

## Supplementary Information

### **Au nanocrystals decorated TiO<sub>2</sub> nanotubes for photocatalytic nitrogen fixation into ammonia**

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## **Materials synthesis**

**Titania nanotubes:** Titania nanotubes, denoted as TiO<sub>2</sub> NT, were prepared by electrospinning method<sup>1</sup>. A coaxial, two-capillary spinneret was used to allow two immiscible liquids to eject in a core-shell mode. Schematic illustration of the setup is displayed in the supporting information (Scheme S1). Paraffin oil (Aldrich, 5 mL) was directed into the inner needle by a syringe as the core whilst ethanol solution (2.5 mL) containing tetrabutyl titanate (Ti(OiPr)<sub>4</sub>, Aldrich, 1 mL), PVP (M<sub>w</sub> ≈ 1 300 000, Aldrich, 0.1 g) and acetic acid (0.5 mL) was loaded into the outer needle by another syringe as the shell. The feeding rates of ethanol solution and paraffin oil were set at 2.2×10<sup>-4</sup> mL/s and 1.1×10<sup>-4</sup> mL/s, respectively. A constant voltage of 15 kV was loaded between the dual nozzle and a piece of aluminum foil which served as a static collector. The distance between the nozzle and the aluminum foil was set at 20 cm. The fibers formed on the aluminum foil were immersed into octane overnight to remove paraffin oil. TiO<sub>2</sub> NT was obtained by calcining these fibers in air at 550 °C for 2 h in a muffle furnace.

**Au nanocrystals anchored titania nanotubes:** Au nanocrystals anchored TiO<sub>2</sub> NT, denoted as Au@ TiO<sub>2</sub> NT were fabricated by a photo-deposition method. Typically, 50 mg as-prepared TiO<sub>2</sub> NT was dispersed into water/ethanol (1:1) solution containing proper amounts of HAuCl<sub>4</sub> (e.g. 1 mg/mL). Sonication and magnetic stirring was applied to gain uniform suspensions. The suspensions were then irradiated by 365 nm UV light for 5 min to allow deposition of Au nanocrystals onto

TiO<sub>2</sub> NT. Color changes from white to purple can be visually inspected during irradiation. The resultant suspensions were centrifuged, washed with deionized water several times and dried in vacuum at 60 °C for 12 h.

### **Materials characterization**

Sample powders were analyzed by X-ray powder diffraction (XRD) techniques to inspect phase purity. A Bruker D8 Focus diffractometer (Bruker, Germany) with radiation Cu K<sub>α1</sub> radiation ( $\lambda = 1.5405 \text{ \AA}$ ) and Cu K<sub>α2</sub> radiation ( $\lambda = 1.5444 \text{ \AA}$ ) was used for XRD analysis. Data collections were carried out using step size of 0.01 ° with duration of 0.1 s at each step. The morphology and EDS spectra of freshly prepared samples were examined by a field emission scanning electron microscope (FESEM, HitachiS4800, Japan) and a transmission electron microscope (TEM, JEOL JEM-2100, Japan). Optical absorption data were collected on a UV-vis spectrophotometer (JASCO-750, Japan) coupled with integrating sphere and data were analyzed using JASCO software suite. BaSO<sub>4</sub> was used as a reference non-absorbing material. Surface conditions were analyzed by X-ray photo electron spectroscopy (XPS, AXIS Ultra DLD) with a monochromatic Al K X-ray source. All bonding energies were adjusted according to adventitious carbon C 1s peak at 284.6 eV. The surface area of as-prepared samples was analyzed on a NOVA 2200e adsorption instrument and were calculated based on the Brunauer-Emmett Teller (BET) model. N<sub>2</sub> temperature-programed desorption (N<sub>2</sub>-TPD) analysis were performed on a chemisorption apparatus (Micromeritics AutoChem II 2920) equipped

with thermal conductivity detector (TCD). Briefly, 0.03 g of sample powders were first pretreated with pure He at a flow rate of 30 mL·min<sup>-1</sup> at 150 °C for 60 min and were cooled down to 50 °C. Pure N<sub>2</sub> was then directed onto these sample powders for 60 min. Residual N<sub>2</sub> was purged with pure He at a flow rate of 50 mL·min<sup>-1</sup> for 30 min. The N<sub>2</sub> TPD measurement was subsequently performed up to 950 °C at a heating rate of 5 °C·min<sup>-1</sup> in pure He. The photoluminescence (PL) spectra were collected on a F-7000 FL Spectrophotometer equipped with a UV lamp of 280 nm as the excitation source. Time-resolved fluorescence decay spectra were acquired on a Horiba FL-1016 spectrophotometer using a 290 nm nanosecond pulse laser as the excitation source. Electron paramagnetic resonance (EPR) spectroscopy was performed on a Bruker EMX-10/12 spectrometer under a 9.65 GHz magnetic field modulation at 293 K with 7 mg sample placed in a quartz ESR tube.

