

## Electronic Supplementary Information

### Controlled synthesis of thorny anatase TiO<sub>2</sub> tubes for construction of Ag-AgBr/TiO<sub>2</sub> composites as highly efficient simulated solar-light photocatalyst

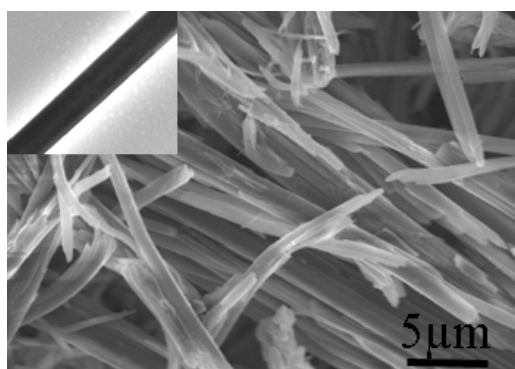
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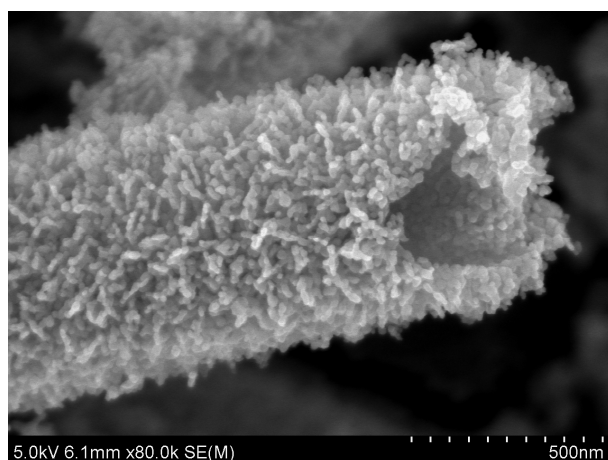
<sup>b</sup> Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, P. R. China

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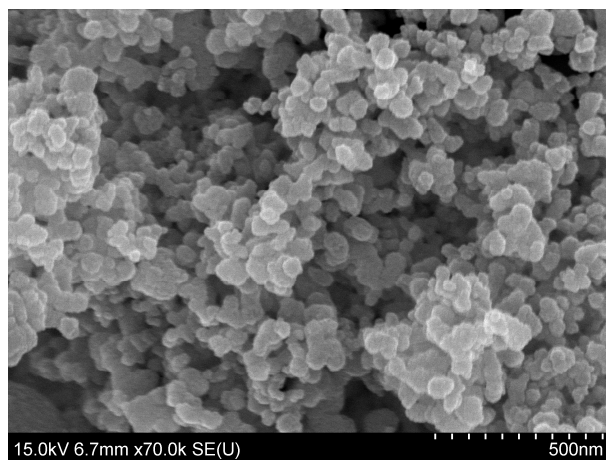
Tel.: +86 451 8660 4330, Fax: +86 451 8667 3647



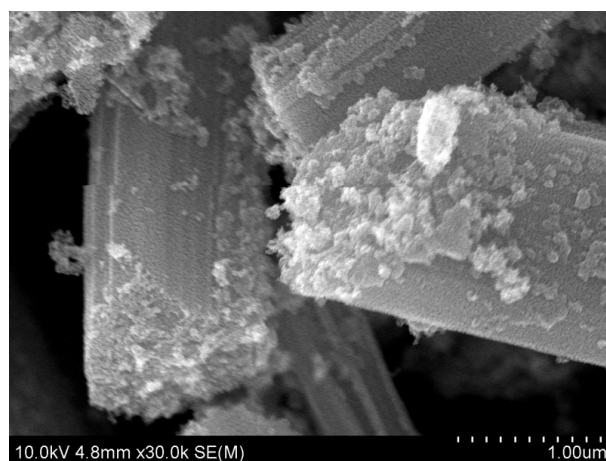
**Fig. S1.** SEM and TEM (inset) images of the rod-like TiOSO<sub>4</sub>·2H<sub>2</sub>O starting material.



