Electronic Supplementary Information

Photoinduced synthesis of Bi_2O_3 nanotubes based on oriented attachment

Yaming Qiu,[1†] Lei Zhang,[1†] Lingmei Liu,[2] Cong Lin,[1] Le Xu,[1] Jian Li,[1] Youyou Yuan,[1] Xin Du,[1] Yu Han[2*] and Junliang Sun[1*]

[1] *College of Chemistry and Molecular Engineering Peking University Yi he yuan Road 5, Beijing 100871, China*

[2] *Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.*

[†] These authors contributed equally to this work.

* Corresponding author. E-mail: junliang.sun@pku.edu.cn, yu.han@kaust.edu.sa

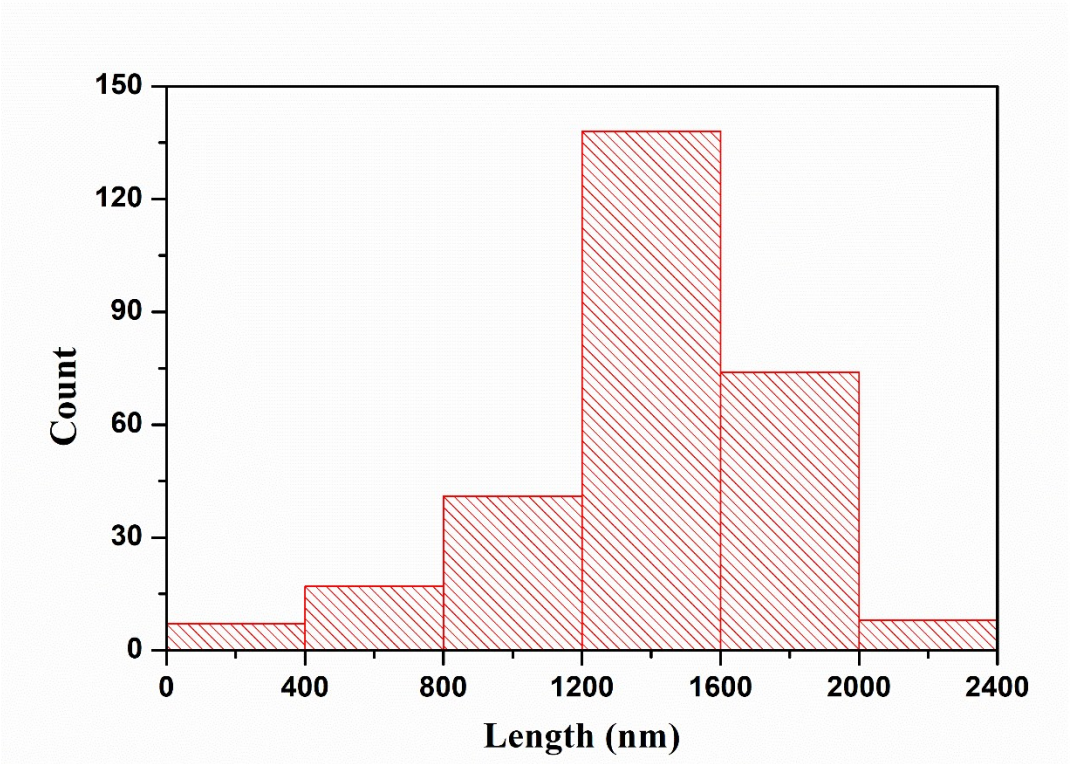


Figure S1. The length histogram of the nanotubes.

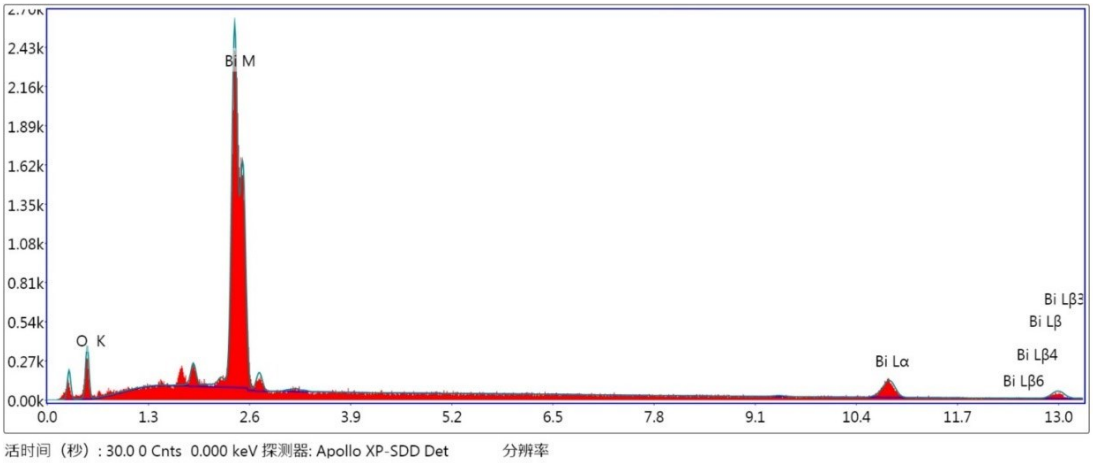


Figure S2. The EDX pattern of the as-synthesized product.

