Supporting information

A Microwave-Assisted Template-Free Route for Large-Scale Synthesis of Photoluminescence Single Crystal $CsPbI_3$ Nanotubes

Weiwei Xiong, [*a] Ziyi Zhang, [b] Yutao Huang, [b] Chenxin Xu, [a] Jiajing Wu [b], Lingling Li,[b] Fenfen Zheng, [*a] Xingcai Wu [*b]

[a] Dr. W. Xiong, C Xu, Dr. F. Zheng,
School of Environmental & Chemical Engineering, Jiangsu University of Science and Technology Zhenjiang, Jiangsu 212003 (P. R. China)
E-mail: xiongweiwei@just.edu.cn; fenfenzheng1108@126.com
[b] Dr. Z. Zhang, Dr. J. Wu, Z. HuangYang, Prof. L. Li, Prof. Dr. X. Wu,
E-mail: wuxingca@nju.edu.cn
School of Chemistry & Chemical Engineering Nanjing University, Nanjing, Jiangsu 210023 (P. R. China)
Supporting information for this article is given via a link at the end of the document.

Experimental

Materials: Cs_2CO_3 (99.9, Aladdin), octadecene (ODE, 90%, Aldrich), oleic acid (OA, 90%, Aldrich), PbI_2 (99%, Aladdin), oleylamine (OLA, Aldrich, 80%), hexane (99.9%, Aladdin). All chemicals were used as received.

Methods:

Preparation of Cesium oleate:

Cesium oleate solution was prepared following the previous approach. Briefly, 0.40 g Cs_2CO_3 and 1.2 mL OA were loaded into a 3-neck flask along with 15 mL ODE, degassed under vacuum at 120 °C for 1h, following a second degassing phase at 150°C under N_2 until all Cs_2CO_3 reacted with OA.

Microwave Assisted Synthesis of double swallow-tail $CsPbI_3$Nanotubes:

ODE (20 mL) and PbI_2 (0.348g), were loaded into 50 mL 3-neck flask and dried under vacuum for 1h at 120 ºC. Dried OLA (2 mL) and dried OA (2 mL) were injected at 120 ºC under N_2. After complete solubilisation of a PbI_2 salt, the temperature was changed to 150 ºC and hot Cs-oleate solution (1.6 mL in ODE, prepared as described above) was quickly injected and the reaction mixture was immediately transferred into the exclusive vitreous vessel with a volume of 30 mL. The high-quality nanotubes were prepared at controlled reaction temperature with different time. After microwave irradiation, the product was allowed to cool to lower than 40 ºC, and $CsPbI_3$ Nanotubes were separated via low speed centrifuge from the crude solution. Finally, the precipitate was re-dispersed in hexane for storage.

Characterization:

UV-vis spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan). Fluorescence spectra were obtained from an F-7000 spectroflurophotometer (Hitachi, Japan). Transmission electron micrographs (TEM) were performed on a JEOL 2010 transmission electron microscope, using an accelerating voltage of 200 kV. Scanning electron micrographs were performed on JEOL JSM-7500 scanning electron microscope with an energy-dispersive X-ray spectrometer. The structures of the materials were confirmed by powder XRD on a Thermo ARL SCINTAG X'TRA diffractometer using a Cu-Kα radiation (λ = 0.15405 nm). Confocal laser scanning microscopy (CLSM) studies were performed using a Leica TCS SP5 microscope (Germany) with excitation at 405 nm. The PL lifetime study was performed by FLS920 with an excitation of 409 nm. The microwave system is from Discover (CEM), and exclusive vitreous vessels with a 30 mL capacity were equipped for use with the system at high temperature and pressure. The standard photolithography technique was used to design the source and drain electrodes with channel about 15 μm by using metal evaporation and a lift-off procedure. The current-voltage and the current-time characteristic curves of the photodetector was measured using a

Model CRX-4K Cryogenic Probe Station (Lake Shore Inc.) and Keithley2636A (Keithley Instruments Inc.).

