Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information for

Branching growth of novel silver phosphate dendrites and the greatly improved photocatalytic activity by the active {110} facets

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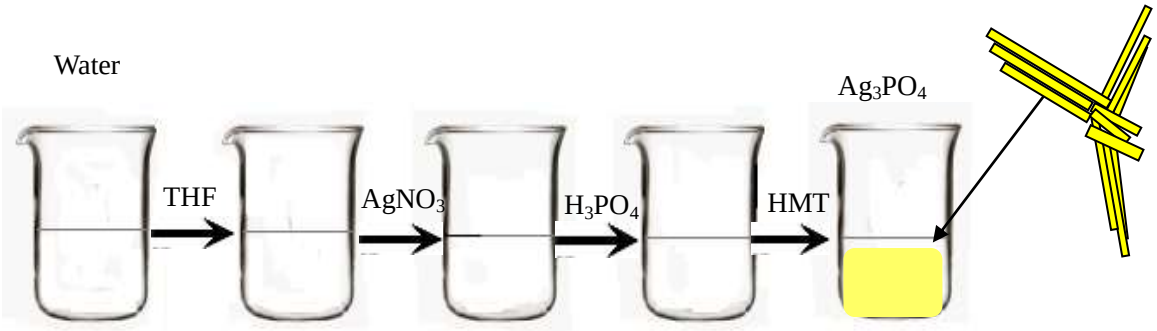
Experimental Section



Scheme S1. Schematic illustration of the preparation process

Schematic S1 shows the preparation process for highly-branched tetrapods (HBT), three-dimensional towers (TDT) and threefold-overlapped tetrapods (TOT).

1. Preparation of the samples

1.1. Threefold-overlapped tetrapods (TOTs). In a typical synthesis, 32 ml deionized water was placed in a breaker, and 8 ml THF was then added. 0.318 g Ag_3NO_4 was added into the mixed solvent above under stirring. Then, 41 μl of 85 wt.% H_3PO_4 was added drop wise to the solution above. Finally, 0.197 g of hexamethylenetetramine (HMT) was introduced into the above solution. The whole process was carried out at room temperature under stirring. The color of the reaction mixture changed from silvery white to golden yellow after injection of the HMT. After stirring for 5 min, the yellow precipitation was collected, washed with deionized water for several times, and dryed at room temperature.

1.2. Three-dimensional towers (TDTs) and highly-branched tetrapods (HBTs). The same procedures as above were taken, but the THF/W volumetric ratios were changed to 0:1 and 0.13:1 while the solvent volumes were kept same (40 ml) for TDT and HBT, respectively.

1.3. Non-overlapped tetrapods (NOTs). NOTs sample is synthesized as our previously reported.[1] In a typical procedure, 3 mmol of 85% H_3PO_4 was dissolved in 80 ml of deionized water and 2.5 mmol of $AgNO_3$ was added under stirring. Then, 37.5 mmol of urea were put into above solution. The resulting precursor was transferred into a Teflon-lined stainless steel autoclave and maintained at 80 ^oC for 24 h. After cooling to room temperature, the yellow precipitation was collected, washed with deionized

water several times, and dried overnight at 60 ^{o}C.

1.4. Irregular Ag_3PO_4. The irregular Ag_3PO_4 particles were synthesized as previously reported.[1] Typically, appropriate amounts of raw powders of Na_2HPO_4 and $AgNO_3$ were thoroughly ground until the initial white changed to yellow.

1.5. N-doped TiO_2 (NTs). Nitrogen doping was conducted as described previously.[2] Typically, 0.5 g of Degauss P25 TiO_2 powders was suspended in ethanol (5 ml). Then, urea (1 g) dissolved in a mixture solvent of both 2.5 ml ethanol and 0.5 ml H_2O was added into the suspension above. The mixture was stirred and heated to completely evaporate the solvent, followed by calcination in air at 400 ^{o}C for 4 h.

2. Photocatalytic degradation reactions

Photocatalytic activities of the samples were evaluated by photocatalytic decomposition of rhodamine B (RhB). Typically, the suitable amounts of powders were put into a solution of RhB (100 ml, 10 mg/L), which was irradiated with a 300W Xe arc lamp equipped with an ultraviolet cut off filter to provide visible light ($\lambda \geq 420$ nm). Because the BET areas of HBTs, TDTs, TOTs, NOTs and NTs are 4.9, 3.2, 3.3, 3.1, 32.2 m^2 g^{-1}, 64 mg of HBTs, 97 mg of TDTs, 94 mg of TOTs, 100 mg of NOTs and 96 mg of NTs are used in the degradation, respectively. According to reference [20], the aim is to keep their surface areas same.

3. Characterization

Scanning electron microscope (SEM) images of the samples were obtained on a Hitachi SU-1510 operated at 120 kV. The samples were coated with 5-nm-thick gold layer before observation. The phase compositions of the samples were determined by X-ray diffractometer (Rigaku D/max-2550VB) using graphite monochromatized Cu K_{α} radiation (λ = 0.154 nm), operating at 40 kV and 50mA. The XRD patterns were scanned in the range of 20-80° (2θ) at a scanning rate of 5 $^{\circ}$min^{-1}. Nitrogen adsorption-desorption isotherms were collected at 77 K using the NOVOE 4000 adsorption apparatus.

References

(1) Wang, J.; Teng, F.; Chen, M. D.; Xu, J. J.; Song, Y. Q.; Zhou, X. L. *CrystEngComm*., **2013**, *15*, 39.