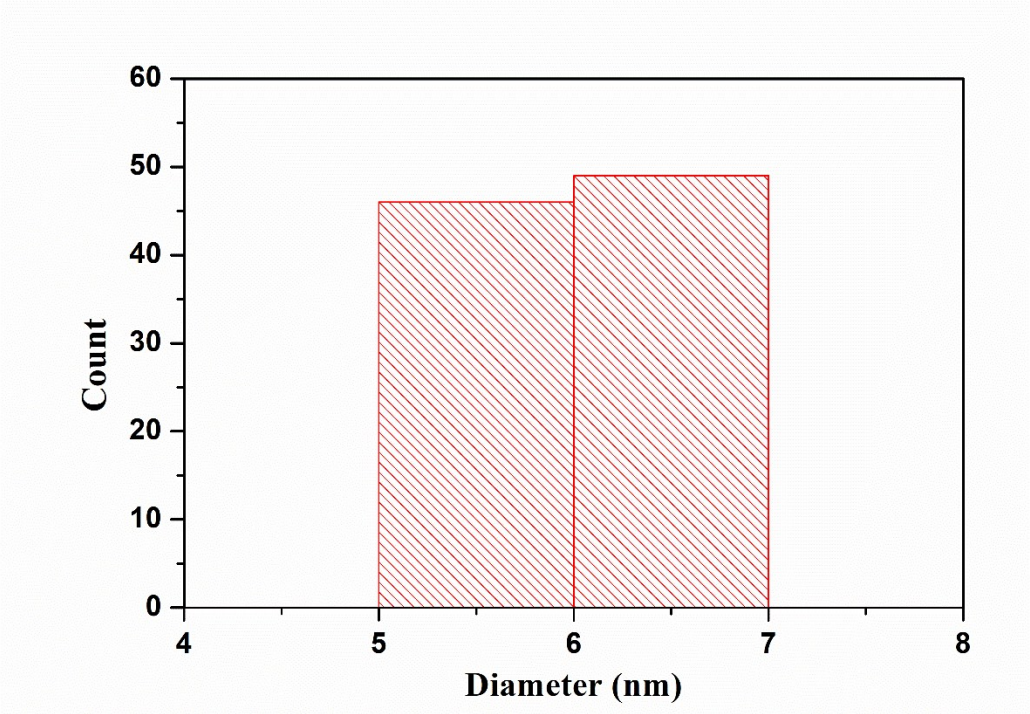


Figure S3. The diameter histogram of the nanotubes.

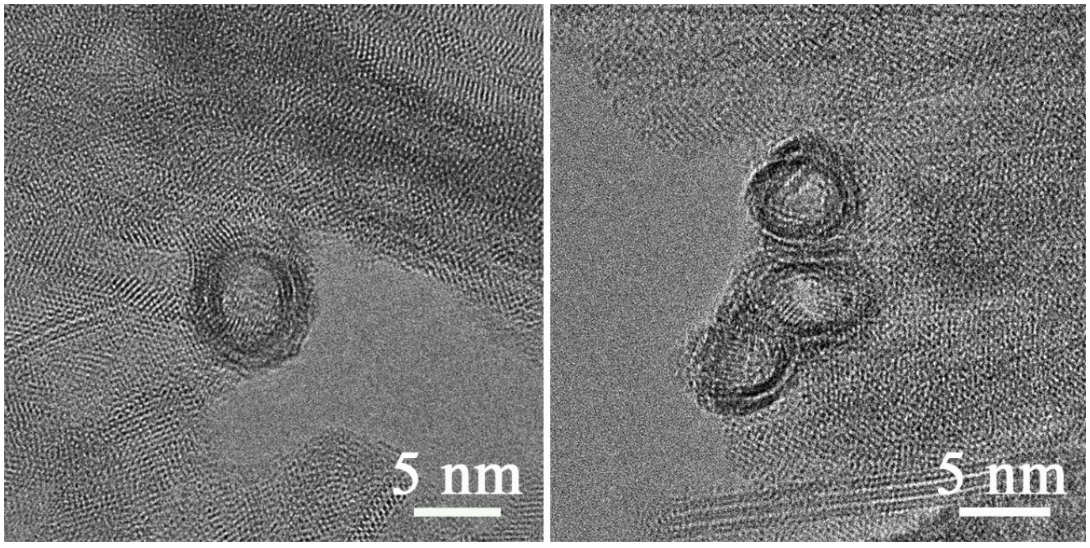


Figure S4. HRTEM images of the cross section of nanotubes showing a multi-walls tubular structure.

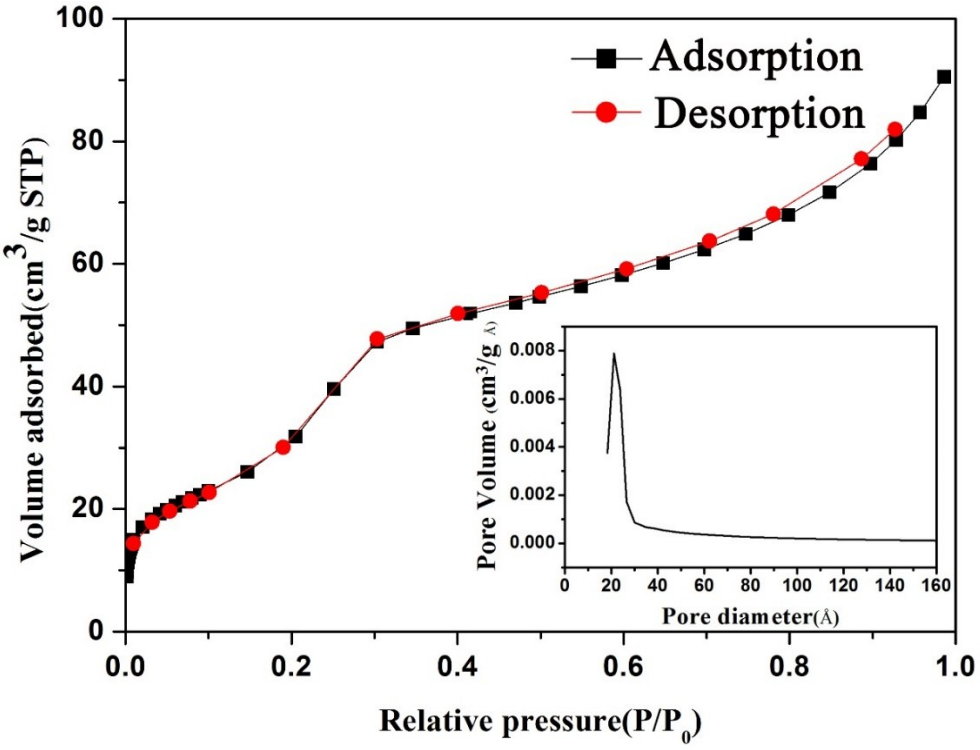


Figure S5. Ar adsorption/desorption isotherms and pore size distribution of Bi_2O_3 nanotubes.