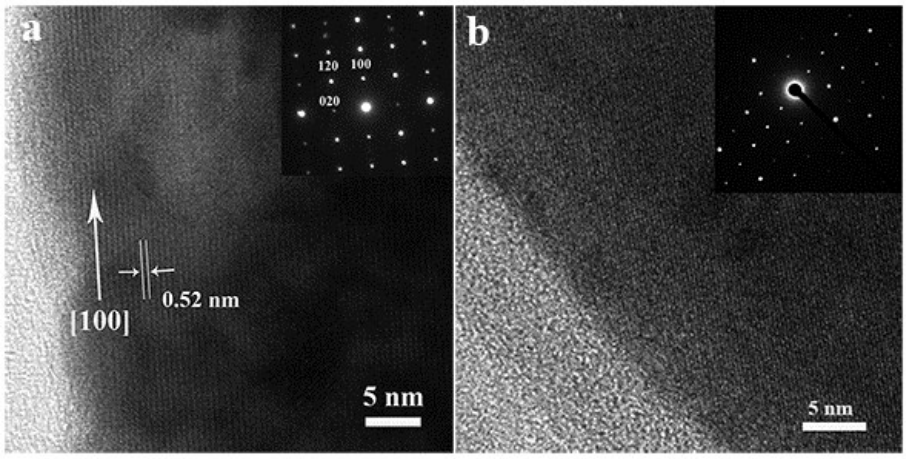

Figure S1. HR-TEM image and corresponding SAED of $CsPbI_3$ nanotubes in different regions.

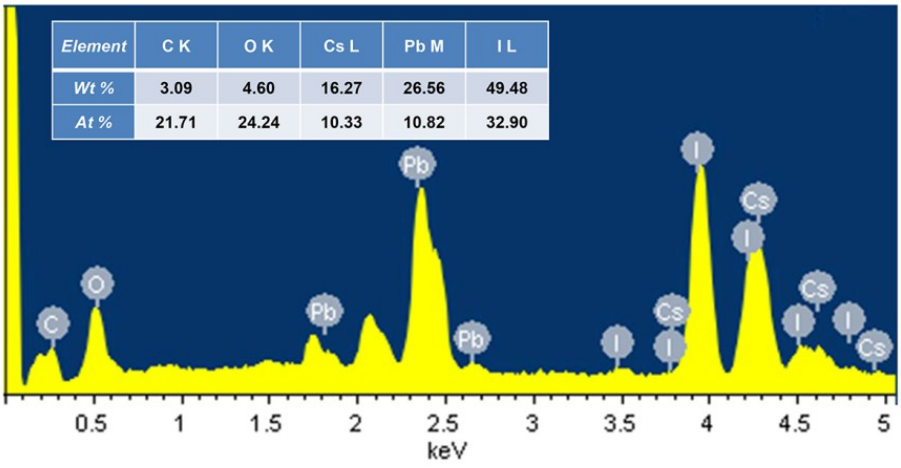

Figure S2. Energy dispersive X-ray spectroscopy analysis of the $CsPbI_3$ nanotubes.

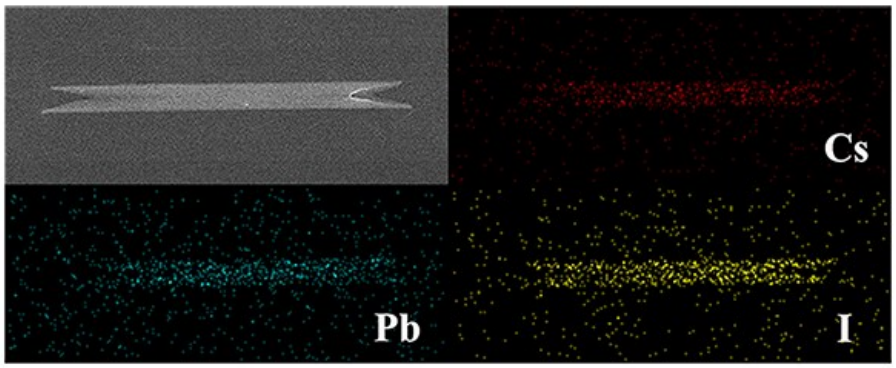

Figure S3. EDS mapping of the nanotubes, showing the uniform elemental distribution of Cs, Pb, I.