(2) Mitoraj, D.; Kisch, H.; *Angew. Chem., Int. Ed.*, **2008**, *47*, 9975.

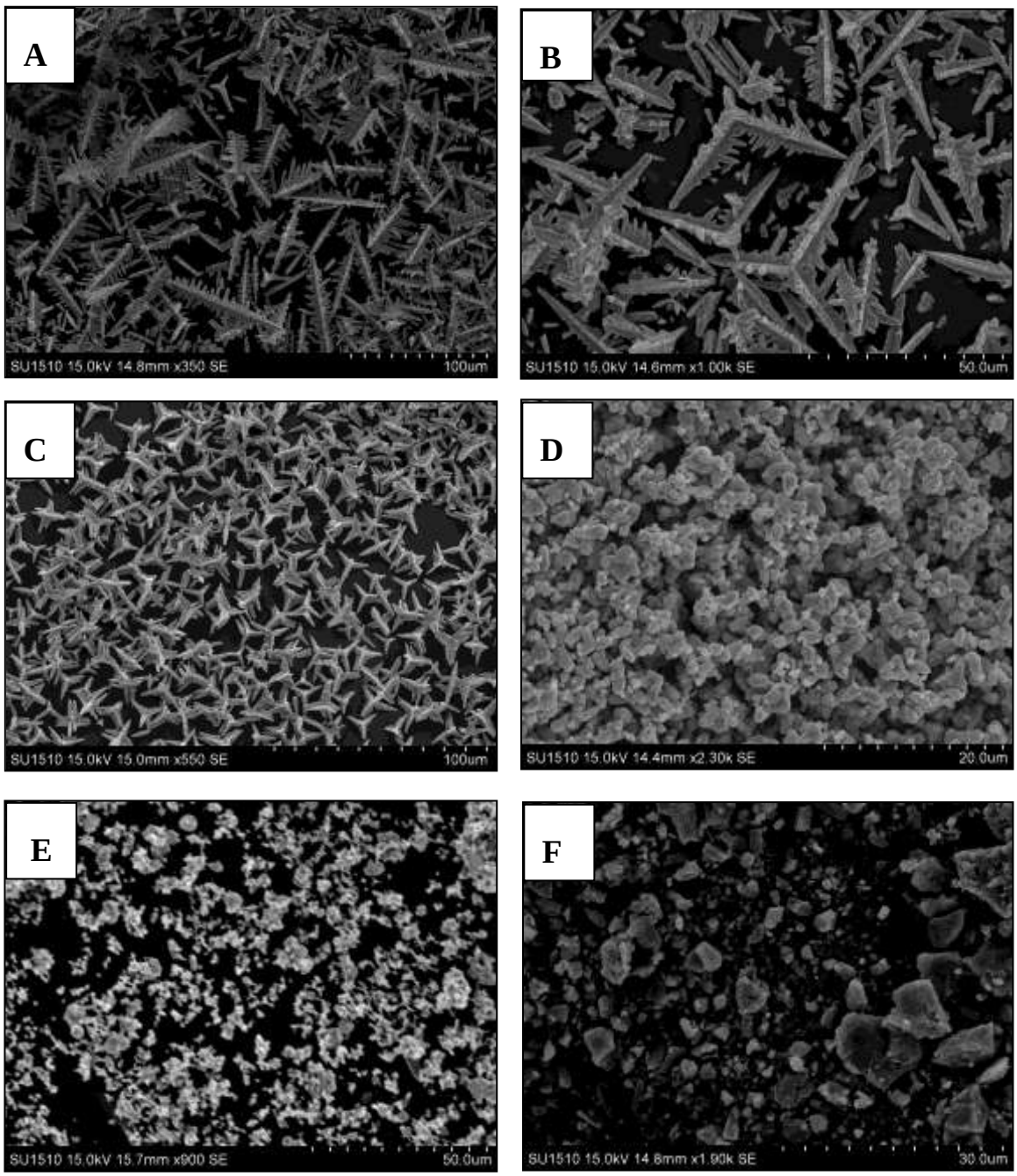


Fig. S1 Low-magnification SEM images of Ag_3PO_4 crystals synthesized at different volume ratios of tetrahydrofuran (THF) to water (W): (A) 0:1; (B) 0.13:1; (C) 0.25:1; (D) 0.5:1; (E) 1:1; (F) 1:0. Reaction temperature: 30 ^oC; Hexamethylenetetramine (HMT)/Ag(I) = 0.75 (molar ratio)

When the volume ratio of THF/W is increased, the morphology of Ag_3PO_4 changes from three-dimensional towers (TDTs) to highly-branched tetrapods (HBTs), threefold-overlapped tetrapods (TOTs), irregular Ag_3PO_4.

