

Supporting information

Spaced TiO₂ Nanotube Arrays Allow for High Performance Hierarchical Supercapacitor Structure

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Experimental

Fabrication of spaced TiO₂ nanotubes: Titanium foils (0.125 mm thickness, 99.6+% purity, Advent Research Materials) were sonicated with water, acetone and ethanol for 15 min. The titanium foils were then dried under nitrogen gas stream. The spaced TiO₂ nanotubes (NTs) were formed by anodizing titanium foils in triethylene glycol electrolyte (TEG) containing NH₄F (0.3 M) and H₂O (3M) at 60 V for 1 h at 60°C. The DC potential was supplied by a VLP 2403 pro, Voltcraft power supply. After anodization, the samples were cleaned and soaked in ethanol for several hours before being dried under nitrogen gas. Then the spaced TiO₂ nanotubes were annealed at 450°C in air for 1 h with a heating and cooling rate of 30°C min⁻¹ using a Rapid Thermal Annealer (Jipelec Jetfirst 100).

Fabrication of reference (close-packed) TiO₂ nanotubes: the reference nanotubes were formed by anodization of titanium foils in ethylene glycol electrolyte containing NH₄F (0.15 M) and H₂O (3 wt.%) at 60 V for 15 min at room temperature.

Nanoparticle decoration: The deposition of TiO₂ nanoparticles on the TiO₂ nanotubes was carried out using a close vessel in an oven at 70°C. TiO₂ nanotube samples were soaked into 7 mL of aqueous TiCl₄ solution (0.1 M) for 30 min. The samples were then washed with H₂O and ethanol before being dried under nitrogen gas. This step was repeated many times to decorate different amounts of TiO₂ nanoparticles. The samples were then annealed at 450°C for 10 min in order to induce crystallization of the particles.

Characterization of the structure: Field-emission scanning electron microscope (FE-SEM, Hitachi S4800) was used to characterize the morphology of the samples. The chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5600, US). X-ray diffraction (XRD) performed with a X'pert Philips MPD (equipped with a

Panalytical X'celerator detector) was employed to examine the crystallographic properties of the materials.

Conductivity measurements: solid-state conductivity measurements were carried out in an adapted scanning electron microscope (SEM, TESCAN LYRA3 XMU) by 2-point measurements using a semiconductor characterization system (Keithley 4200-SCS). Tungsten tips were used as electrical contacts between TiO₂ tube tops and the titanium substrate. Resistivity values were then obtained from the I-V curves by ramping the potential from -2 V to 2 V at a sweep rate of 5 mV s⁻¹.

Dye loading measurements: Dye adsorption was conducted by immersing the samples in a 300 mM solution of Ru-based dye (cis-bis (isothiocyanato) bis(2,2-bipyridyl 4,4-dicarboxylato) ruthenium(II) bistetrabutylammonium) at 40°C for 1 day. The dye solution was a mixture of tert-butyl alcohol and acetonitrile. Subsequently, the samples were rinsed with ethanol to remove non-chemisorbed dye. Then the samples were soaked in an aqueous solution of 5 mL KOH (10 mM) for 30 min. The concentration of desorbed dye was measured spectroscopically (by using a Lambda XLS UV/VIS spectrophotometer, PerkinElmer) at $\lambda = 520$ nm.

Electrochemical measurements: The electrochemical measurements were conducted by cyclic voltammetry (CV) and galvanostatic charge/discharge tests in a three-electrode configuration. The working electrode was TiO₂ nanotubes with an exposure area of 1 cm². A Pt sheet acted as a counter electrode and a Ag/AgCl (1 M KCl) as a reference electrode. Mott-Schottky measurements were performed at 100 Hz. All the measurements were carried out in an aqueous Na₂SO₄ (0.5 M) solution at room temperature. The areal capacitance was calculated from CV curves according to below equation:^[1]

$$C = \frac{Q}{\Delta V \times A} \quad (1)$$

where C (mF cm^{-2}) is the areal capacitance, Q (C) is the average charge during 1 cycle, ΔV (V) is the potential range and A (cm^2) is the surface area of the working electrode.

The areal capacitance measured by charge/discharge curves were calculated according to below equation:

$$C = \frac{I \times t}{\Delta V \times A} \quad (2)$$

where C (mF cm^{-2}) is the areal capacitance, I (mA) is the discharge current, t (s) is the discharging time, ΔV (V) is the potential range and A (cm^2) is the surface area of the working electrode.

Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 100 kHz to 10 mHz with the amplitude of 10 mV peak-to-peak using AC signals at open circuit potential. The curves were fitted with Zfit-EC-Lab 10.44 spectrum analyzer (simplex method).

References

- [1] X. Lu, G. Wang, T. Zhai, M. Yu, J. Gan, Y. Tong, Y. Li, *Nano Lett.* **2012**, *12*, 1690.

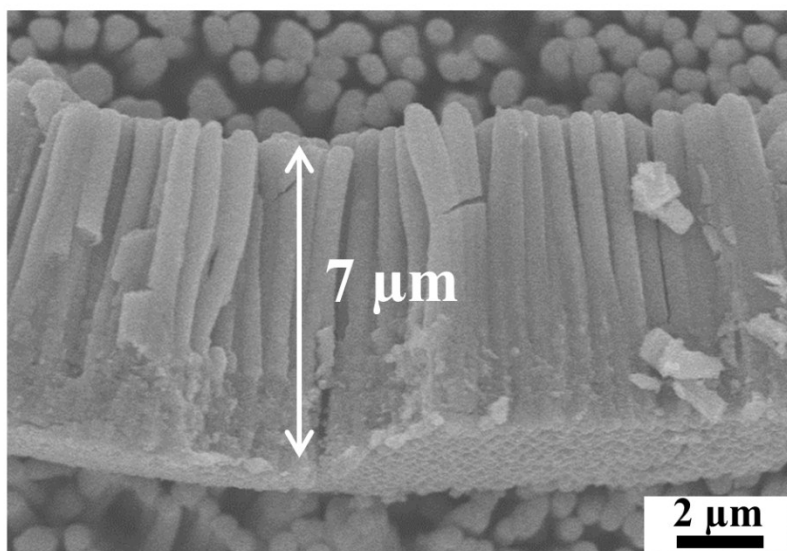


Figure S1 SEM image of cross-sectional hierarchical structures.

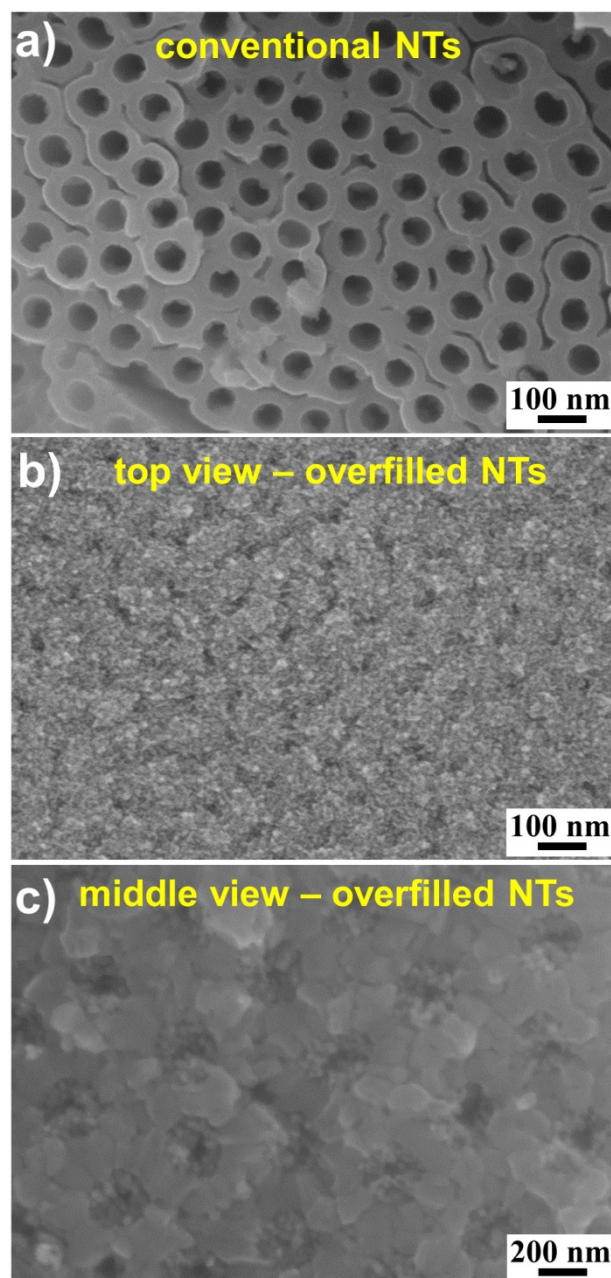


Figure S2 SEM images of reference TiO_2 NTs a) before and b), c) after decoration of TiO_2 nanoparticles. The NTs are formed by anodizing Ti in ethylene glycol-based electrolyte containing NH_4F and H_2O .