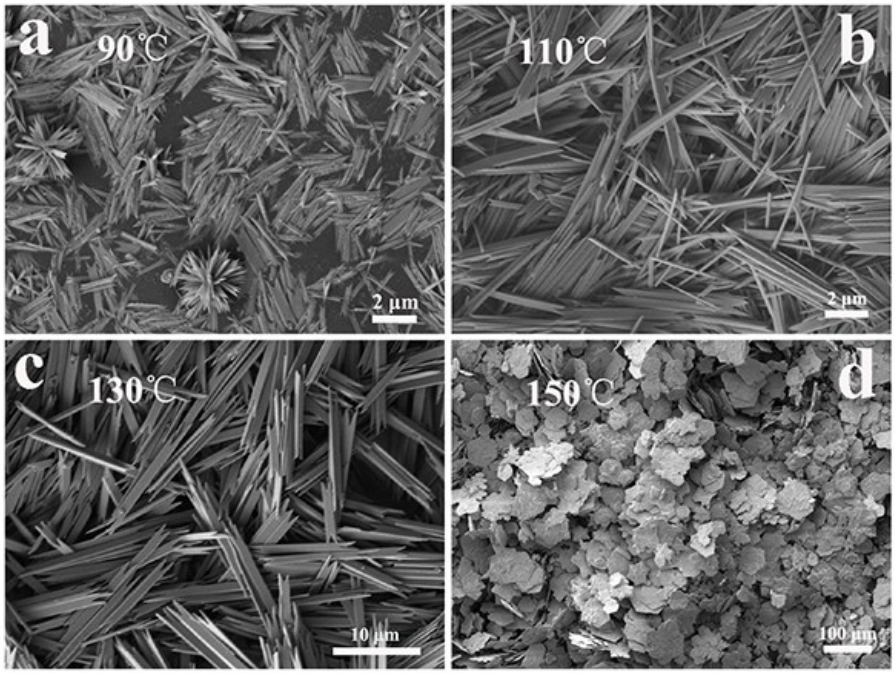

Figure S4. Representative SEM images of the as-prepared $CsPbI_3$ nanotubes synthesized with different reaction temperature with a fixed reaction time of 30 min.

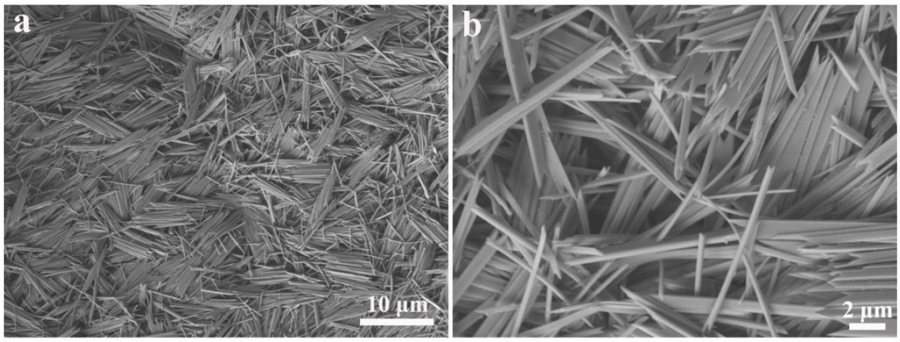

Figure S5. Representative SEM images of the as-prepared $CsPbI_3$ nanotubes synthesized at 110℃under different magnifications.