### **Nitrogen photofixation**

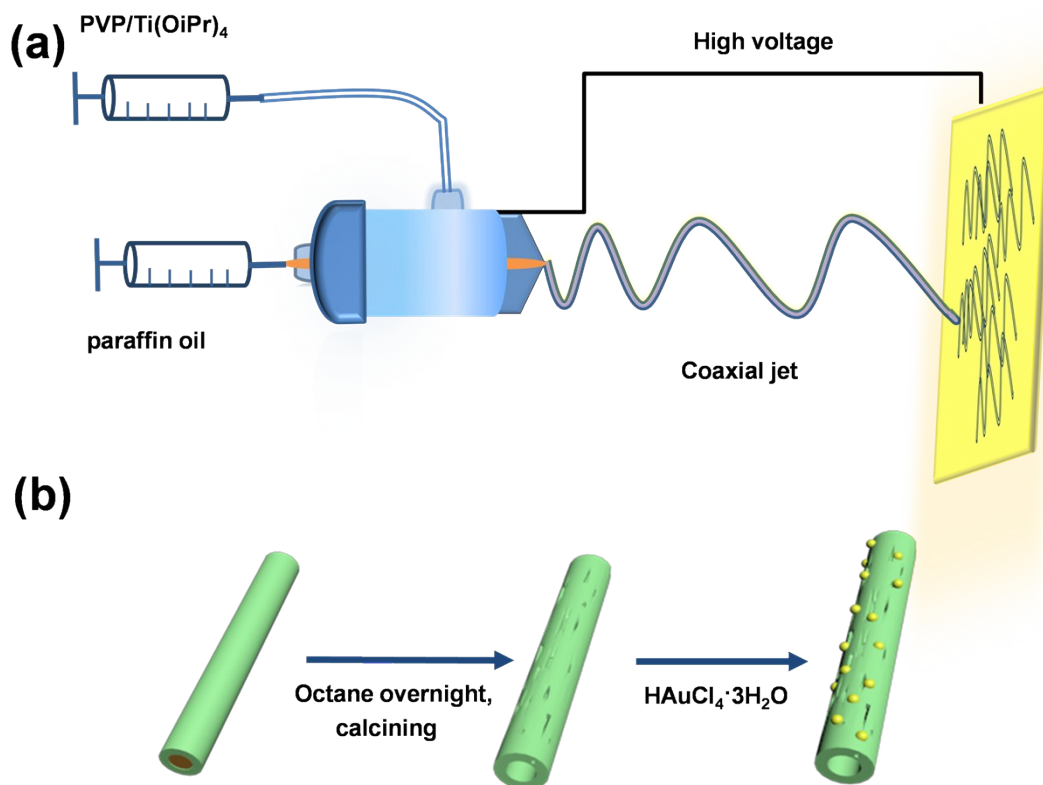
Nitrogen photofixation experiments were performed in a home-made glass reactor with a quartz window on the top. In a typical experiment, 30 mg sample powders were ultrasonically dispersed into 100 mL deionized water to form suspensions. The suspensions were sealed in the reactor which was purged with ultrapure N<sub>2</sub> gas at a flow rate of 60 mL/min. The experiment was started after N<sub>2</sub> purging for 30 min. Water jacket was applied to the reactor to maintain the temperature around 25 °C. A 500 W high-pressure mercury lamp (NbeT, Merc-500) was used as the light source. 5 mL of aliquot was taken out from the reactor every 1 h for ammonia analysis. The