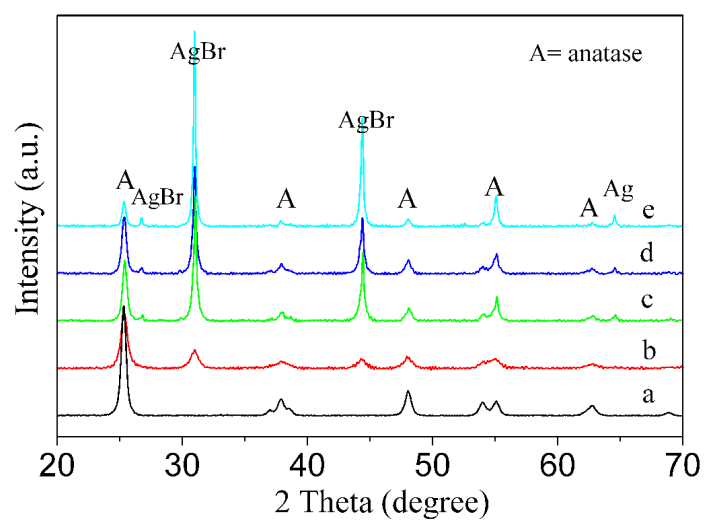
**Fig. S2.** High magnification SEM of the as-obtained thorny TiO<sub>2</sub> tube obtained from the calcined precursors (24 h solvothermal reaction).



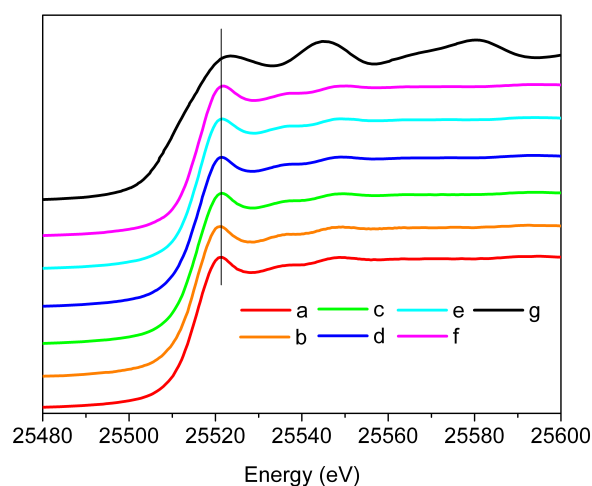
**Fig. S3.** SEM image of the prepared titanium glycerolate precursor using crushed TiOSO<sub>4</sub>·2H<sub>2</sub>O starting material.



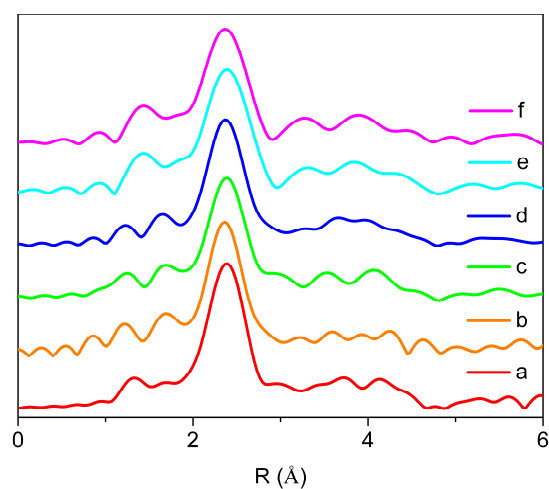
**Fig. S4.** SEM image of the precursor prepared without using glycerol.