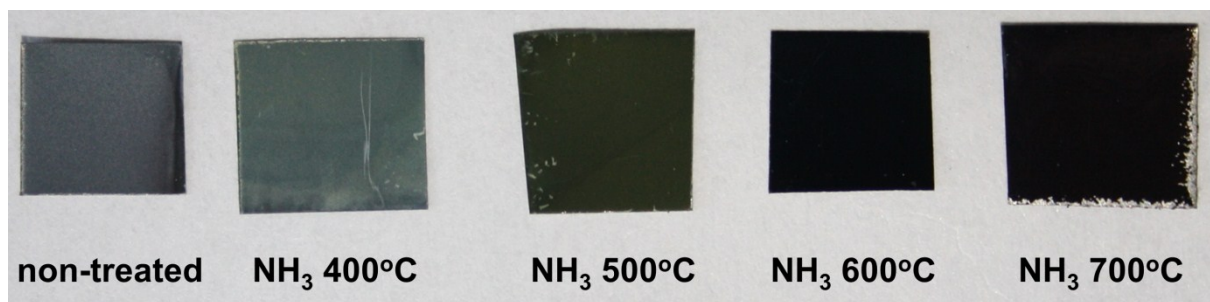


Figure S3 Optical images of TiO₂ samples without/with NH₃ treatment at different temperatures.

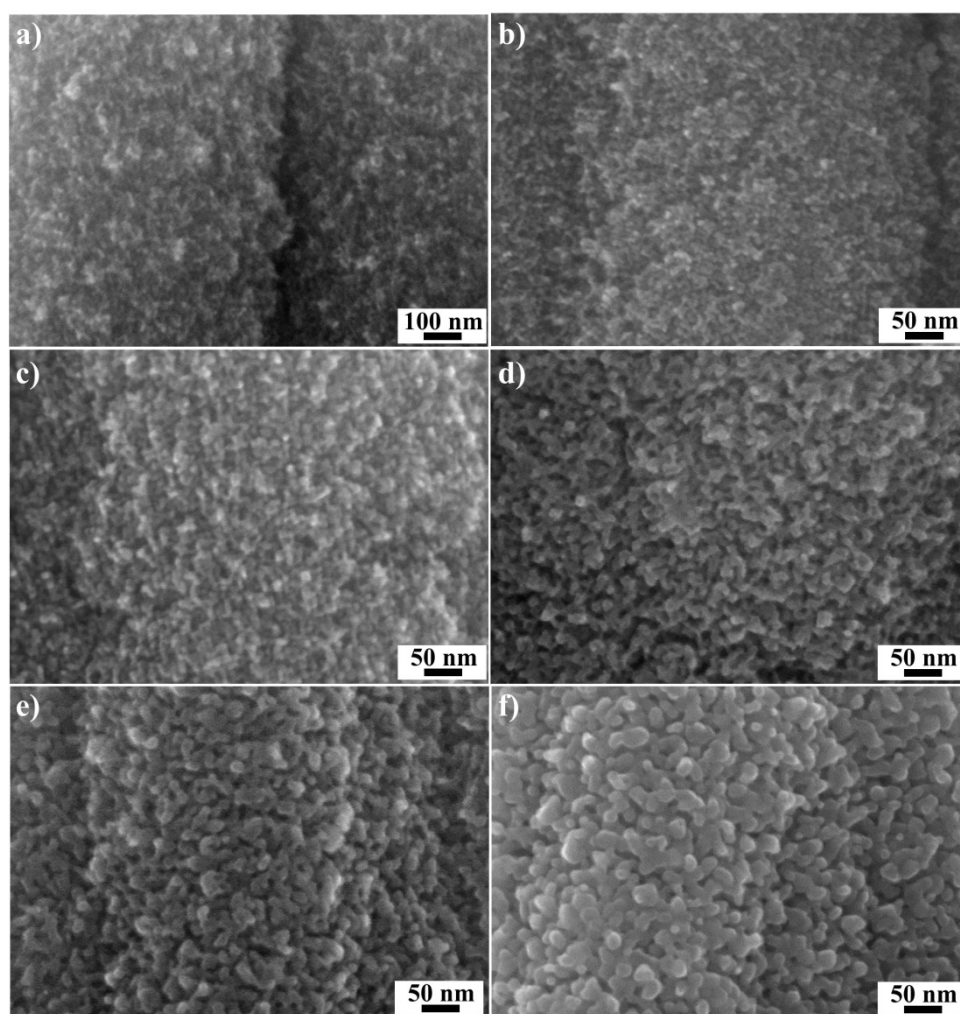


Figure S4 SEM images of: a) nanoparticle-decorated TiO₂ NTs (8 layers of nanoparticles) and nanoparticle-decorated TiO₂ NTs annealed in NH₃ at: b) 400, c) 500, d) 600, e) 700 and f) 800°C.