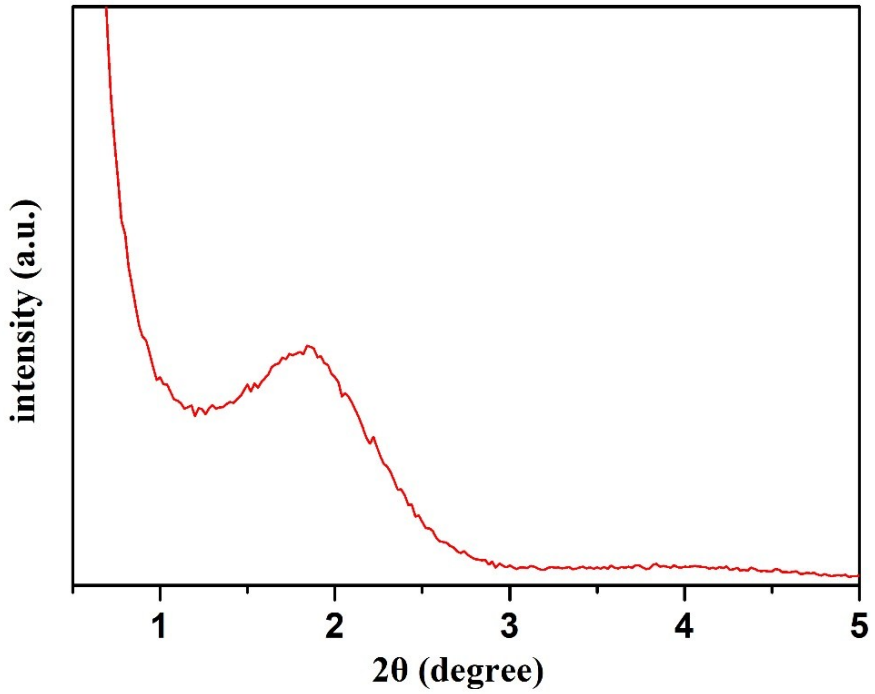


Figure S6. Small angle PXRD pattern of Bi_2O_3 nanotubes.

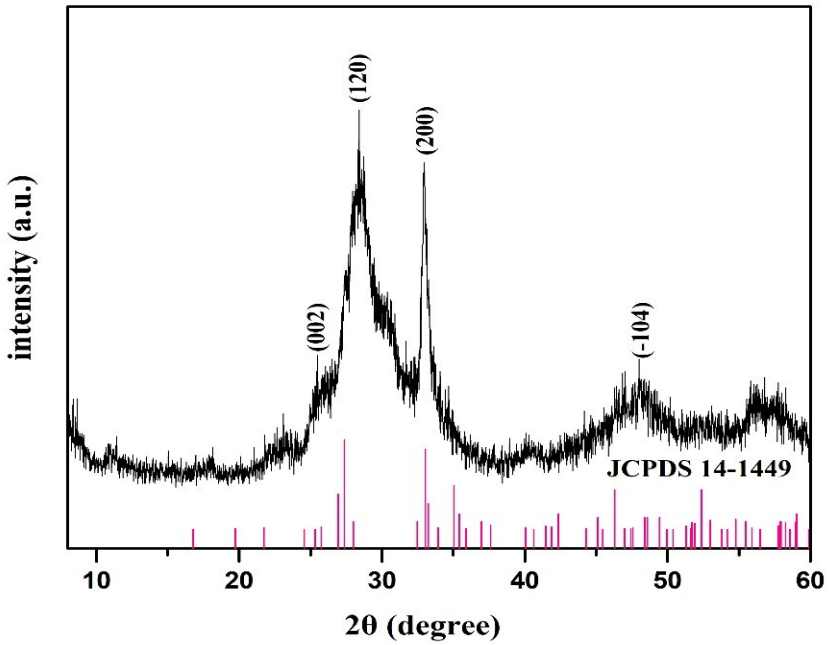


Figure S7. The X-ray diffraction pattern of the as-synthesized product. All peaks are indexed to α-Bi_2O_3 (JCPDS 14-1449).