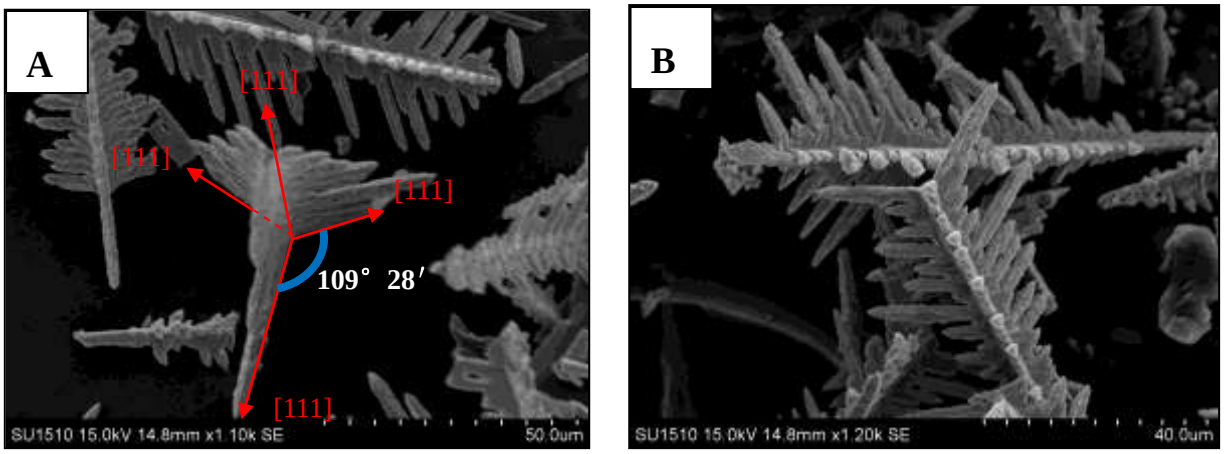


Fig. S2 SEM images of three-dimensional towers (TDTs)

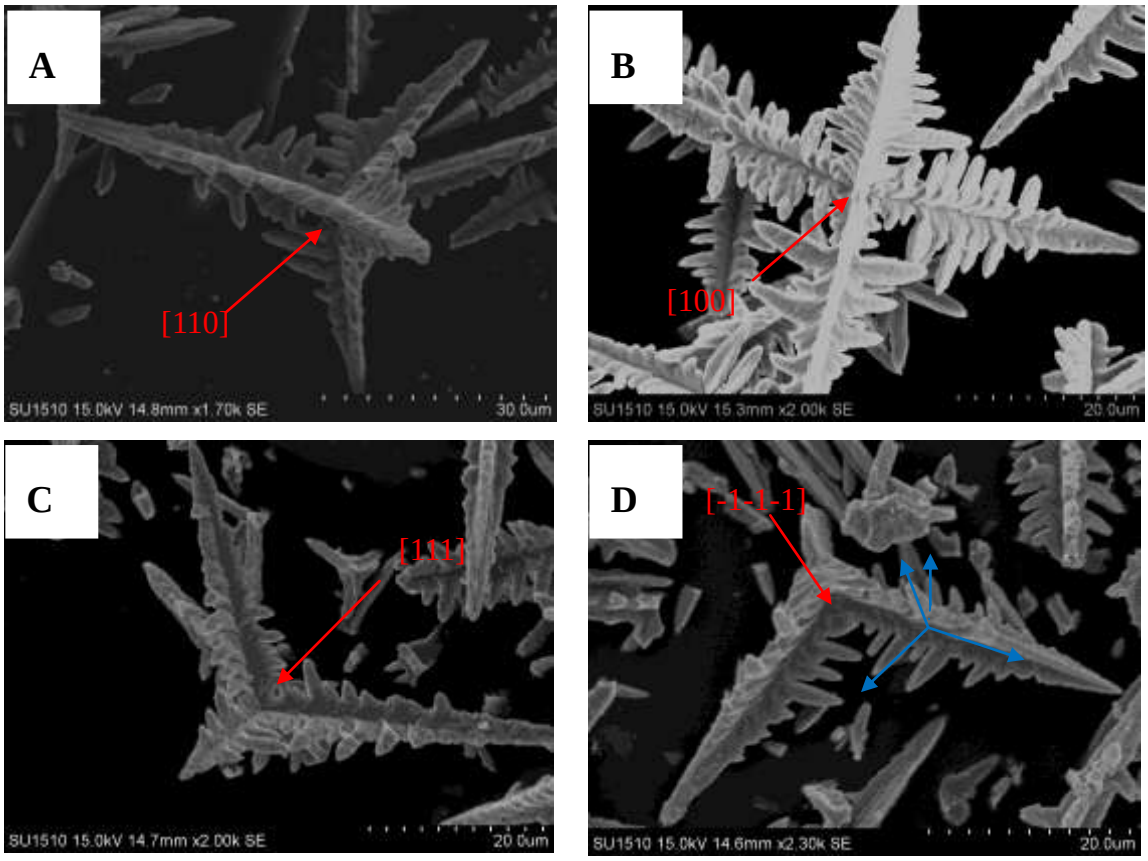


Fig. S3 SEM images of highly-branched tetrapods (HBTs) viewed along different directions: (A) [110]; (B) [100]; (C) [111]; (D) [-1-1-1]

From the SEM images, we can observe that the four shafts of HBT stretch along four [111] directions and they have further branched through a secondary growth process.