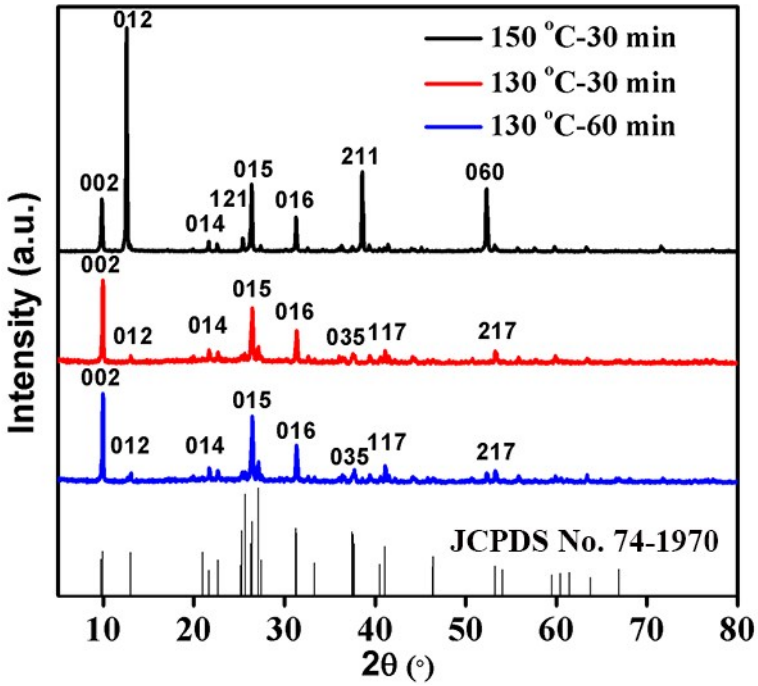

Figure S6. XRD patterns of the nanotubes at different reaction temperature and different reaction time.

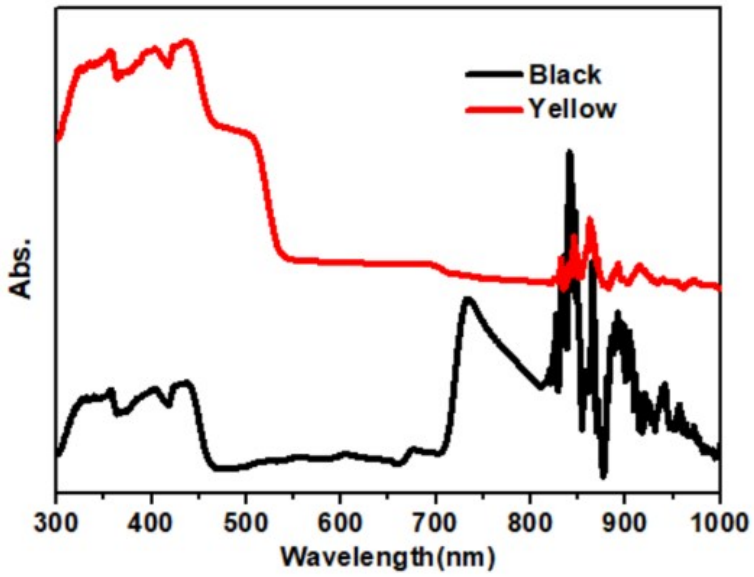

Figure S7. UV-vis absorption spectrum of the nanotubes before and after heating (330℃) treatment in a vacuum.