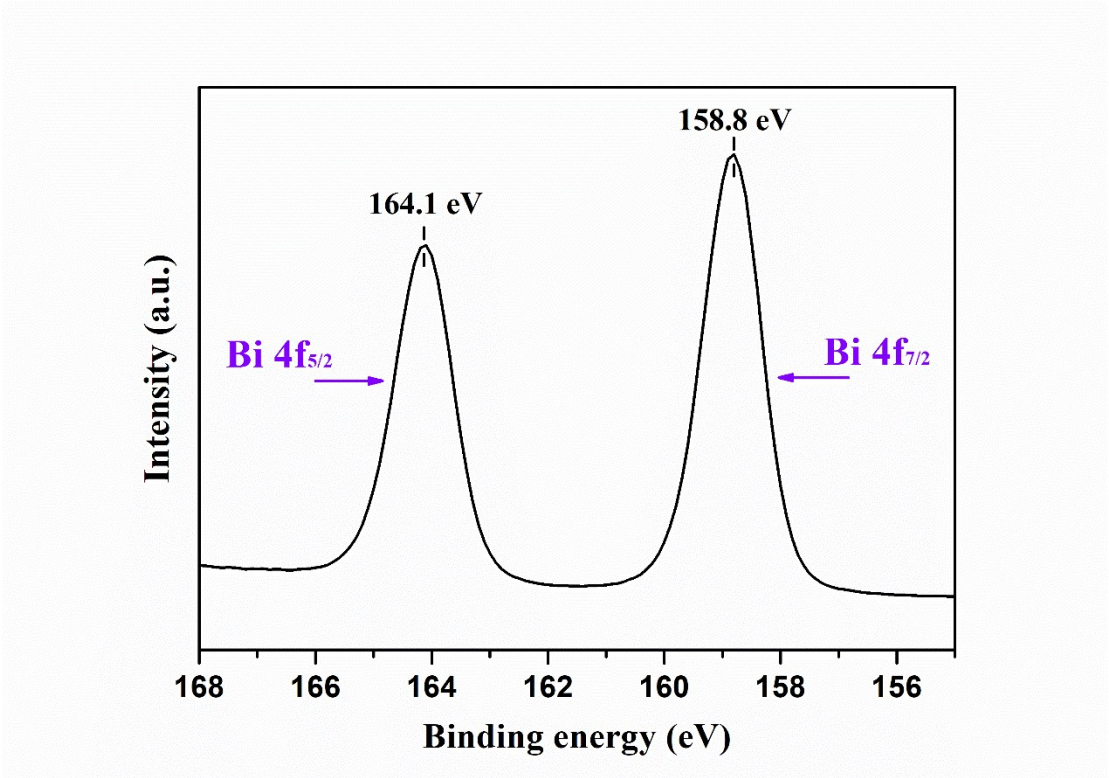


Figure S8. XPS spectra of the as-synthesized product.

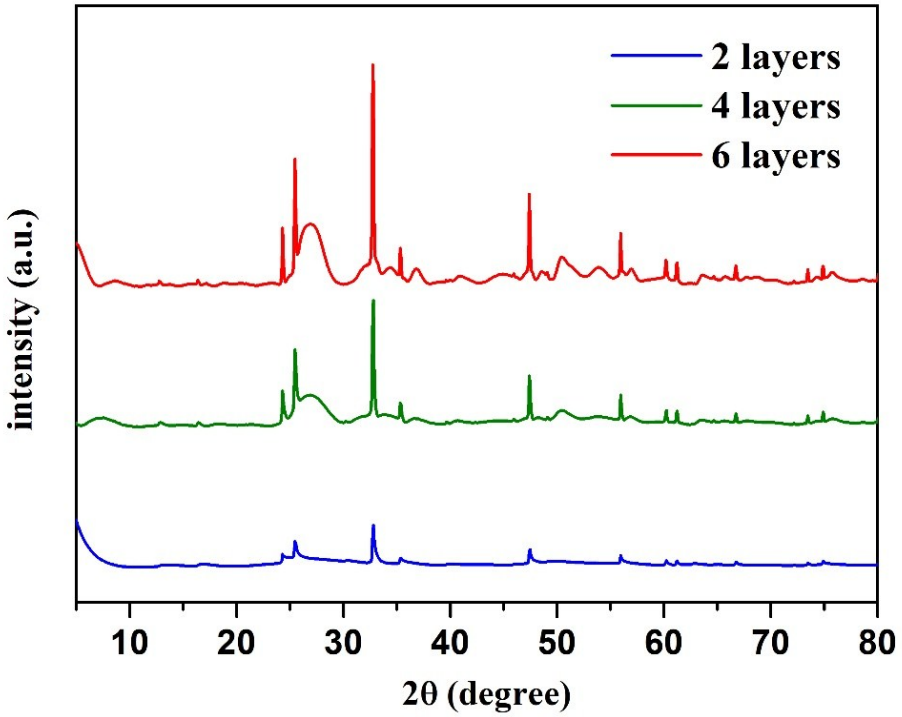


Figure S9. The PXRD simulation of 2, 4 and 6 layers of α-Bi_2O_3 nanosheets.

Discuss program[1] was used in the calculation of the PXRD of thin layer α-Bi_2O_3 (2, 4, and 6 layers of α-Bi_2O_3 nanosheets). The cll file can be edit from the cif file of α-Bi_2O_3, the super cell we calculated is 100 x 1 x 100 , 100 x 2 x 100 and 100 x 3 x 100 for 2, 4, and 6 layers of α-Bi_2O_3 nanosheets respectfully.

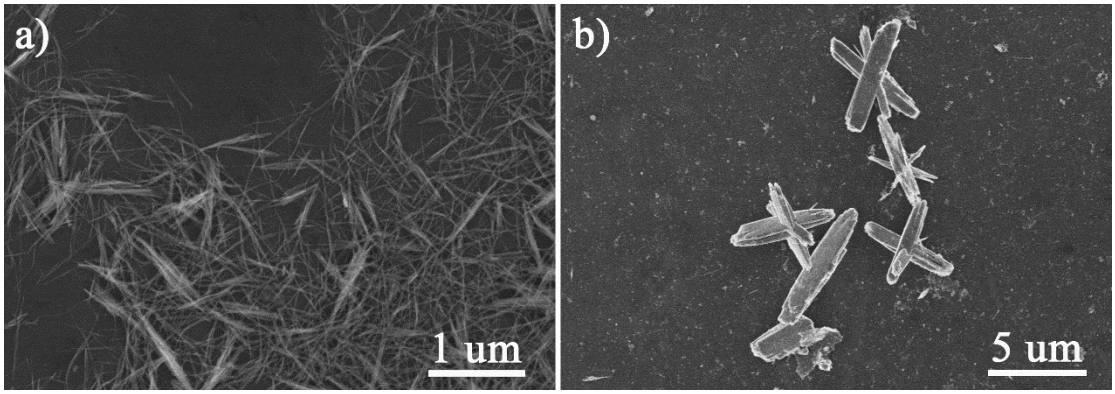


Figure S10. The morphology of Bi_2O_3 under UV conditions for irradiances of 50 and 200 mW/cm^2, respectively. a) nanotubes, b) bulk. It proved that the UV light would accelerate the crystallization process. Besides, the crystallization process would be faster with the increase of the irradiance of light.