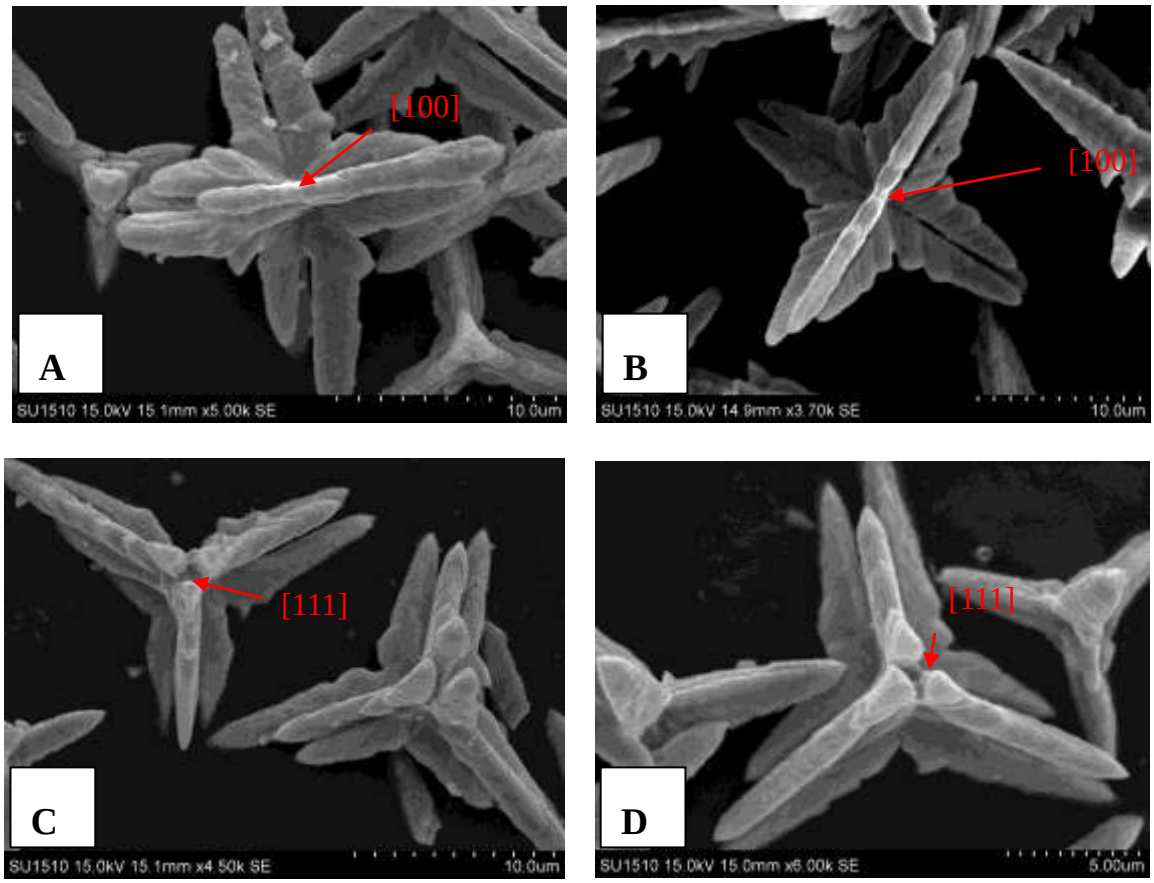


Fig. S4 SEM images of threefold-overlapped tetrapods (TOTs) viewed along different directions: (A, B) [100]; (C, D) [111]

From the SEM images, we can observe that along each [111] direction, three-overlapped branches are parallel to one another. The twelve branches are about 5-8 μm in length and 500 nm in diameter.

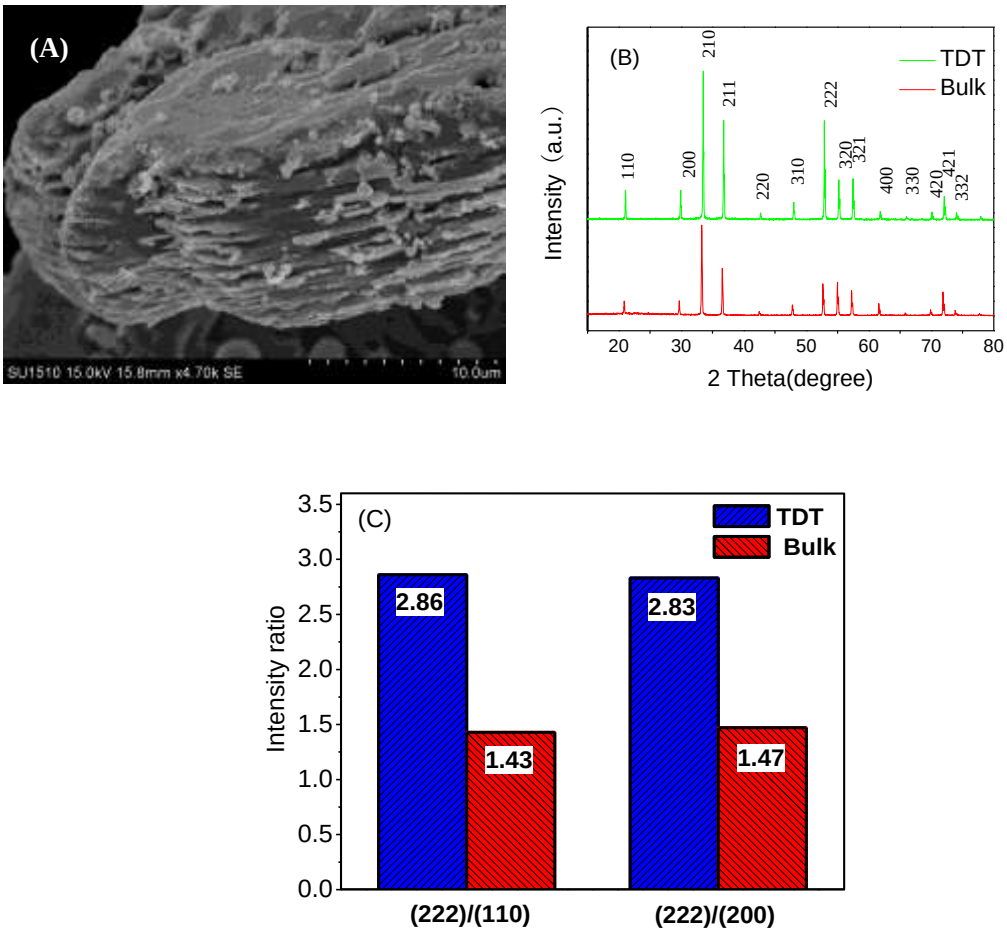


Fig. S5 (A) SEM image of bulk Ag_3PO_4, (B) XRD patterns of TDT and the bulk, and (C) Intensity ratios of (222)/(110) and (222)/(200) peaks of TDT and the bulk

