

## Electronic Supplementary Information (ESI)

### **A facile step for heterogeneous crystal structure in hierarchical architecture with vacancy-driven defects by oriented attachment growth mechanism**

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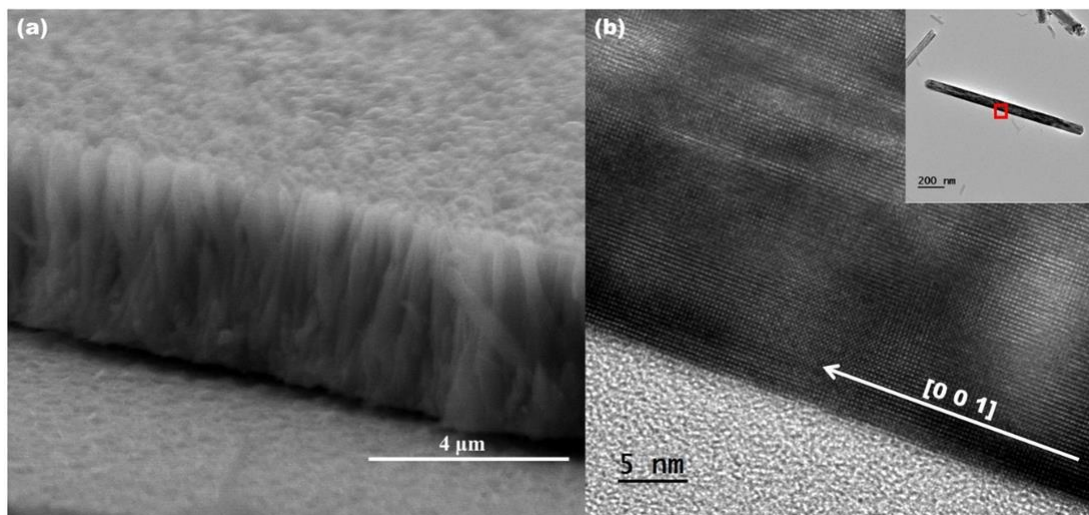
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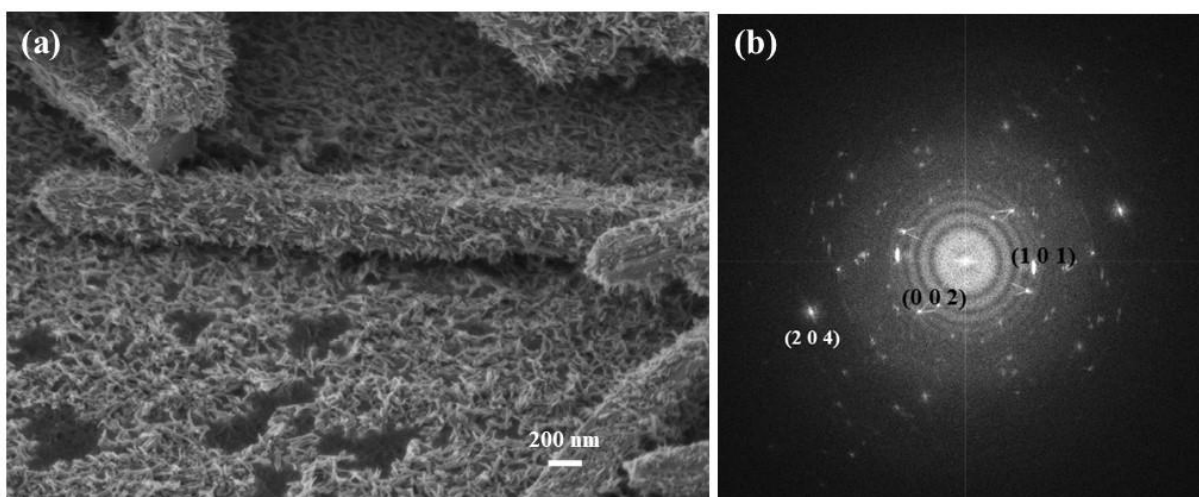
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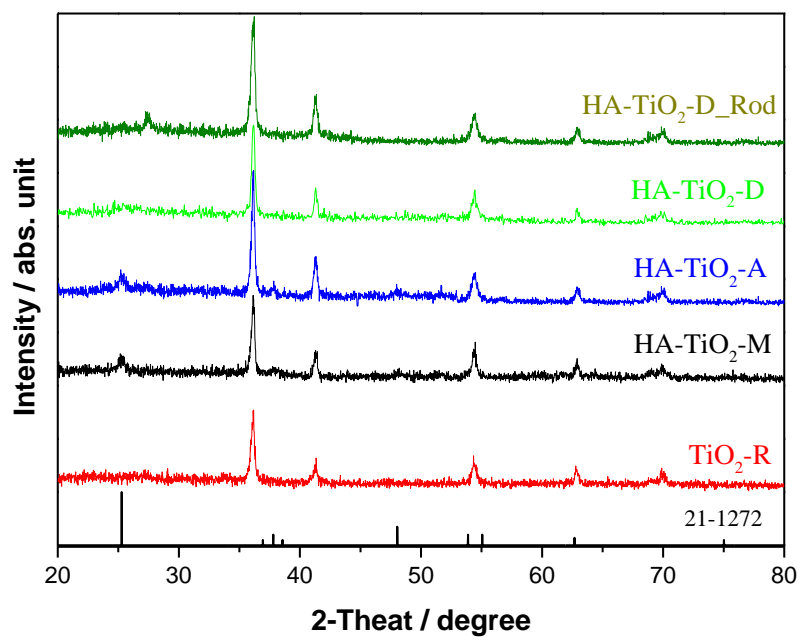
E-mail: [jguo@lbl.gov](mailto:jguo@lbl.gov); [yhliou@ntu.edu.tw](mailto:yhliou@ntu.edu.tw)