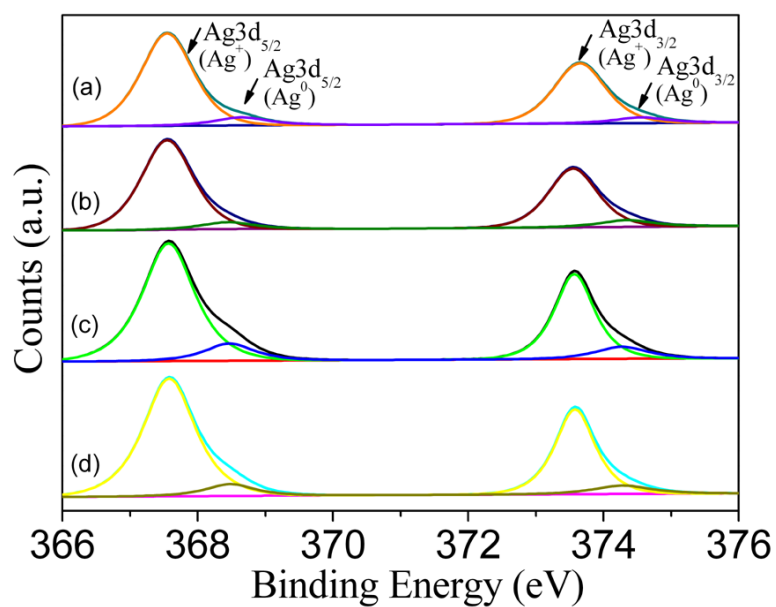
**Fig. S5.** XRD patterns of the different samples, a) thorny  $\text{TiO}_2$  tube, b) 5%Ag-AgBr/ $\text{TiO}_2$ , c) 10%Ag-AgBr/ $\text{TiO}_2$ , d) 15%Ag-AgBr/ $\text{TiO}_2$  and e) 20%Ag-AgBr/ $\text{TiO}_2$ .



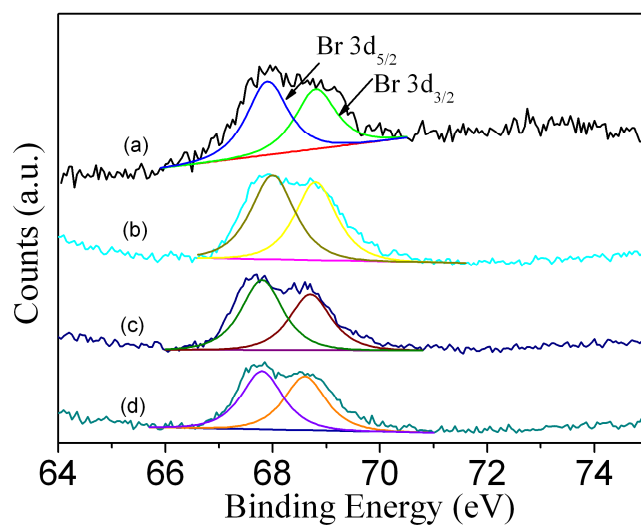
**Fig. S6.** Comparison of the Ag *K* - edge XANES spectra of the different samples. a) AgBr, b) 5% Ag-AgBr/TiO<sub>2</sub>, c) 10% Ag-AgBr/TiO<sub>2</sub>, d) 15% Ag-AgBr/TiO<sub>2</sub>, e) 20% Ag-AgBr/TiO<sub>2</sub>, f) 10% Ag-AgBr/TiO<sub>2</sub> after photocatalytic reaction, g) Ag foil.



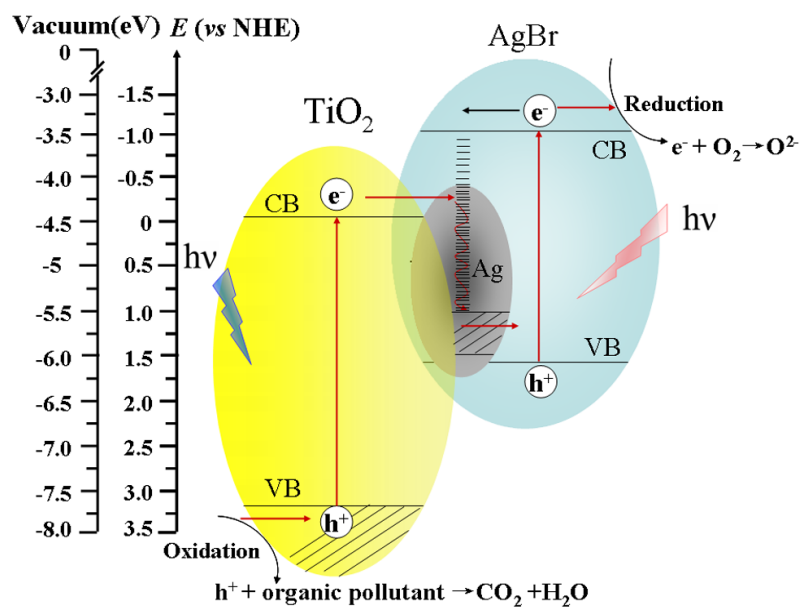
**Fig. S7** Comparison of the Fourier-transformed EXAFS spectra for different samples: a) AgBr, b) 5% Ag-AgBr/TiO<sub>2</sub>, c) 10% Ag-AgBr/TiO<sub>2</sub>, d) 15% Ag-AgBr/TiO<sub>2</sub>, e) 20%Ag-AgBr/TiO<sub>2</sub>, f) 10% Ag-AgBr/TiO<sub>2</sub> after photocatalytic reaction.