For TDTs, the peak intensity ratios of (222) to (110) and (222) to (200) are 2.86 and 2.83, respectively; whereas 1.43 and 1.47 for the bulk one. The results mean that {111} crystal facets may preferentially grow. As demonstrated in our previous study [*Wang, J.; Teng, F.; Chen, M. D.; Xu, J. J.; Song, Y. Q.; Zhou, X. L. CrystEngComm.*, ***2013***, *15, 39.*], both shaft and secondary branches grow alone [111] direction. The angle between the shaft and secondary branch is about $109^{o}28'$.

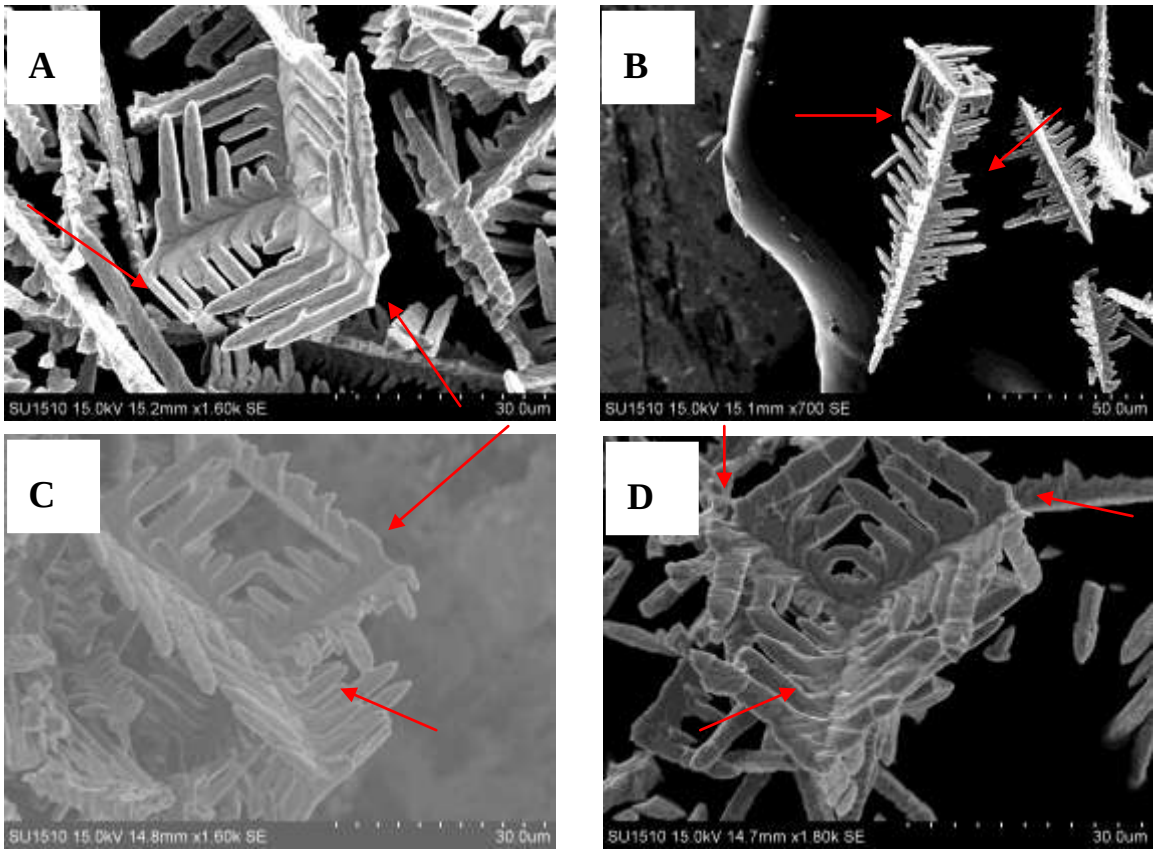


Fig. S6 SEM images of the fractured HBT found in TDT sample

A few of fractured HBT are found in TDT sample, which further verify our conjecture that TDTs result from the fractured branch of HBT.