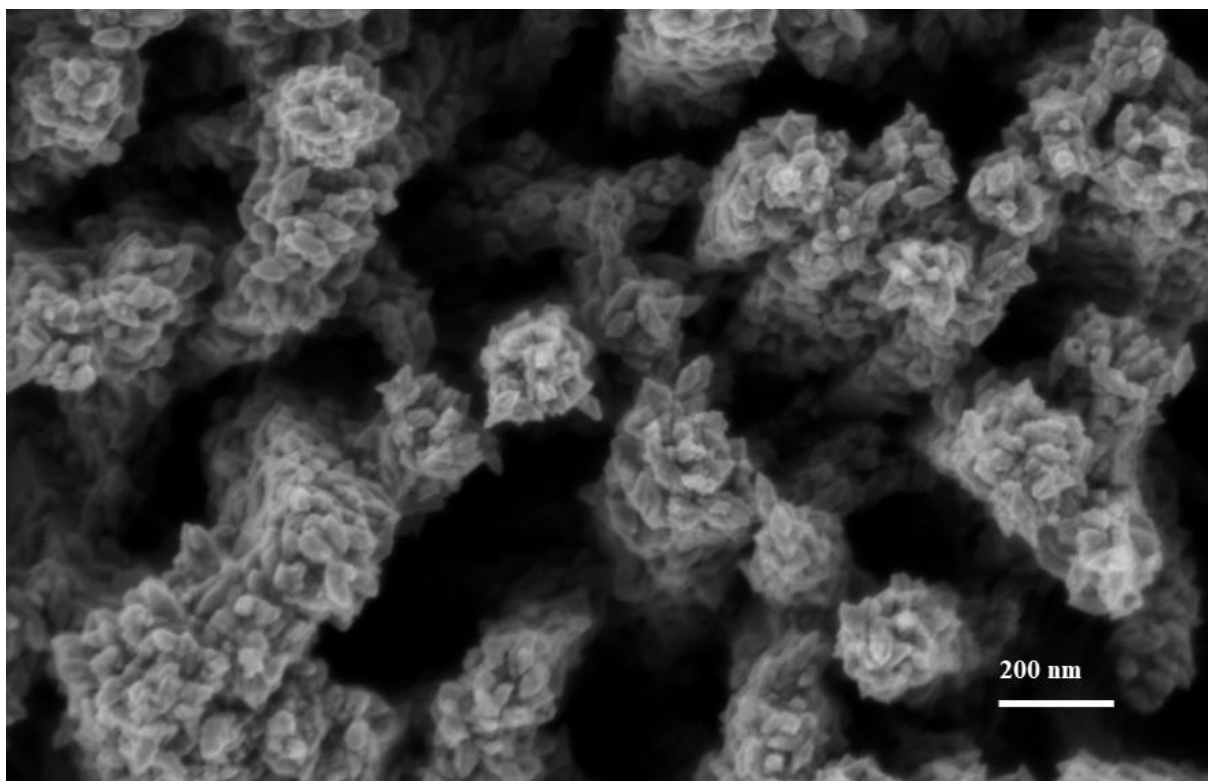
**Figure S1.** (a) The side view SEM images of TiO<sub>2</sub>\_R. (b) HRTEM images of tetragonal-rutile phase nanorod with a [0 0 1] growth direction taken from the inset red square.