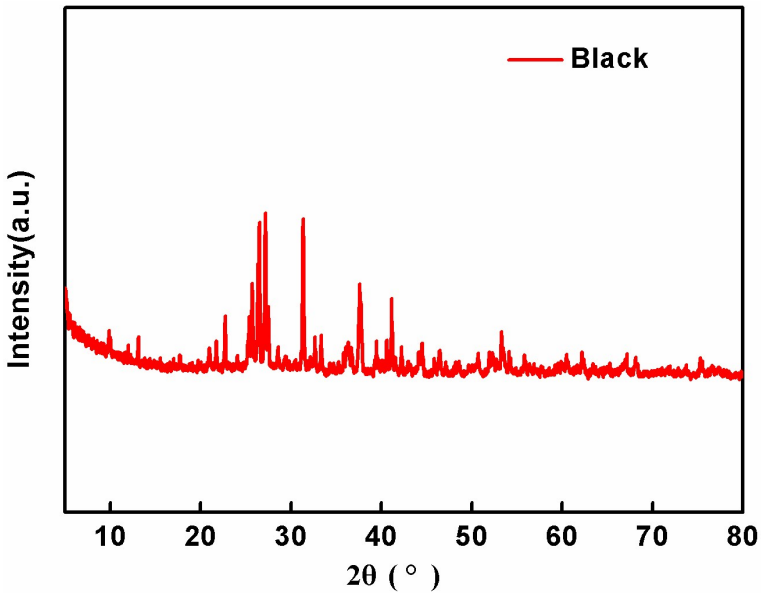

Figure S8. XRD patterns of the nanotubes after heating treatment(330℃).

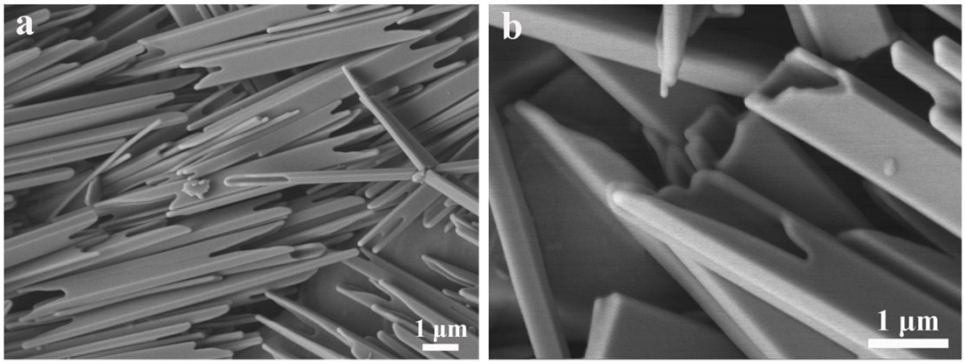

Figure S9. Representative hollow SEM images of the as-prepared $CsPbI_3$ nanotubes.

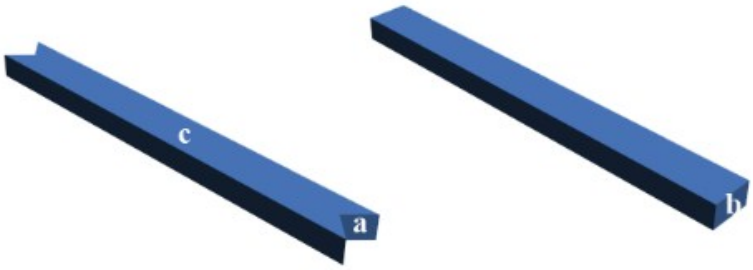

Figure S10. The schematic illustration for the formation of the swallow-tail ends

With regard to the formation of the swallow tail ends, we speculate that their formation and growth processes are related to the interplay between kinetics and thermodynamics control. Because in the initial growth stage, both ends of the nanotubes present swallow-tail topographic characteristics with a good symmetry, related to the known cell type. We believe that the four inner surfaces of the cusps have the same crystal plane (denoted as crystal plane a in Figure S8), leading to a lower energy compared to the closed ends (denoted as crystal plane b in Figure S8). Under thermodynamic control, the nanotubes grow along the crystal plane c, meanwhile, the kinetics ensures a relatively slow grow rate, leading to the nanotubes growing along the inner surfaces of the cusps and maintain the exposure of the same crystal face. All these ensure that the nanotubes appear to have similar swallowed tail ends at different stages of growth

(different lengths). In addition, we believe that I^- ions play a vital role in the formation of nanotubes with swallowed tail ends since we failed to obtain similar $CsPbBr_3$ nanotubes under the same experimental conditions.