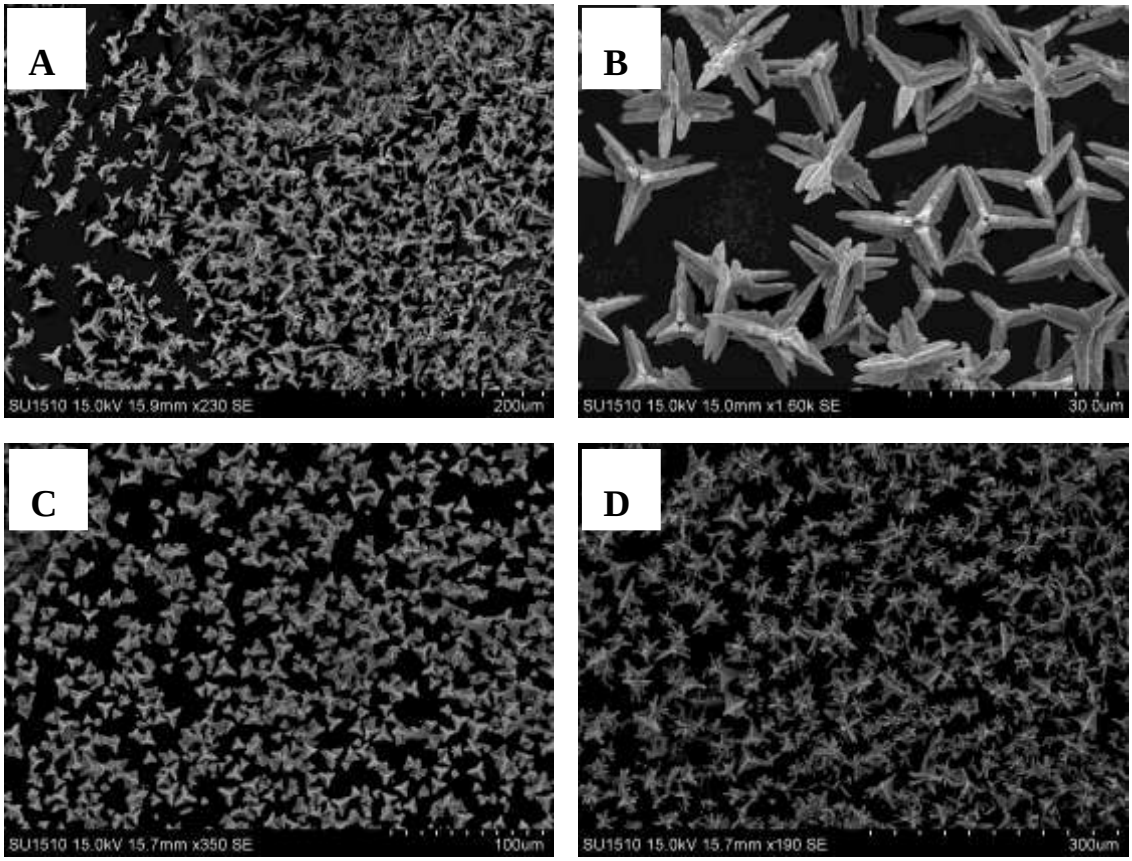


Fig. S7 Low-magnification SEM images of Ag_3PO_4 samples synthesized at different HMT/Ag(I) molar ratios: (A) 0.5:1; (B) 0.75:1; (C) 1 and 1.25:1; (D) 1.5:1

As the amount of HMT increases, the morphology of Ag_3PO_4 crystal changes from three-overlapped tetrapods to the pitted tetrahedrons, poly-arms.

Table 1 pH values of the reaction system at different HMT/Ag(I) molar ratios

HMT/Ag(I) (molar ratio)	PH
0/1	0.21
0.5/1	4.04
0.75/1	4.10
1.25/1	4.60
1.5/1	4.82

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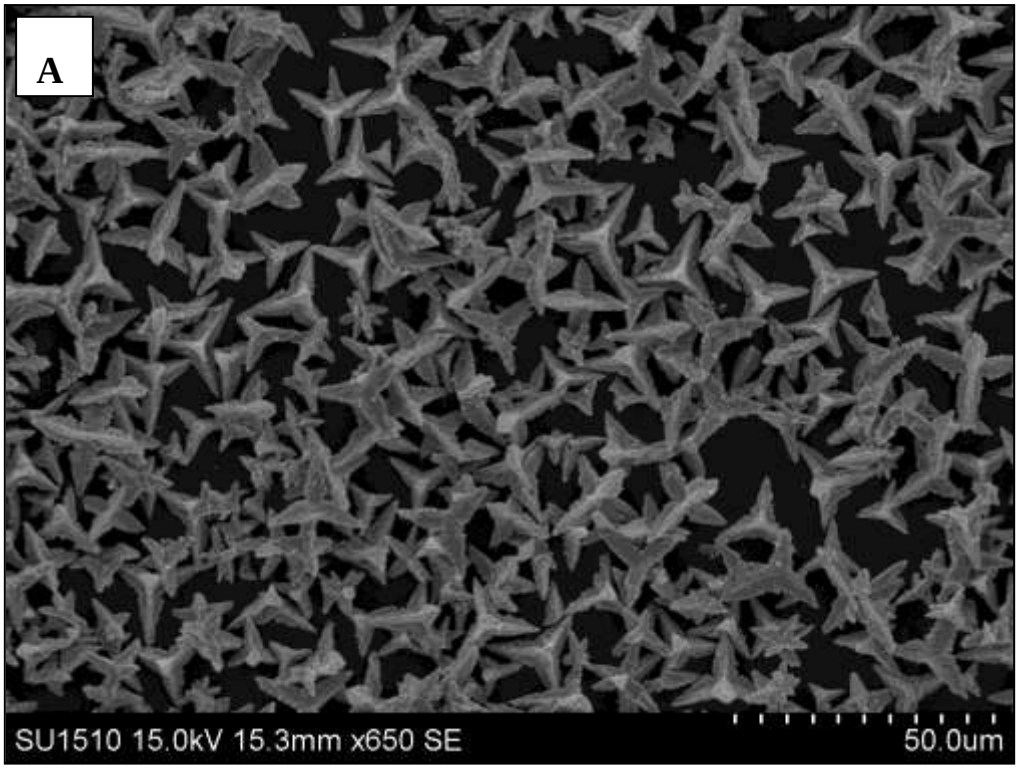