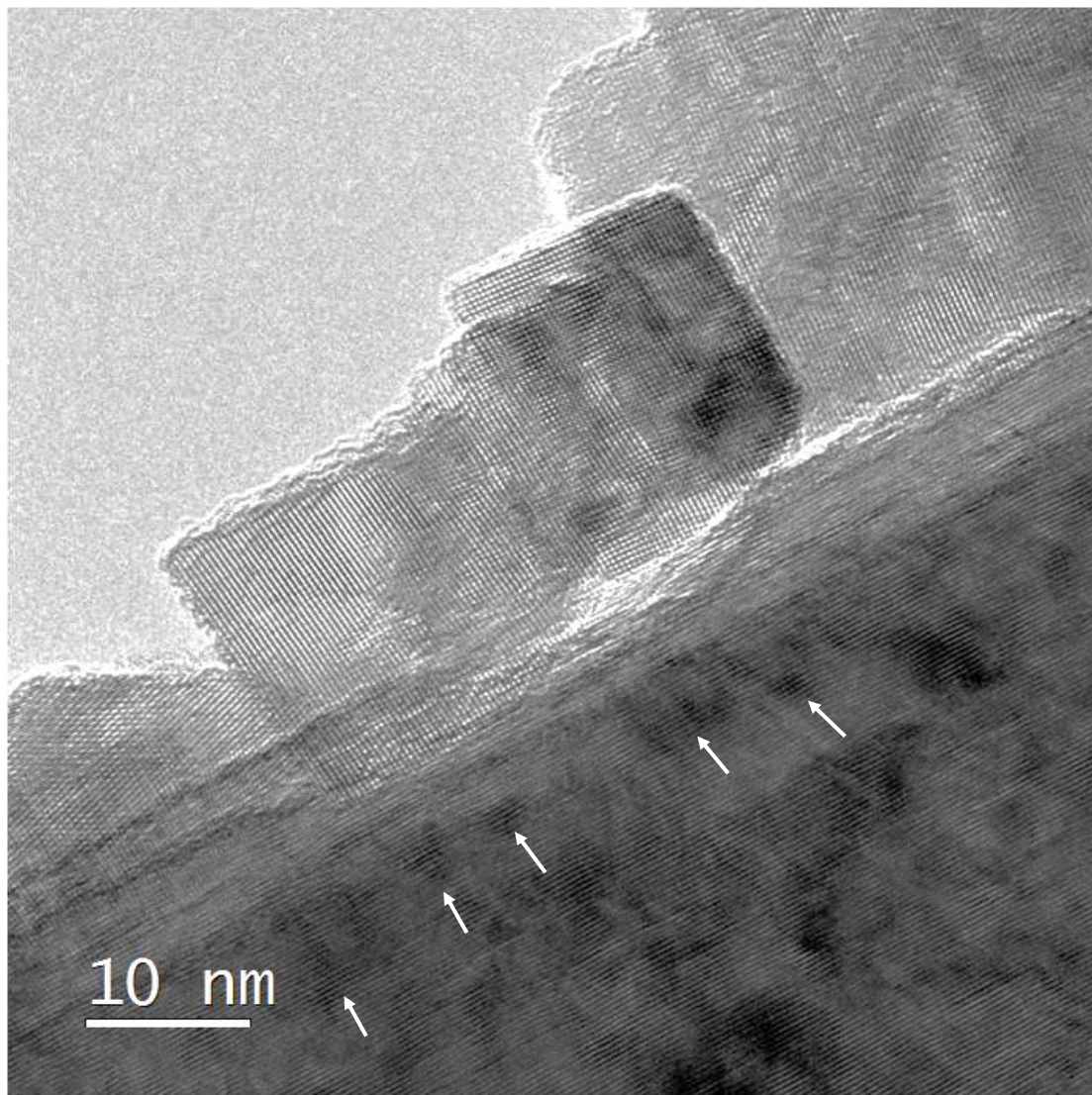
**Figure S2.** (a) FESEM images of HA\_TiO<sub>2</sub>\_M. (b) The corresponding fast Fourier transform pattern of Figure 1d reveals the rings contributed by multiple sub-nano structures can be indexed to anatase diffraction planes of (0 0 2) and (1 0 1).