ammonia analysis was performed using the indo-phenol blue method<sup>2</sup>. Specifically, the aliquot was filtered using a 0.22 $\mu$ m filter to remove sample powders. 0.2 mL salicylic acid solution (50 g/L), 80  $\mu$ L of sodium nitroferricyanide (10 g/L) and 80  $\mu$ L of 0.05 M sodium hypochlorite was added sequentially into the supernatant. After aging at 25 °C for 1 h, the supernatant was analyzed by a Shimadzu UV-2450 UV-Vis spectrometer to collect its UV-Vis absorption spectrum. The absorption at 697 nm was used to determine the concentration of indophenol blue. The concentration-absorbance curve was calibrated using standard ammonia chloride solution with a series of concentrations. The fitting curve ( $y = 65.79x - 2.94$ ,  $R^2 = 0.9999$ ) shows good linear relation of absorbance value with ammonia concentration by three independent calibrations (Figure S1). Other product of nitrogen photofixation such as  $N_2H_4$  was also detected by a colorimetry method with p-dimethylaminobenzaldehyde<sup>3</sup>. No  $N_2H_4$  signal was detected for a 5 h illumination period. Isotopic labelled experiments were performed by replacing  $H_2O$  with  $D_2O$  for nitrogen photofixation and other experiment conditions were kept the same. Monochromatic light was used to determine the apparent efficiency of nitrogen photofixation and was generated by filtering the output of 500 W high-pressure mercury lamp (NbeT, Merc-500) with bandpass filter at 350 nm, 420 nm, 450 nm, 550 nm and 600 nm, respectively. Apparent quantum efficiency was calculated according to following equation:

$$AQE = \frac{3 \times \text{ammonia produced per hour}}{\text{photon flux per hour}} \times 100\%$$

## **Photoelectrochemical analysis**

The photoelectrochemical measurements were performed via a Zahner electrochemical workstation using a standard three-electrode quartz cell with a 300 W Xenon lamp (Perfect Light, PLX-SXE300) coupled with AM1.5 filter as a light source. Sample photo-electrodes were fabricated by an electrophoretic deposition method: two pieces of clean fluorine doped tin oxide (FTO) glass ( $30 \times 10$  mm) were immersed into 50 ml acetone solution containing 50 mg ultrasonically dispersed sample powders and 20 mg iodine. The two pieces of glass were aligned in parallel with 10 mm distance and conductive sides facing inward. A constant electric bias was applied between the glasses under potentiostatic control (Keithley 2450 Source meter) for 3 min. The glass at anode side was quickly deposited with sample powders and was used as photo-electrode. The photo-electrode was calcined at 473 K for 10 min for the removal of iodine absorbed. Diluted  $\text{TiCl}_4$  (Alfa Aesar, 99.9%) methanol solution (10 mM) was dropped onto the electrodes and was dried in air. The procedure was repeated six times in order to minimize the exposure of naked FTO. The photo-electrode was then calcined at 673 K for 1 h to strengthen interconnection between individual particles. The as-prepared photo-electrode, Pt foil ( $10 \times 10$  mm) and Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. An aqueous solution of  $\text{K}_3\text{PO}_4/\text{K}_2\text{HPO}_4$  (0.1 M, pH = 12.66) was used as an electrolyte and a buffer. The incident light was rectified by an electronic timer and shutter (DAHENG, GCI-73).



Scheme S1. (a) Schematic illustration of electrospinning setup for the preparation of TiO<sub>2</sub> nanotubes; (b) procedures for the fabrication of Au nanoparticle anchored TiO<sub>2</sub> nanotubes.