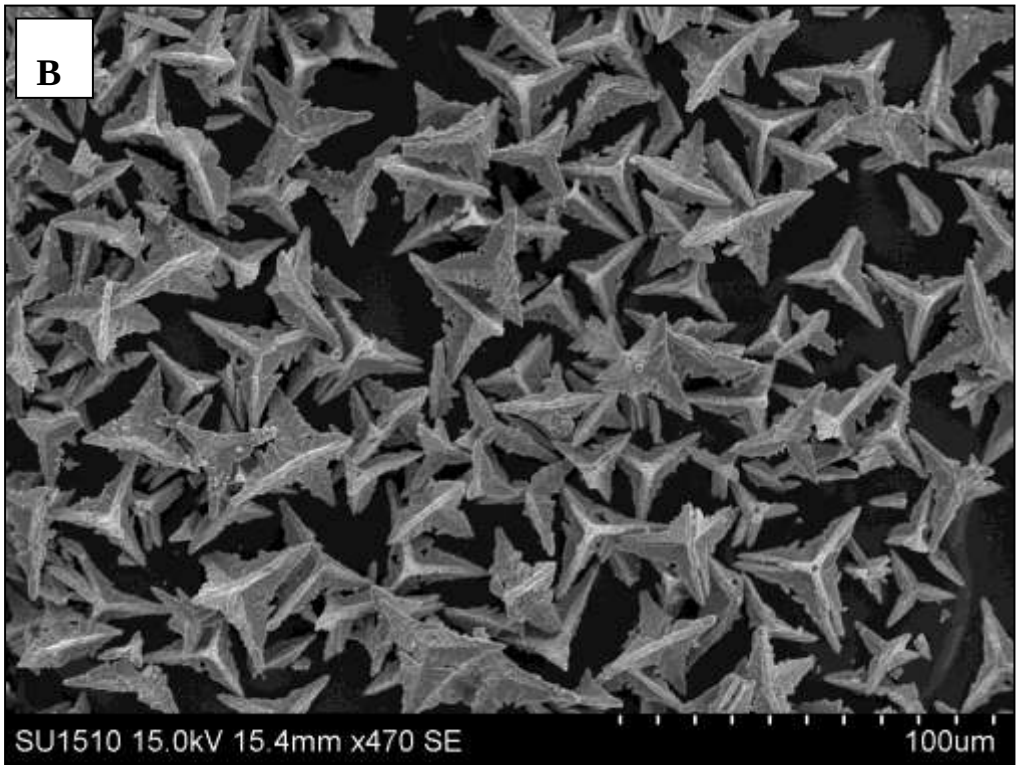

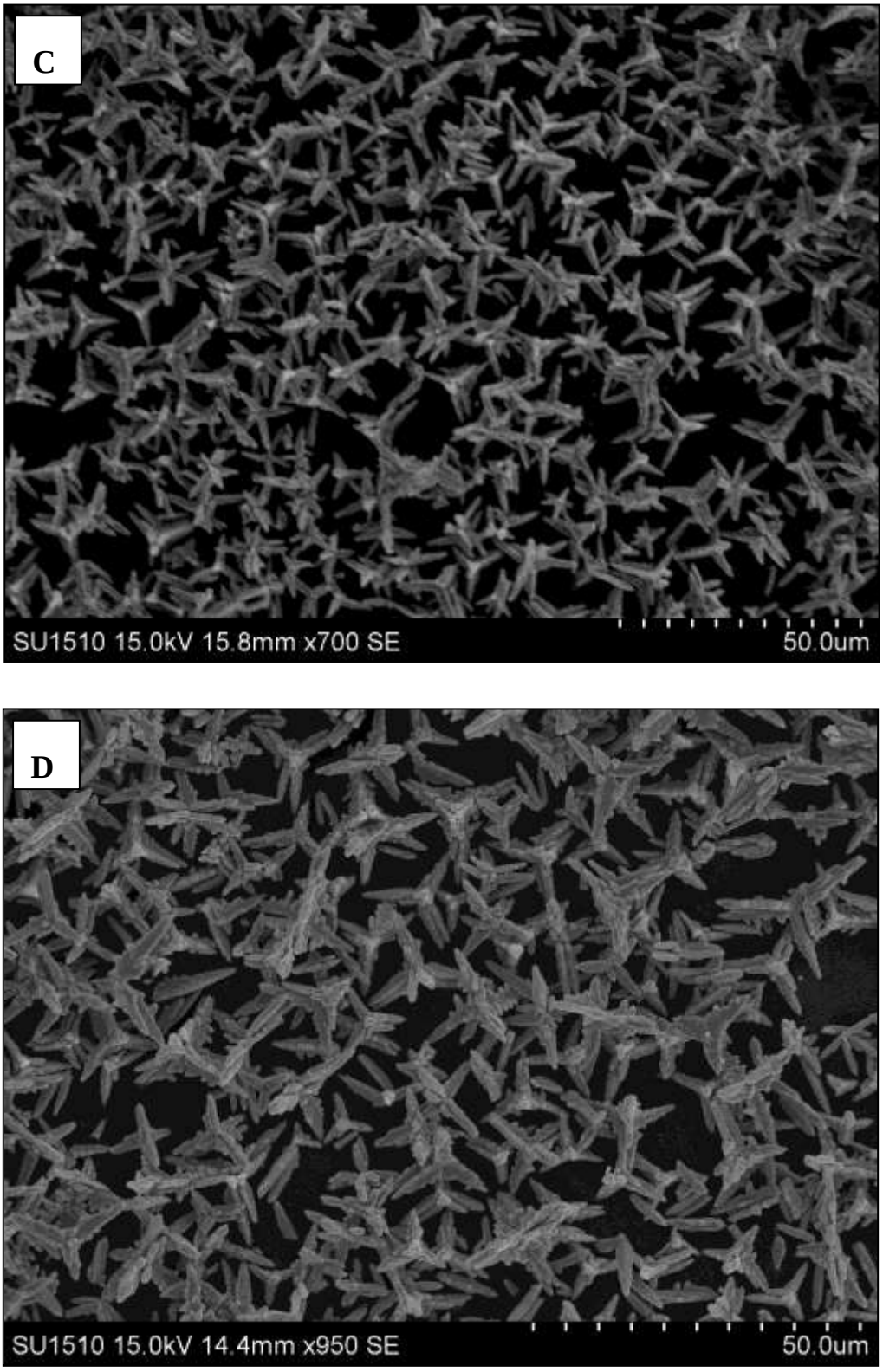

Fig. S8 Low-magnification SEM images of Ag_3PO_4 samples synthesized at different temperatures: (A) 15 ^oC; (B) 20 ^oC; (C) 30 ^oC; (D) 45 ^oC

At lower temperatures, the tetrapods with wide leaves form; with increasing the

temperature, each wide leaf of tetrapods gradually transform into three independent branches, and