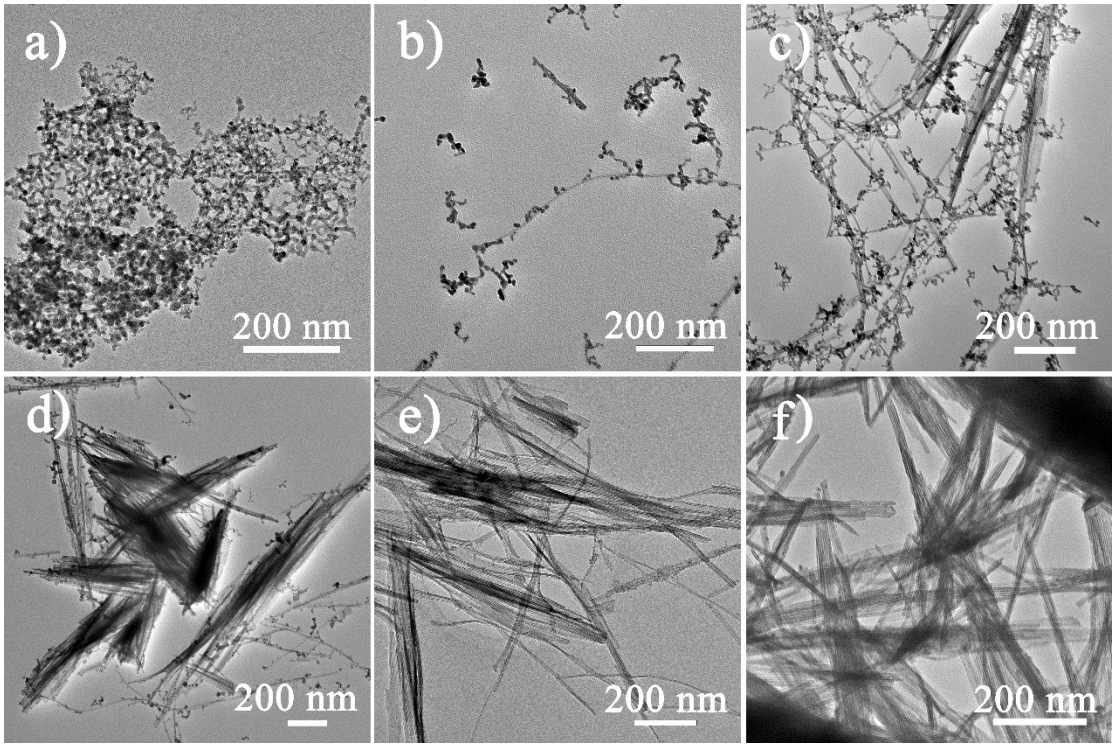


Figure S11. TEM images of the intermediate products at different growth stages under the condition of 50 mW/cm^2 ultraviolet radiation. a) precursor, b) 3 min, c) 10 min, d) 20 min, e) 40 min, and f) 60 min. The results show that the amorphous structures decrease and the nanotubes increase with the prolongation of reaction time.

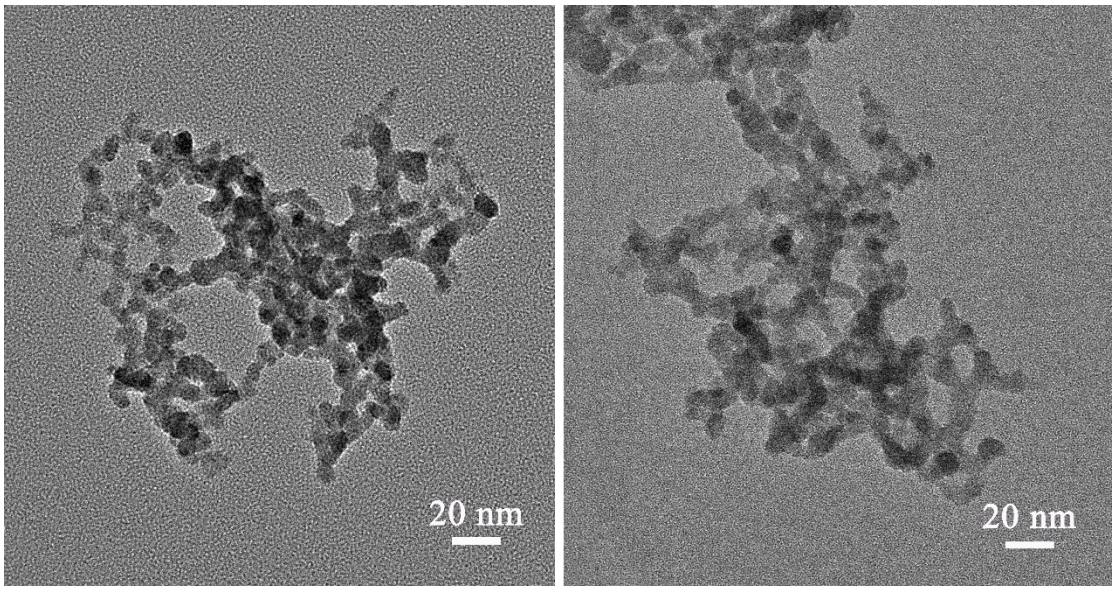


Figure S12. TEM images of the as-synthesized precursor.