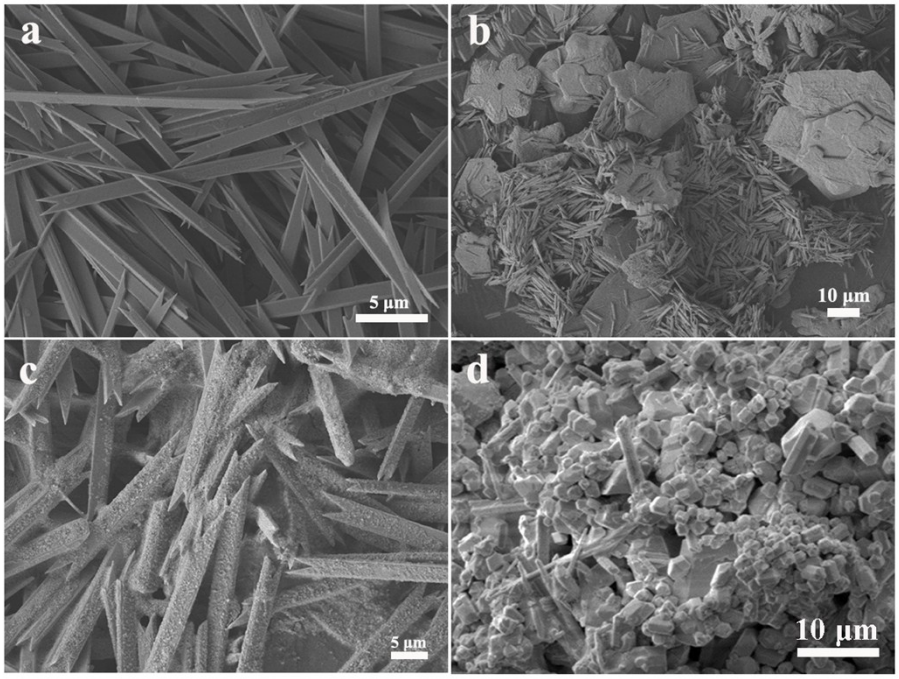

Figure S11. Representative morphologies of the $CsPbI_3$ (a, b, c) and PbI_2 (d) with different synthetic conditions (see Table S1).

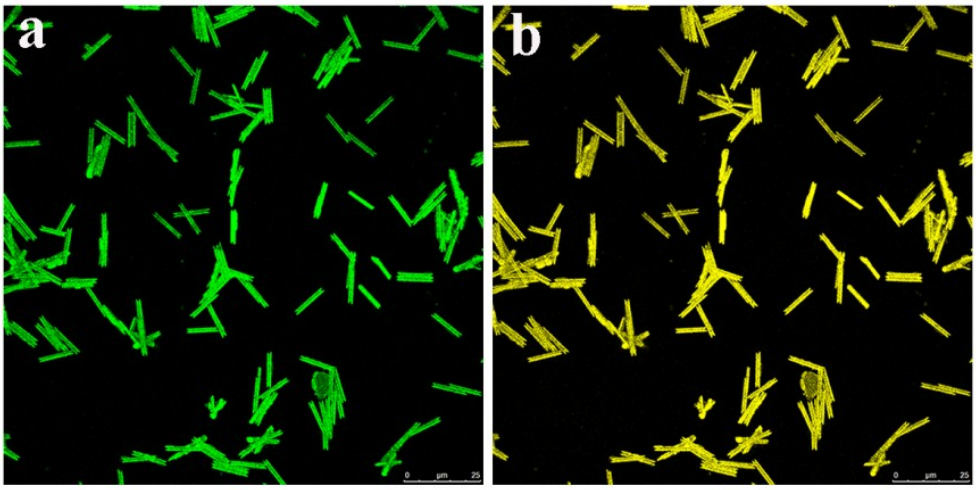

Figure S12. Confocal microscopy images of the nanotubes with different collected channels in the 425-475 nm spectral window and 520-570 nm spectral window, respectively.