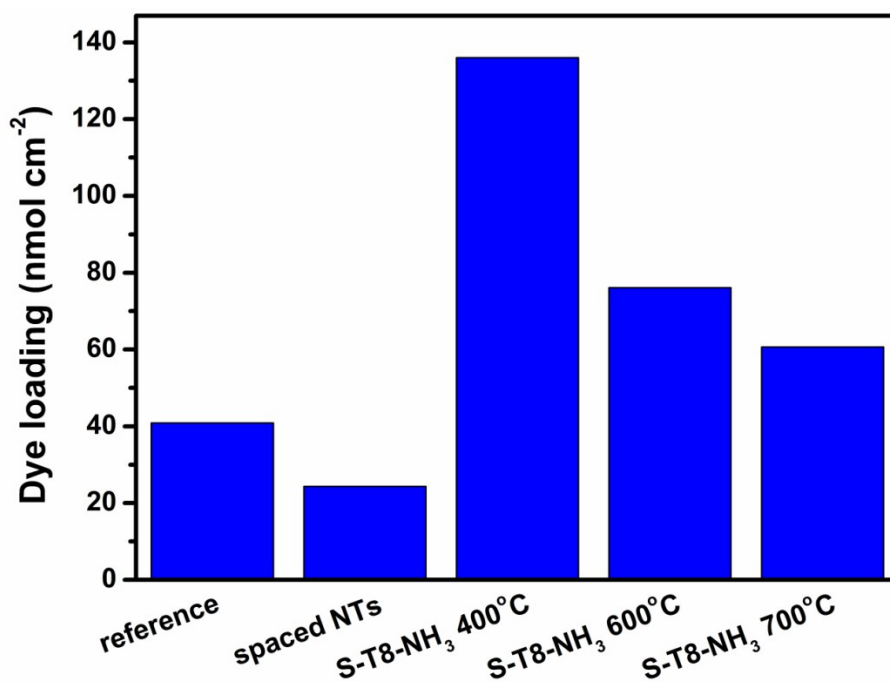


Figure S5 Dye loading measurements for: reference TiO₂ NTs (formed in ethylene glycol-based electrolyte), spaced NTs (formed in TEG-based electrolyte) and hierarchical TiO₂ NTs (decorated with 8 layers of TiO₂ nanoparticles) annealed in NH₃ at 400, 600 and 700°C.

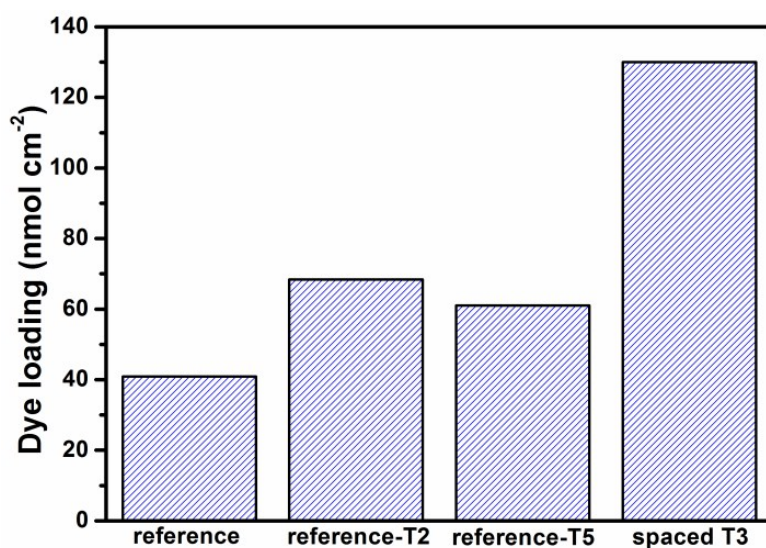


Figure S6 Dye loading measurements for: reference TiO₂ NTs (formed in ethylene glycol-based electrolyte) without and with TiO₂ nanoparticles (2 and 5 layers), and spaced NTs with 3 layers of TiO₂ nanoparticles.