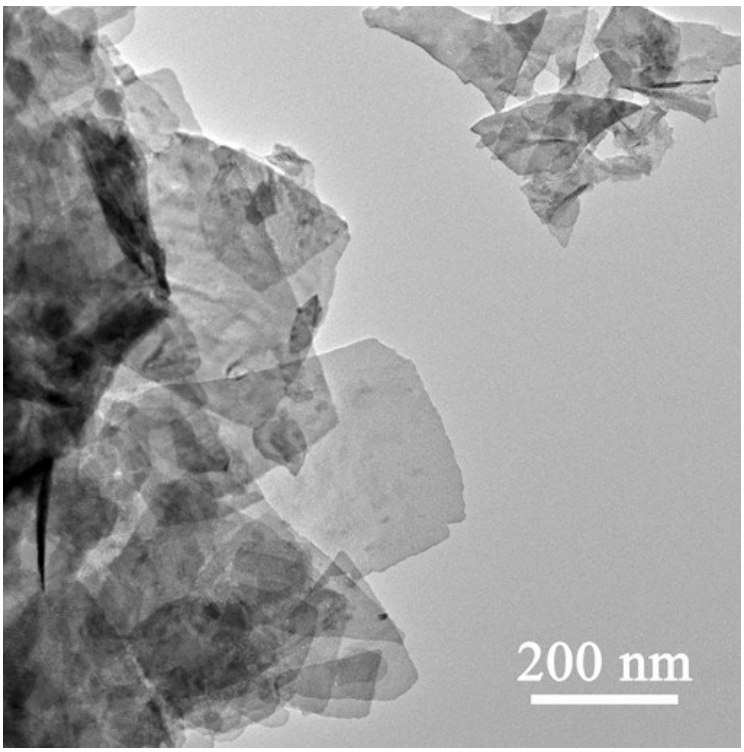


Figure S13. TEM image of the $Bi_2O_2CO_3$ nanosheets.

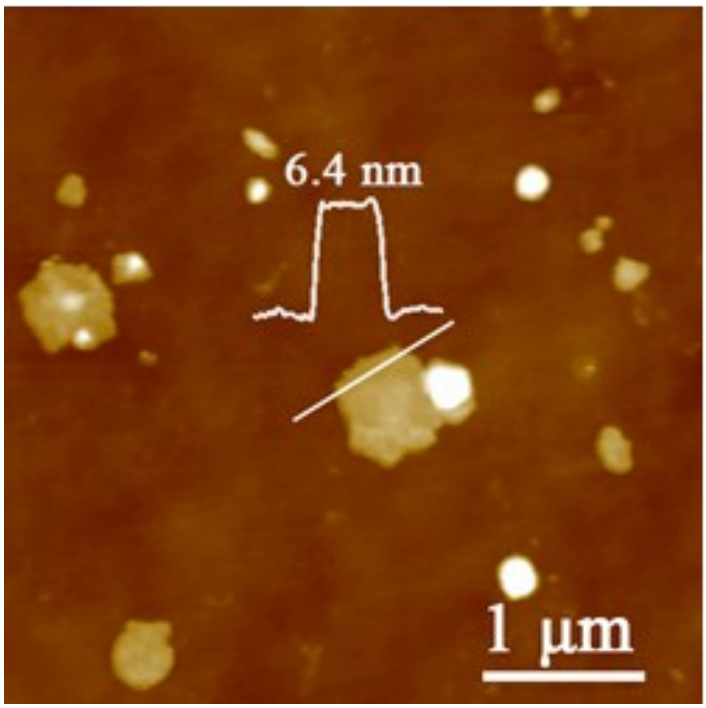


Figure S14. AFM image of the $Bi_2O_2CO_3$ nanosheets.