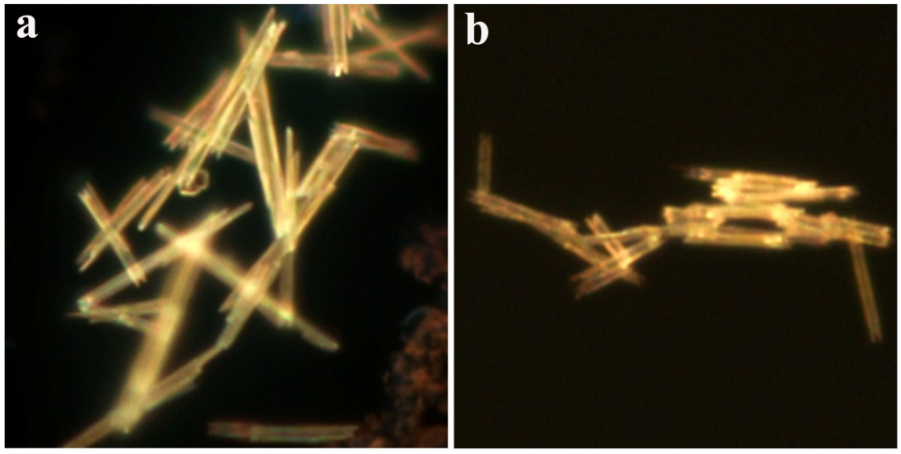

Figure S13. Microphotographs of $CsPbI_3$ nanotubes under excitation at 365 nm.

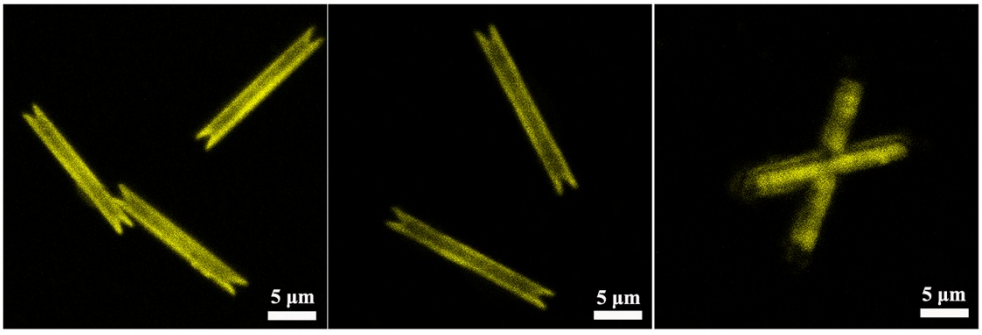

Figure S14. Confocal microscopy images of the nanotubes with the same control parameters. (a)fresh preparation; (b) stored in hexane at 4 ℃ for 10 months; (c)

Exposed in air at room temperature for one month.

Table S1. Synthetic conditions and obtained morphologies of nanomaterial in Figure S11.

ODE (mL)	Oleylamine (mL)	Oleic acid (mL)	Reaction Temperature (℃)	Reaction Time (min)	Morphology	Nanotube Yield (%)
20	2	2	130	30	**(a)** Nanotubes	99%
20	2	3.2	130	30	**(b)** Nanotubes and nanoflakes	30~40%
20	3.2	2	130	30	**(c)** Nanotubes and nanocubes	60~70%
0	10	10	130	30	**(d)** Large nanoparticles and nanorods	0%