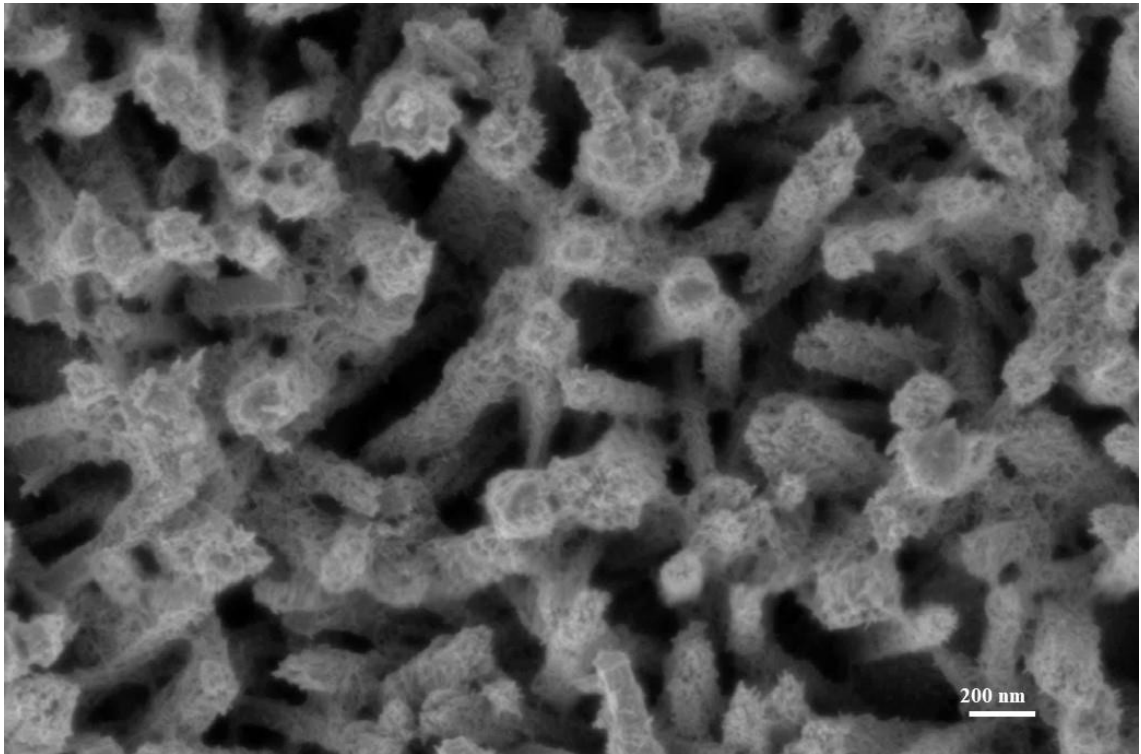
**Figure S3.** XRD pattern of rutile TiO<sub>2</sub> and HA\_TiO<sub>2</sub> series. The tetragonal anatase phase (JCPDS No. 21-1272) was listed as reference.