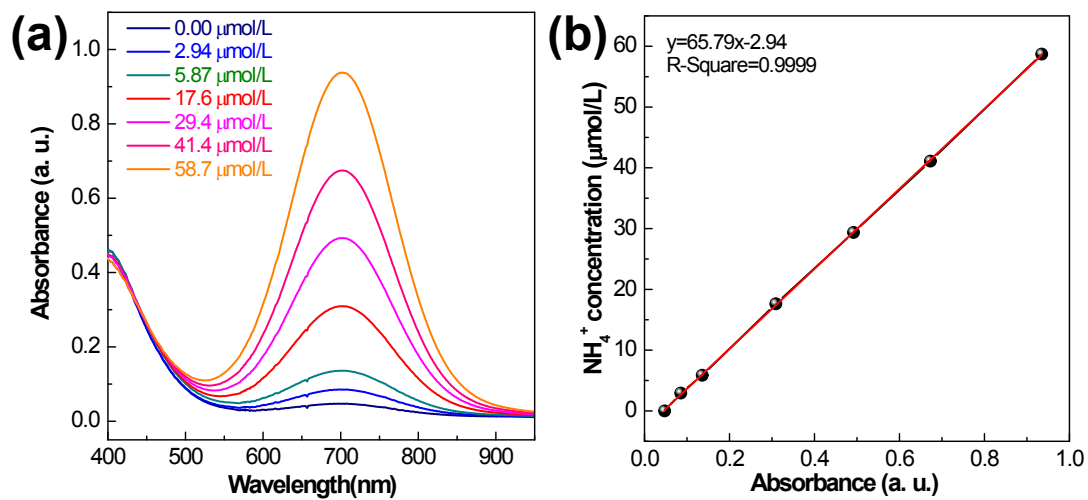


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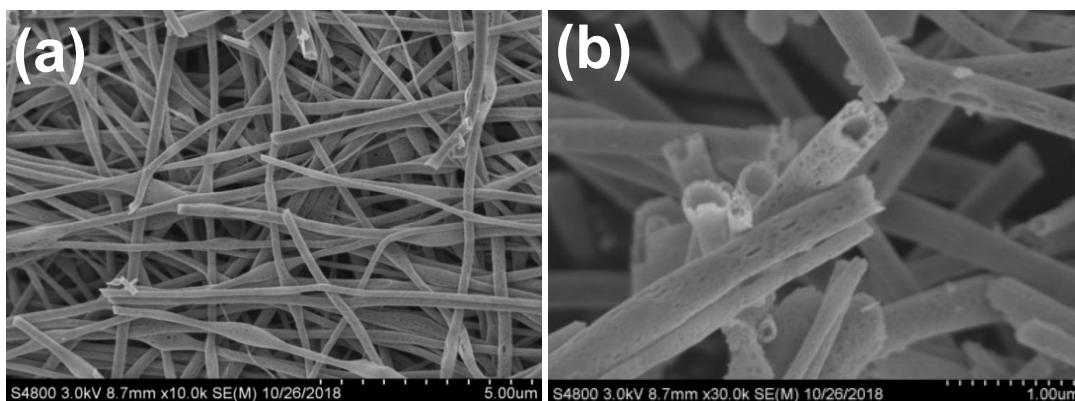


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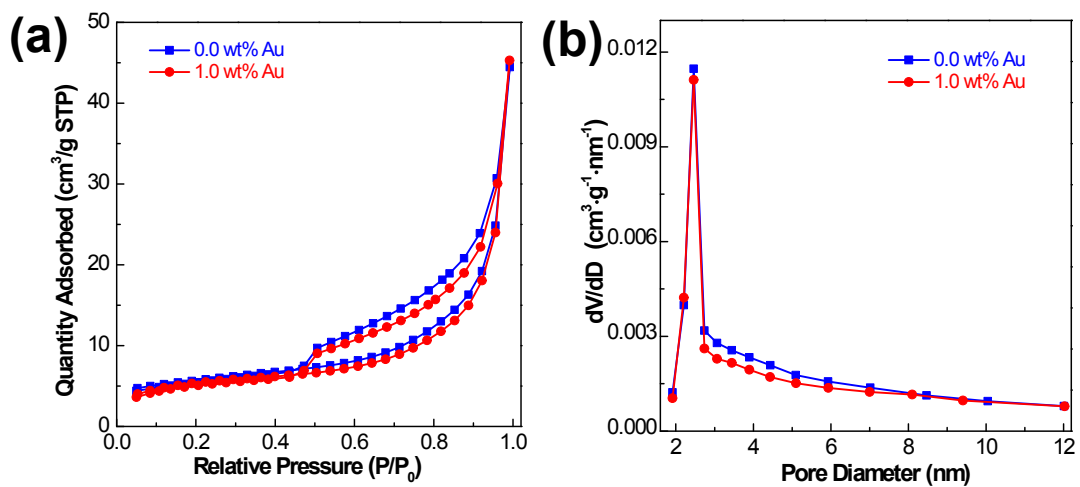


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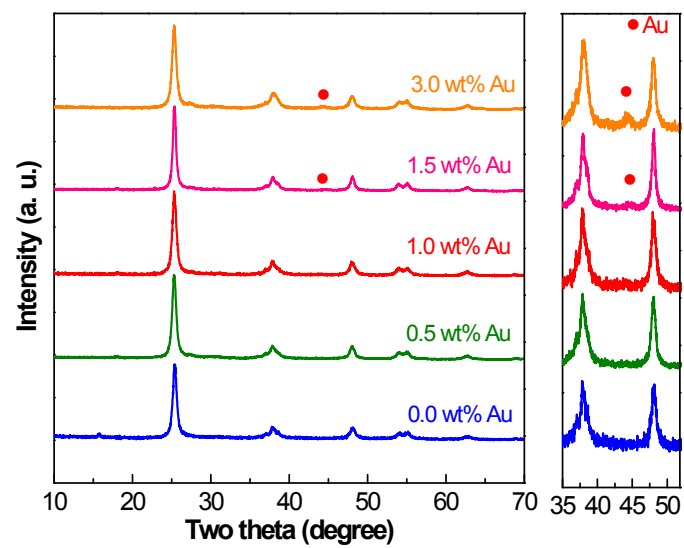