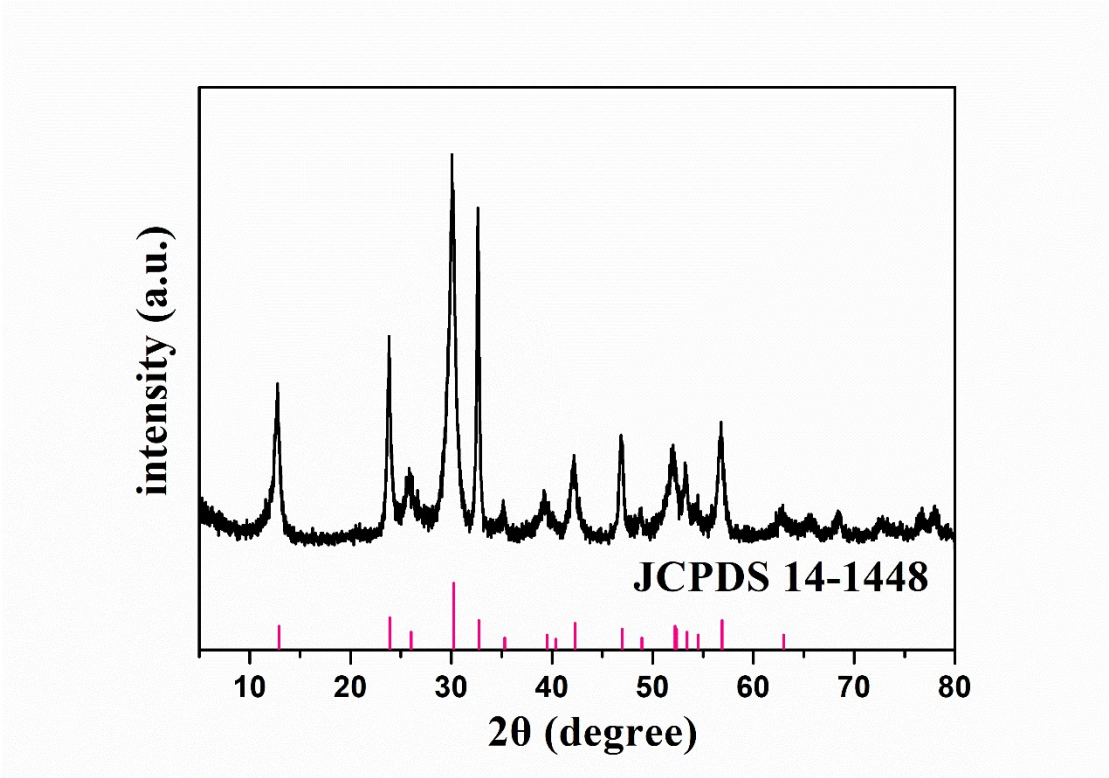


Figure S15. The X-ray diffraction pattern of the recycled catalyst. All peaks are well indexed to $Bi_2O_3CO_3$ (JCPDS 14-1448).

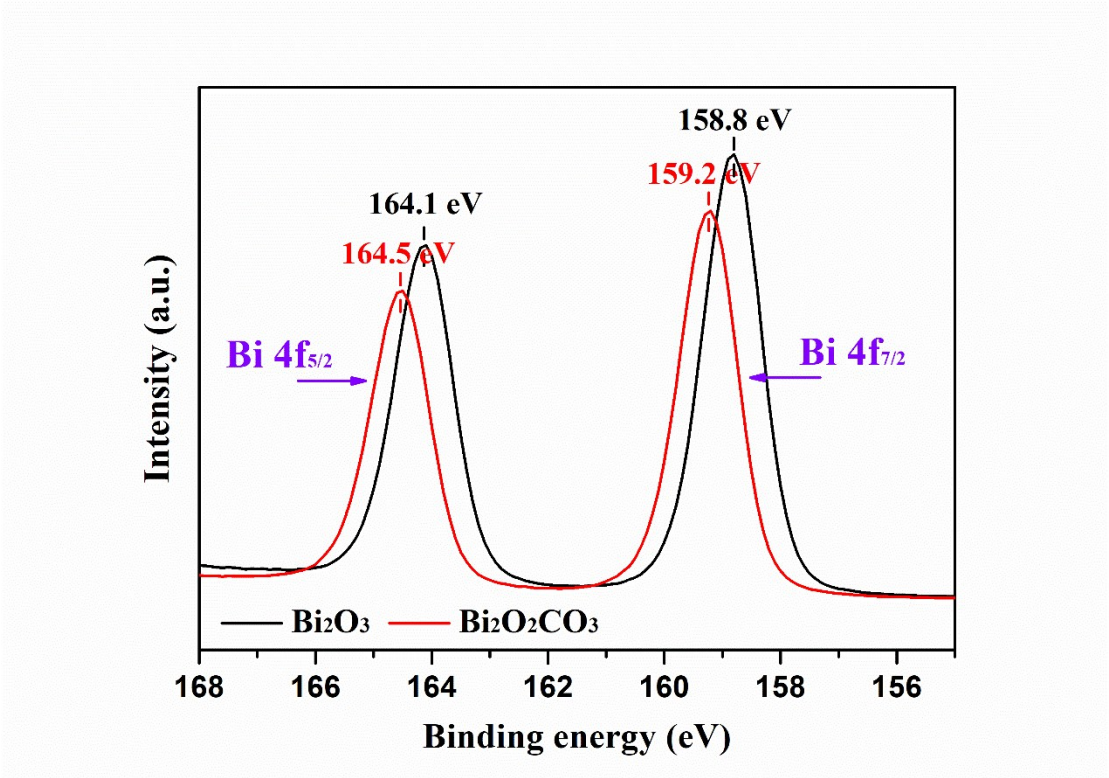


Figure S16. XPS spectra of the nanotubes and nanosheets.

