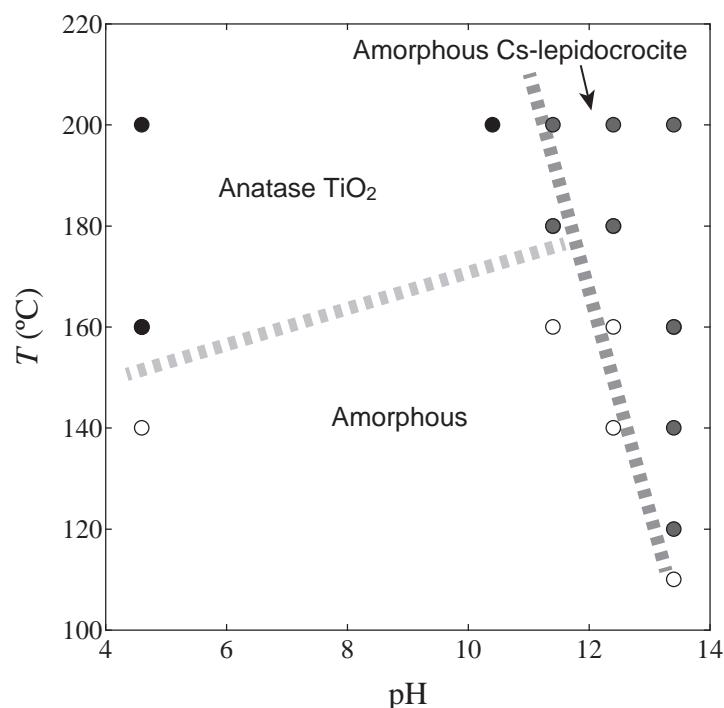


Figure S2. The phase diagram for hydrothermal treatment temperature and solution pH dependences. The pH of the solution was controlled by using CsOH and CsNO_3 in water. The phase boundary has not strictly determined yet, however, it is clear that the amorphous Cs-lepidocrocite phase appear at higher pH region above $\text{pH} = 11$. The samples prepared by this region can be converted to the crystallized Cs-lepidocrocite phase after annealing at above $600\text{ }^\circ\text{C}$.

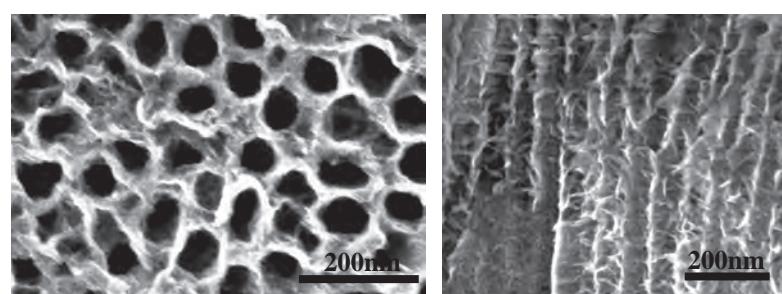


Figure S3. The FESEM image for the sample prepared by hydrothermal treatment at $180\text{ }^\circ\text{C}$ for 2 h in 80 mM CsOH using ethanol/water mixed solution ($\text{C}_2\text{H}_5\text{OH:H}_2\text{O} = 2:1$, v/v).

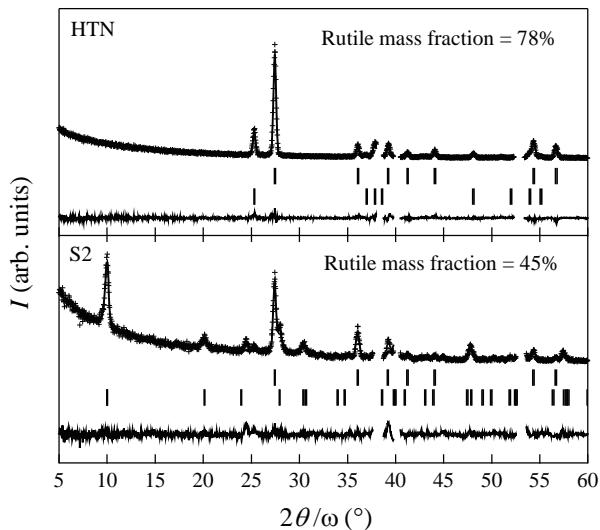


Figure S4. The X-ray diffraction patterns for the S2 and HTN. The obtained patterns were analyzed by using Rietveld method. The calculated and observed diffraction profiles are shown at the top with the solid line and the cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities. The signals from the Ti foil were excluded. The S2 was refined as two mixture phases of Cs-lepidocrocite and rutile TiO_2 . The good agreement of simulation was obtained when it was including specific orientations of (001)- (100)- and (110)-directions. The mass fraction of Cs-lepidocrocite phase was evaluated to be 55%. The HTN was refined two mixture phases of anatase and rutile TiO_2 . The mass fraction of rutile phase was evaluated to be 78%.

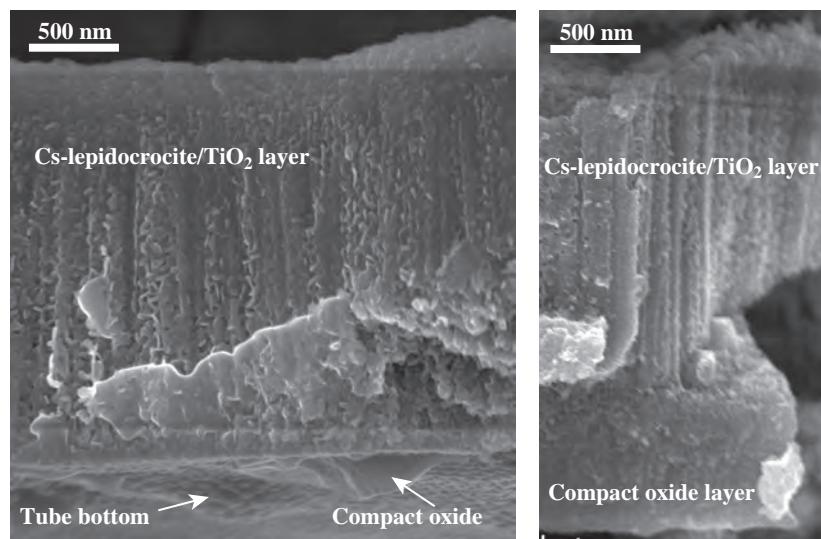


Figure S5. The cross-sectional FESEM image for the S2. The formation of compact layer was confirmed underneath the nanotubular structure with thickness of 700–900 nm. This compact layer would be derived from rutile TiO_2 due to oxidation of the Ti substrate high temperature annealing as reported in previous literature (A. Tighineanu *et al.*, Chem. Phys. Lett. **494** (2010) 260.). The XRD diffraction which showed mixture of Cs-lepidocrocite and TiO_2 rutile phases (Figs. 4 and S4) also supports this.

Dye absorption/desorption procedure

For the evaluation of surface area, we employed dye absorption/desorption experiments. Ru-based N719 dye (*cis*-bis (isothiocyanato) bis (2,2-bipyridyl 4,4-dicarboxylato) ruthenium (II) bis-tetrabutylammonium) was used. The obtained samples were immersed for 1 day at 40 °C in a mixture of acetonitrile and tert-butyl alcohol (1:1,v/v) containing a 300mM N719 dye (Solaronix SA, Switzerland). After dye-absorption, the samples were rinsed acetonitrile to remove non-chemisorbed dye. Dye desorption measurements were carried out by immersing the samples in 5ml of 10mM KOH for 1 h followed by the concentration measurements by UV-VIS spectrometer at 520 nm.