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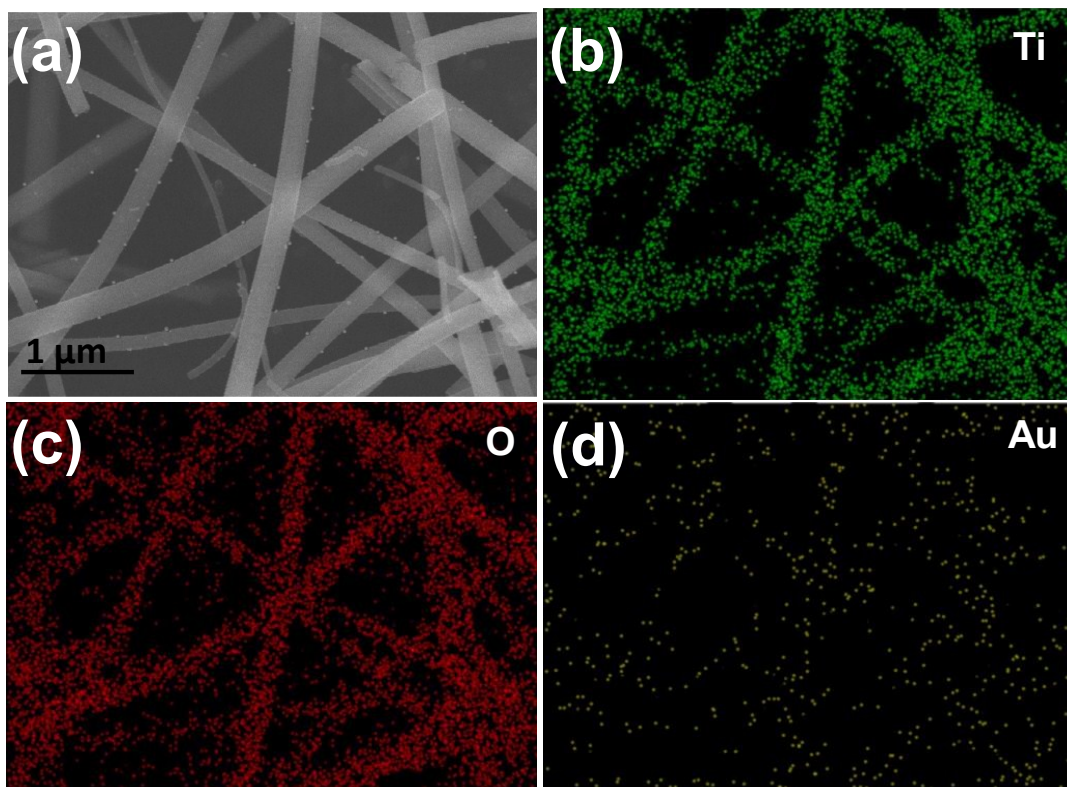


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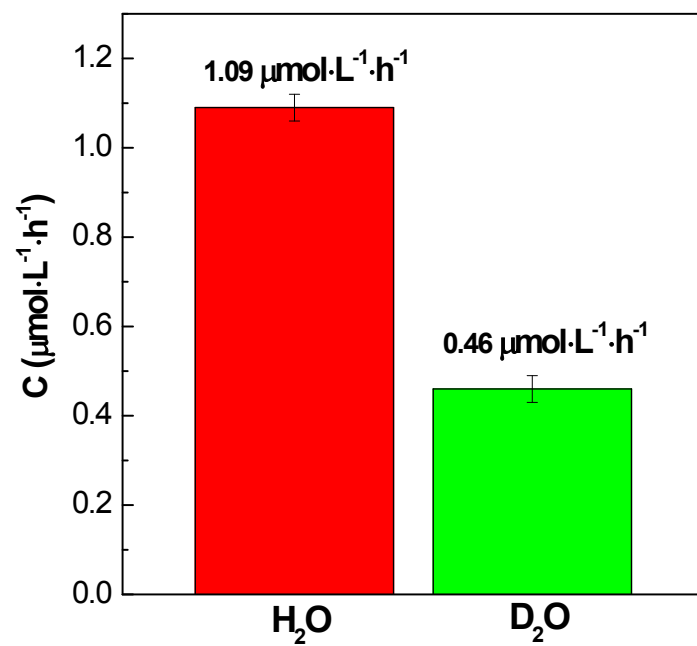


