## Supporting Information for

## Phase control of hierarchically structured mesoporous anatase TiO<sub>2</sub> microspheres covered with {001} facet<sup>†</sup>

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Figure S1. XRD patterns of the  $TiO_2$  microspheres prepared in 4N HCl (red) and HNO<sub>3</sub> (black) solutions.



Figure S2. SEM images of TiO<sub>2</sub> microsphere prepared in 30 mL of 4 M HCl solution.



Figure S3. SEM images of TiO<sub>2</sub> microsphere prepared in 30 mL of 4 M HNO<sub>3</sub> solution.



Figure S4. High-resolution TEM image of MATS synthesized for 1 hour.



Figure S5. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 30min.



Figure S6. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 1 hour.



Figure S7. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 2 hours.



Figure S8. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 3 hours.



Figure S9. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 5 hours.



Figure S10. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 10 hours.



Figure S10. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 15 hours.



Figure S10. SEM images of  $TiO_2$  microspheres prepared from a reaction from 0.5 mL TBT in 30 mL of 2 M  $H_2SO_4$  solution heated at 180 °C for 24 hours.



Figure S11. TEM and HRTEM images of small pieces of MATS.



Figure S12. FE-SEM images of MATS obtained at different amount of TBT. A 0.25 ml, B 0.5 ml, C 1.0 ml, and D 1.5 ml TBT was added into 30 ml 2 mol/L  $H_2SO_4$  at  $180^{\circ}C$  for 5 hours.