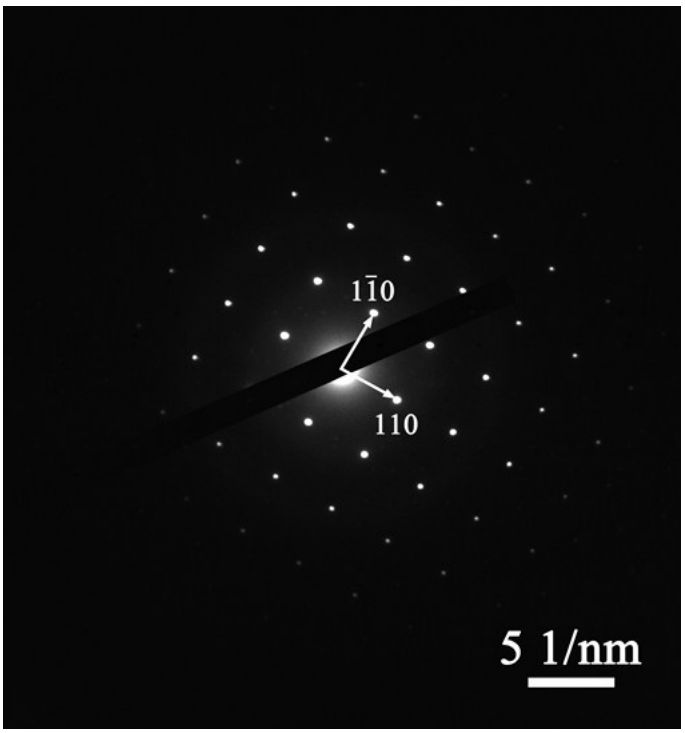
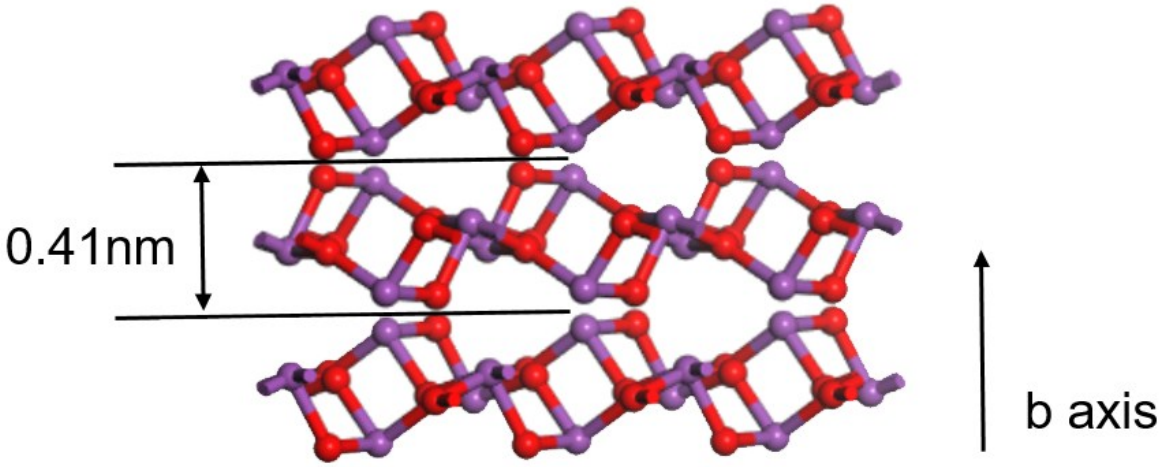
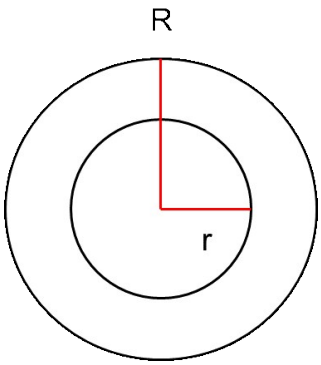


Figure S17. The selected area electron diffraction pattern of the $Bi_2O_2CO_3$ nanosheets.



Scheme S1. The illustration of one layer of α-B_2O_3.



Scheme S2. Cross-section of the nanotube model.

Theoretical calculation of surface area for α-Bi_2O_3 nanotubes.

The density of α-B_2O_3 is 9.372 g/cm^3. If the volume of 1 g α-B_2O_3 is V, surface area is S, and the length of the tube is L, then:

$V=（1/9.372）\times 10^{-6}\ m^3$

$V= (\pi R^2 - \pi r^2)L$

$S = 2\pi RL + 2\pi rL$

$V= \pi L(R^2 - r^2) = \pi L(R + r)(R - r)$

$S= 2\pi L(R + r)$

$V= S/2 \times (R - r) = 1.067 \times 10^{-7}\ m^3$

R-r= 1.5-2 nm

$S= 106.7\text{-}142.3\ m^2$

Method Section

The tube model of Bi_2O_3 nanotubes

The cif file of the tube model is calculated from the cif file of α-Bi_2O_3. Single layer tube model is built from a×1×c unit cell of α-Bi_2O_3, the nanosheet rolled up perpendicular to the c axis to form the Bi_2O_3 nanotube. The coordinate transformation is achieved by the MATLAB program. Multilayer tube model is built from several single layer tube models.

HRTEM image simulation

TEM simulator[2] was used in the HRTEM image simulation. Four layers' tube pdb file is used for the input file of TEM simulator. Specifically, the four layers' tube has a external diameter of 6.2 nm which is built from the combination of 6.2 nm, 5.2 nm, 4.2 nm and 3.2 nm single layer tube. The 6.2 nm single layer tube model is built from 61 × 1 × 25 unit cell of α-Bi_2O_3. The 5.2 nm single layer tube model is built from 61 × 1 × 21 unit cell of α-Bi_2O_3. The 4.2 nm single layer tube model is built from 61 × 1 × 17 unit cell of α-Bi_2O_3. The 3.2 nm single layer tube model is built from 61 × 1 × 13 unit cell of α-Bi_2O_3.

Simulation parameter: the acceleration voltage is 300 kV, the magnification is 300k, the chromatic aberration is 0 mm, the spherical aberration is 0.5 mm.

DFT calculation

CASTEP program package[3] was used in the calculation to obtain the band structures, densities of state (DOS), and partial densities of state (PDOS) of α-Bi_2O_3. the band structure of Bi_2O_3 was calculated by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerh (PBE) function was adopted for the exchange–correction potential. The projector augmented wave potentials and the cut energy of 380 eV were used with the core electrons replaced by ultrasoft pseudopotentials. Both the atomic positions and the unit cell were allowed to relax simultaneously within the symmetry constraints imposed by the $P\,1\,2_1/c\,1$ space groups for α-Bi_2O_3. The respective k-point sets of 5 x 3 x 4 was used for α-Bi_2O_3.

1. T. Proffen and R. B. Neder, *J. Appl. Cryst.*, 1997, **30**, 171-175.
2. H. Rullgård, L.-G. Öfverstedt, S. Masich, B. Daneholt, and O. Öktem, *J. Microsc.*, 2011, **243**, 234-256.
3. M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.: Condens. Matter*, 2002, **14**, 2717–2744.