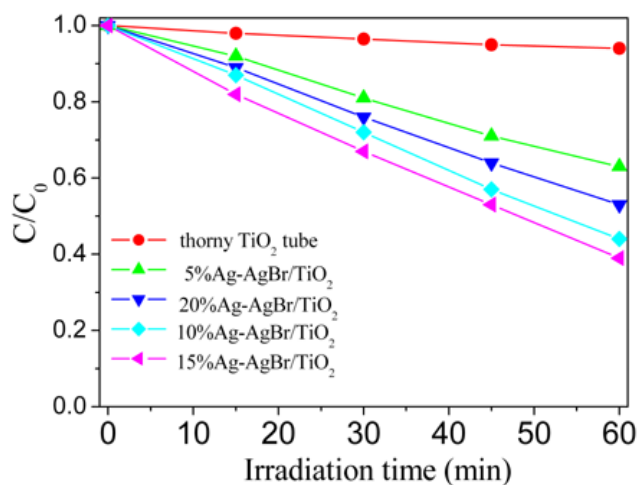
**Fig. S8.** XPS spectra of Ag 3d of the different samples, (a) 5%Ag-AgBr/TiO<sub>2</sub>, (b) 10%Ag-AgBr/TiO<sub>2</sub>, (c) 15%Ag-AgBr/TiO<sub>2</sub>, (d) 20%Ag-AgBr/TiO<sub>2</sub>.



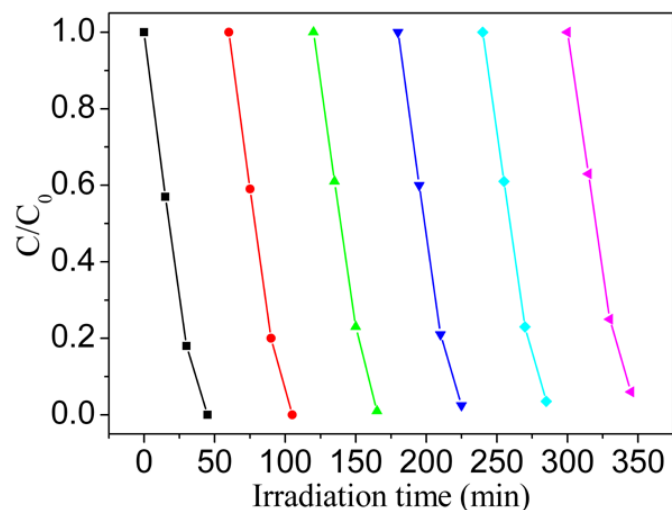
**Fig. S9.** XPS spectra of Br 3d of the different samples, (a) 5%Ag-AgBr/TiO<sub>2</sub>, (b) 10%Ag-AgBr/TiO<sub>2</sub>, (c) 15%Ag-AgBr/TiO<sub>2</sub>, (d) 20%Ag-AgBr/TiO<sub>2</sub>.



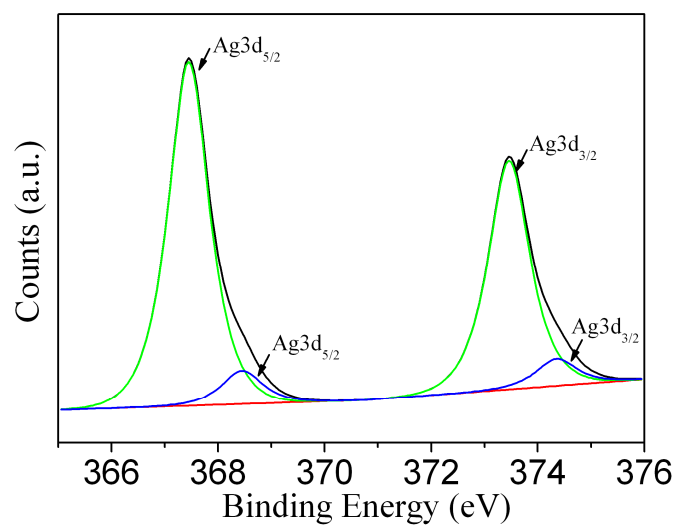
**Fig. S10.** Schematic diagram for the charge separation in Ag-AgBr/TiO<sub>2</sub> composites system under simulated solar light irradiation.