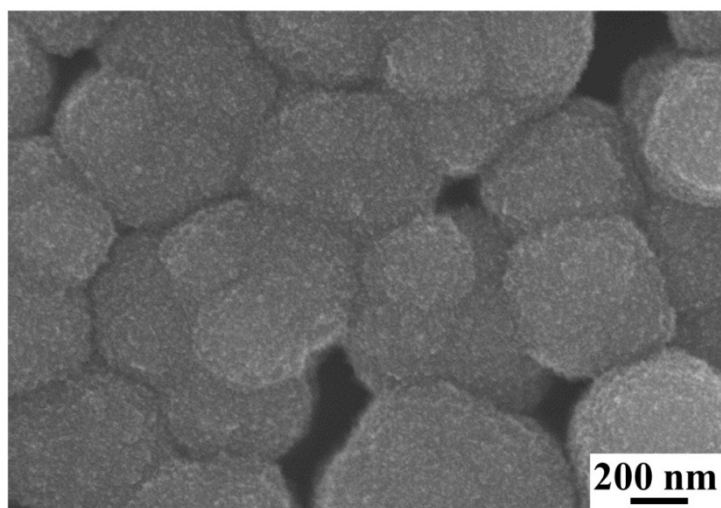


Figure S7 SEM image of hierachical TiO_2 nanotubes after 10 times of TiCl_4 treatment.

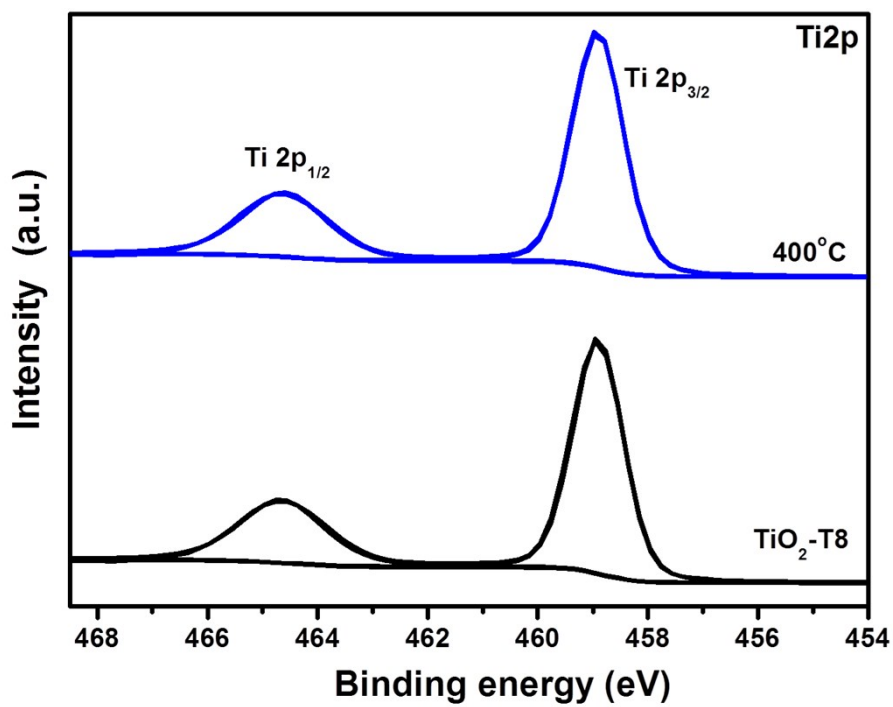


Figure S8 $\text{Ti}2p$ high resolution XPS spectra for the particle-decorated TiO_2 NTs ($\text{TiO}_2\text{-T8}$) and particle-decorated TiO_2 NTs annealed in NH_3 at 400°C .

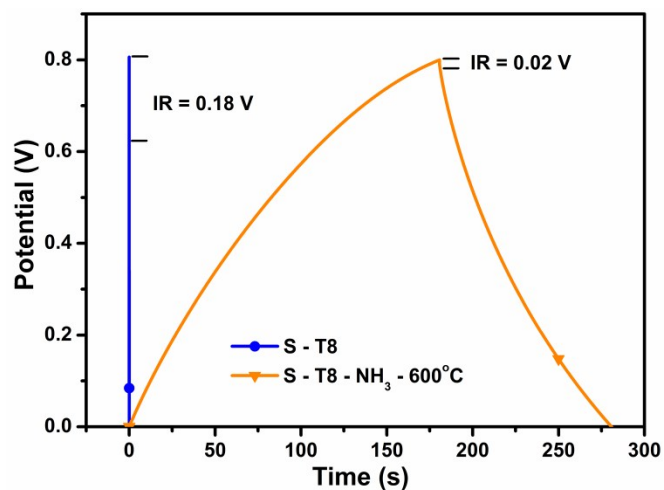


Figure S9 Galvanostatic charge/discharge curves of TiO_2 samples measured at a current density of $200 \mu\text{A cm}^{-2}$. NH_3 treatment was conducted at 600°C for 1 h.