finally become overlapped tetrapods. It seems that the crystals form through the complicated process of dissolution – recrystallization – splitting growth. It is reasonable that reaction temperature generally has a significant influence on the kinetics and thermodynamics of nucleation and growth, leading to different morphologies.

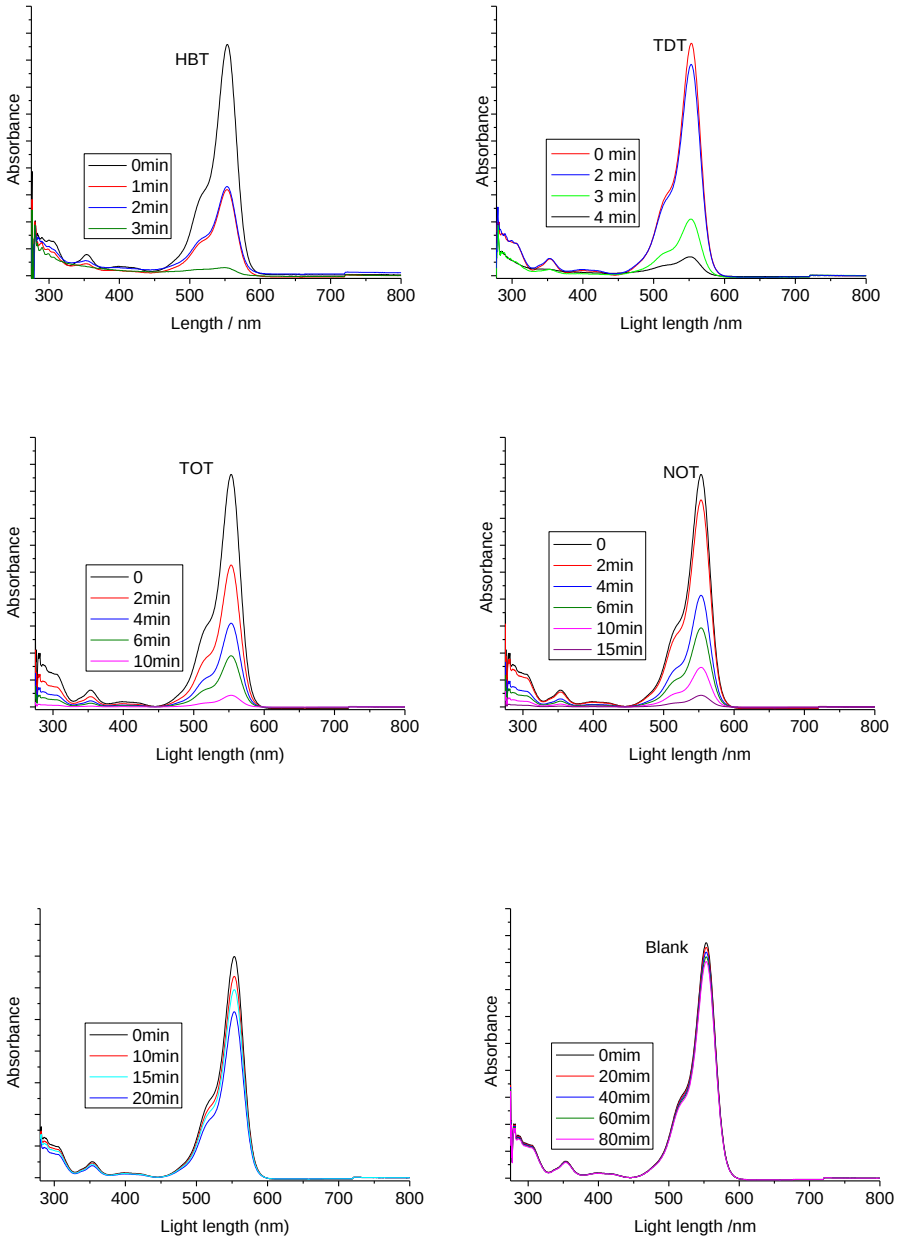

Fig. S9 The absorption spectra of RhB