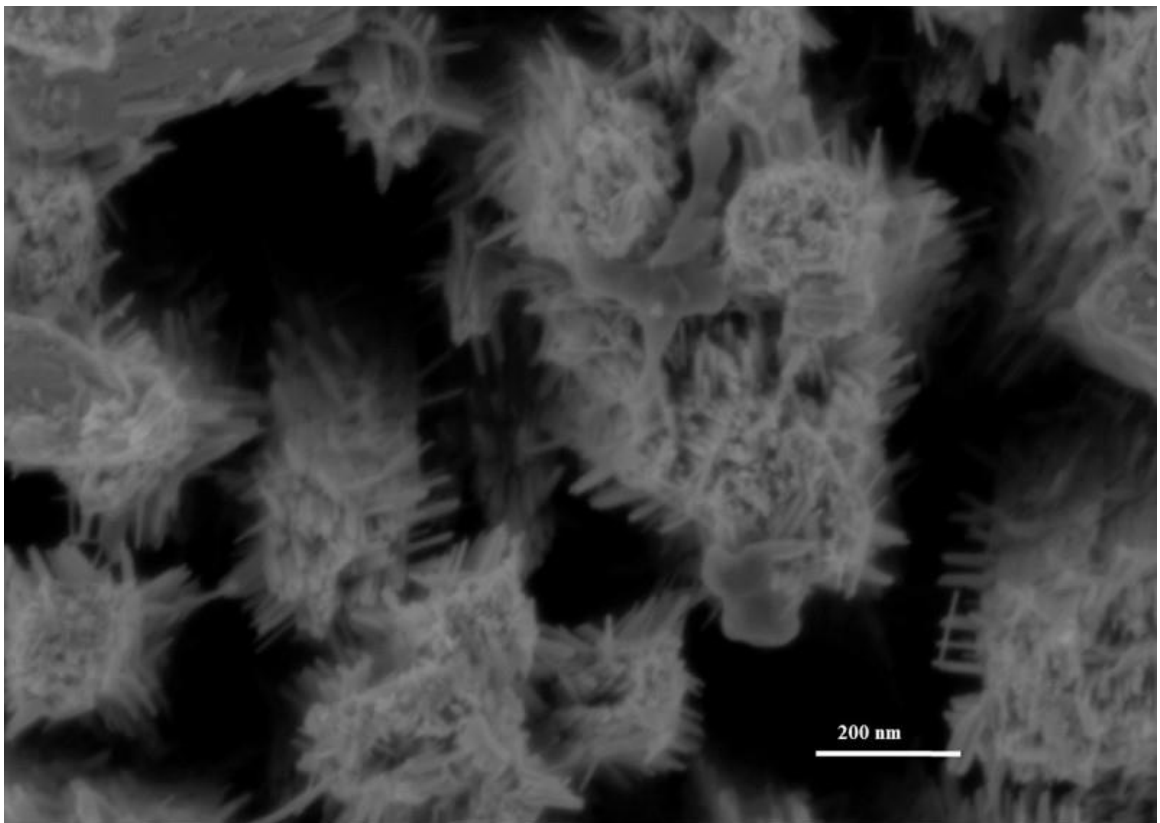
**Figure S4.** The FESEM image of nanorod arrays attached with rhombic sub-nano structures.