**Fig. S11.** Photocatalytic degradation of phenol as a function of irradiation time in the presence of different photocatalysts under visible light irradiation.



**Fig. S12.** Cycling runs in the photodegradation of phenol in the presence of 10%Ag-AgBr/TiO<sub>2</sub> composite under simulated solar light irradiation; addition of phenol.



**Fig. S13.** XPS spectrum of Ag 3d of the 10%Ag-AgBr/TiO<sub>2</sub> after photocatalytic degradation of phenol under simulated solar light irradiation.

**Table S1.** Fit parameters of Ag EXAFS spectra of the different samples. a) AgBr, b) 5%Ag-AgBr/TiO<sub>2</sub>, c) 10%Ag-AgBr/TiO<sub>2</sub>, d) 15%Ag-AgBr/TiO<sub>2</sub>, e) 10%Ag-AgBr/TiO<sub>2</sub> after photocatalytic reaction.

|   | Shell | N <sup>[a]</sup> | R <sup>[b]</sup> | $\sigma^2 (10^{-3} \text{ \AA}^2)$ <sup>[c]</sup> | $\Delta E_0 \text{ (eV)}$ <sup>[d]</sup> |
|---|-------|------------------|------------------|---------------------------------------------------|------------------------------------------|
| a | Ag-Br | 3.1±0.8          | 2.78±0.01        | 13.3±2.3                                          | -3.6±1.5                                 |
| b | Ag-Br | 1.9±0.2          | 2.78±0.02        | 9.0±3.8                                           | 0.8±0.7                                  |
|   | Ag-Ag | 0.1±0.1          | 2.87±0.01        | 7.0±1.5                                           | 4.9±1.3                                  |
| c | Ag-Br | 1.8±0.2          | 2.78±0.01        | 8.8±4.1                                           | 0.5±0.5                                  |
|   | Ag-Ag | 0.3±0.1          | 2.87±0.01        | 3.6±1.6                                           | 6.6±3.5                                  |
| d | Ag-Br | 1.8±0.3          | 2.78±0.02        | 8.5±3.0                                           | -1.0±0.3                                 |
|   | Ag-Ag | 0.2±0.1          | 2.87±0.01        | 4.9±1.2                                           | 5.5±0.7                                  |
| e | Ag-Br | 1.5±0.2          | 2.78±0.02        | 13.1±2.7                                          | 1.4±0.7                                  |
|   | Ag-Ag | 0.6±0.1          | 2.90±0.01        | 12.4±1.6                                          | 6.1±1.3                                  |

[a] Coordination number; [b] Distance between absorber and backscatter atoms; [c] Debye–Waller factor; [d] Inner potential correction.

**Table S2.** The surface element kind and content in the different photocatalysts

| sample                      | surface element | Content (mol%) |
|-----------------------------|-----------------|----------------|
| 5% Ag-AgBr/TiO <sub>2</sub> | Ag <sup>0</sup> | 1.12           |
|                             | Ag <sup>+</sup> | 3.71           |
|                             | Br <sup>-</sup> | 3.42           |
| 10%Ag-AgBr/TiO <sub>2</sub> | Ag <sup>0</sup> | 2.11           |
|                             | Ag <sup>+</sup> | 7.62           |
|                             | Br <sup>-</sup> | 7.32           |
| 15%Ag-AgBr/TiO <sub>2</sub> | Ag <sup>0</sup> | 3.11           |
|                             | Ag <sup>+</sup> | 11.52          |
|                             | Br <sup>-</sup> | 11.31          |
| 20%Ag-AgBr/TiO <sub>2</sub> | Ag <sup>0</sup> | 4.11           |
|                             | Ag <sup>+</sup> | 15.52          |
|                             | Br <sup>-</sup> | 15.16          |