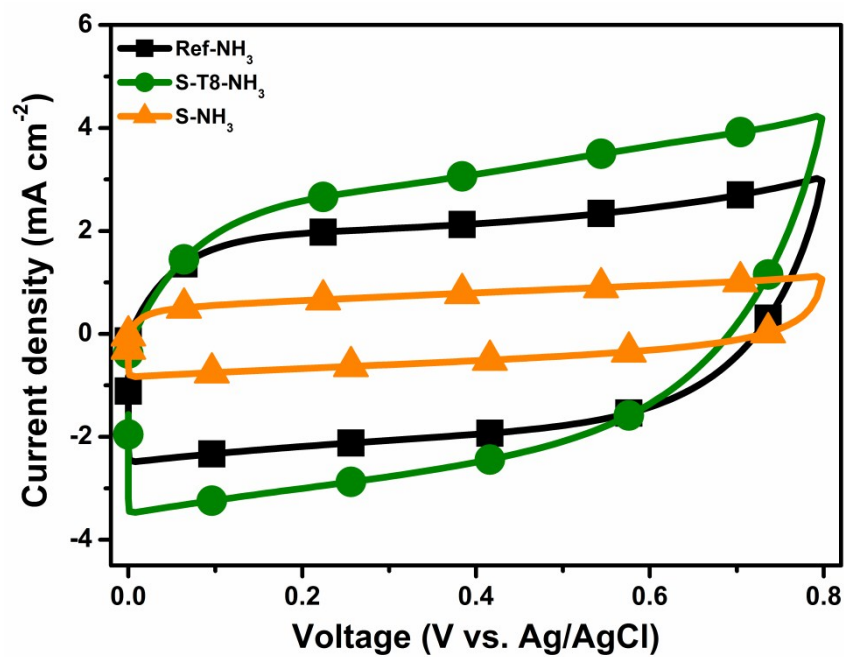


Figure S10 CV curves at a scan rate 100 mV s^{-1} of reference TiO_2 NTs and spaced TiO_2 NTs with/without TiO_2 nanoparticles. All samples are annealed in NH_3 at 600°C for 1 h.

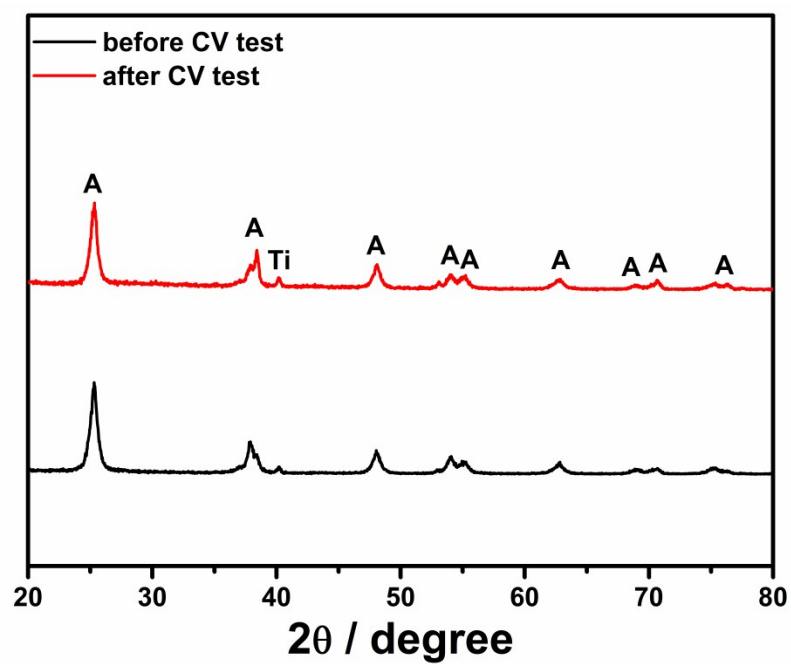


Figure S11 XRD spectra of hierarchical structures before and after CV tests.