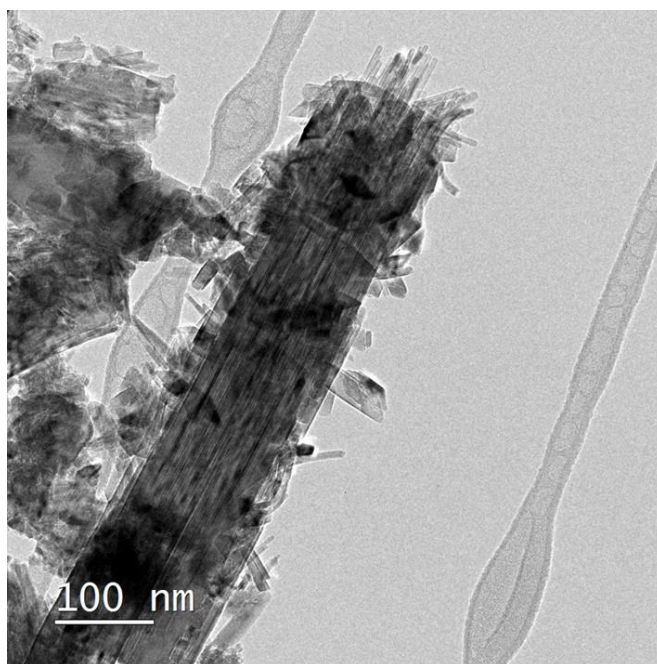
**Figure S5.** The lattice plane of the rutile nanorod was shifted by the attached sub-nano structures (white arrow indicated).



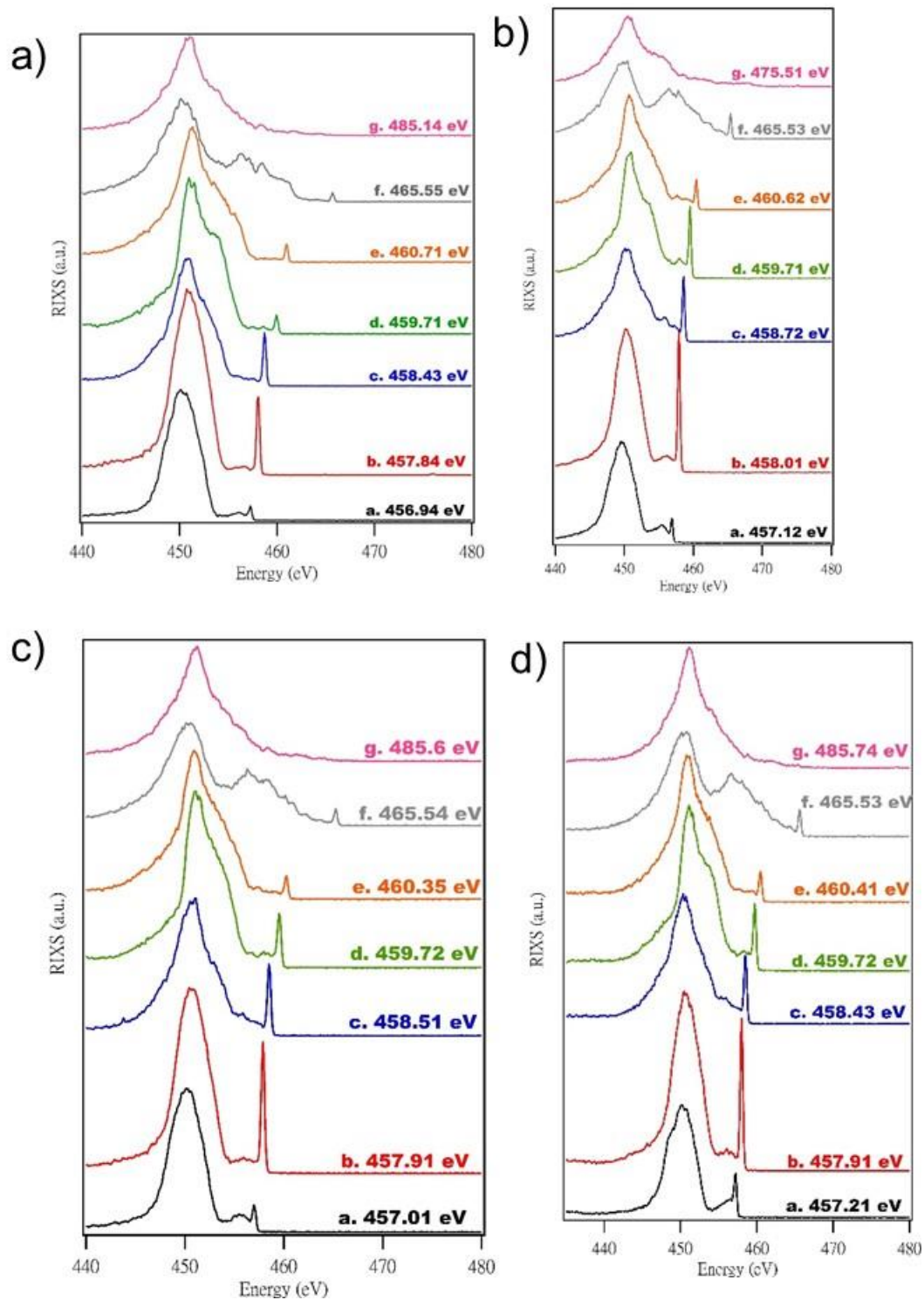
**Figure S6.** The FESEM image of nanorod arrays attached with spindle-like sub-nano structures.