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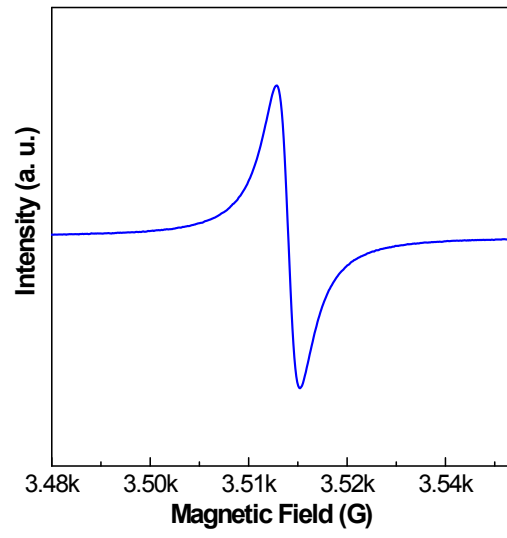


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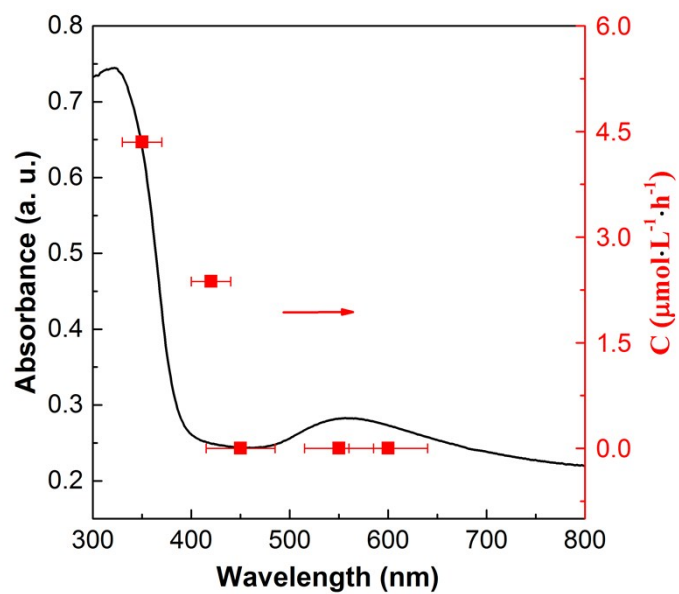


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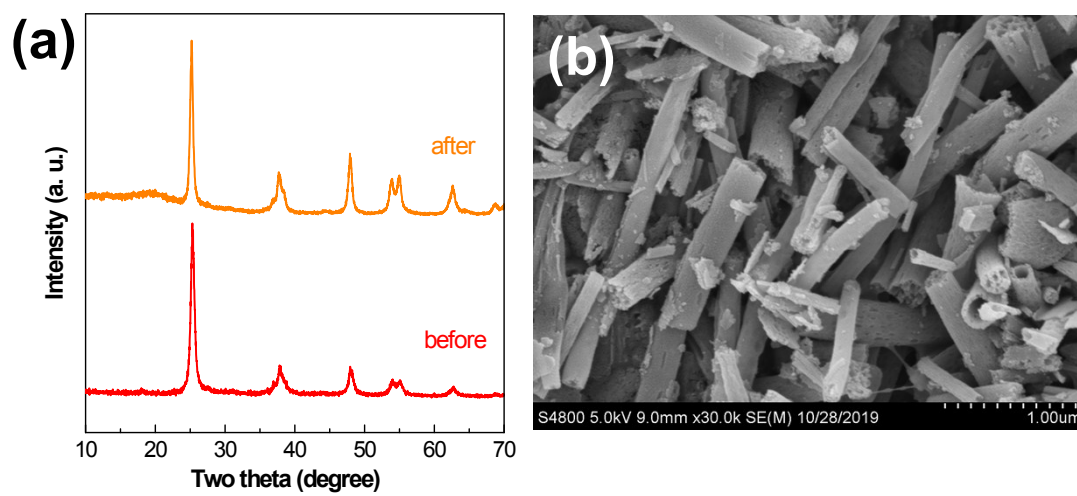


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