**Figure S7.** The FESEM image of nanorod arrays attached with rod-like sub-nano structures.

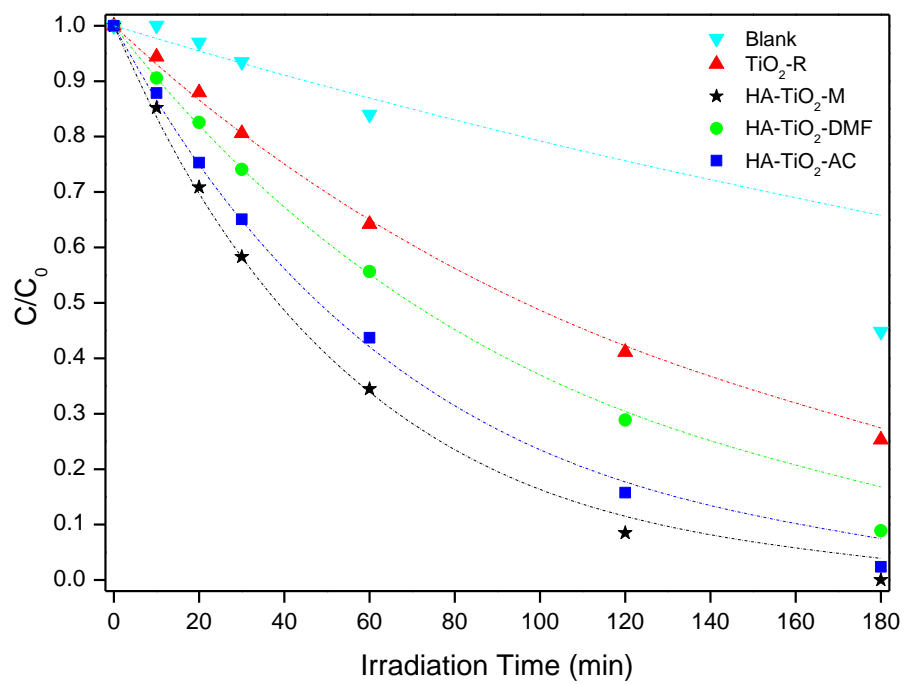


**Figure S8.** The TEM image of synthesis of HA\_TiO<sub>2</sub> without TiCl<sub>4</sub> aqueous solution pre-treatment.



**Figure S9.** Ti 2p RIXS spectra of (a) TiO<sub>2</sub>\_R, (b) HA\_TiO<sub>2</sub>\_M, (c) HA\_TiO<sub>2</sub>\_A, and (d) HA\_TiO<sub>2</sub>\_D.





**Figure S10.** The UV-driven photocatalytic activity test with pseudo first-order rate model  $k_{obs}$ .