Supporting Information for

Controllable growth of novel $BiPO_4$ dendrites by an innovative approach and high energy facets-dependent photocatalytic activity

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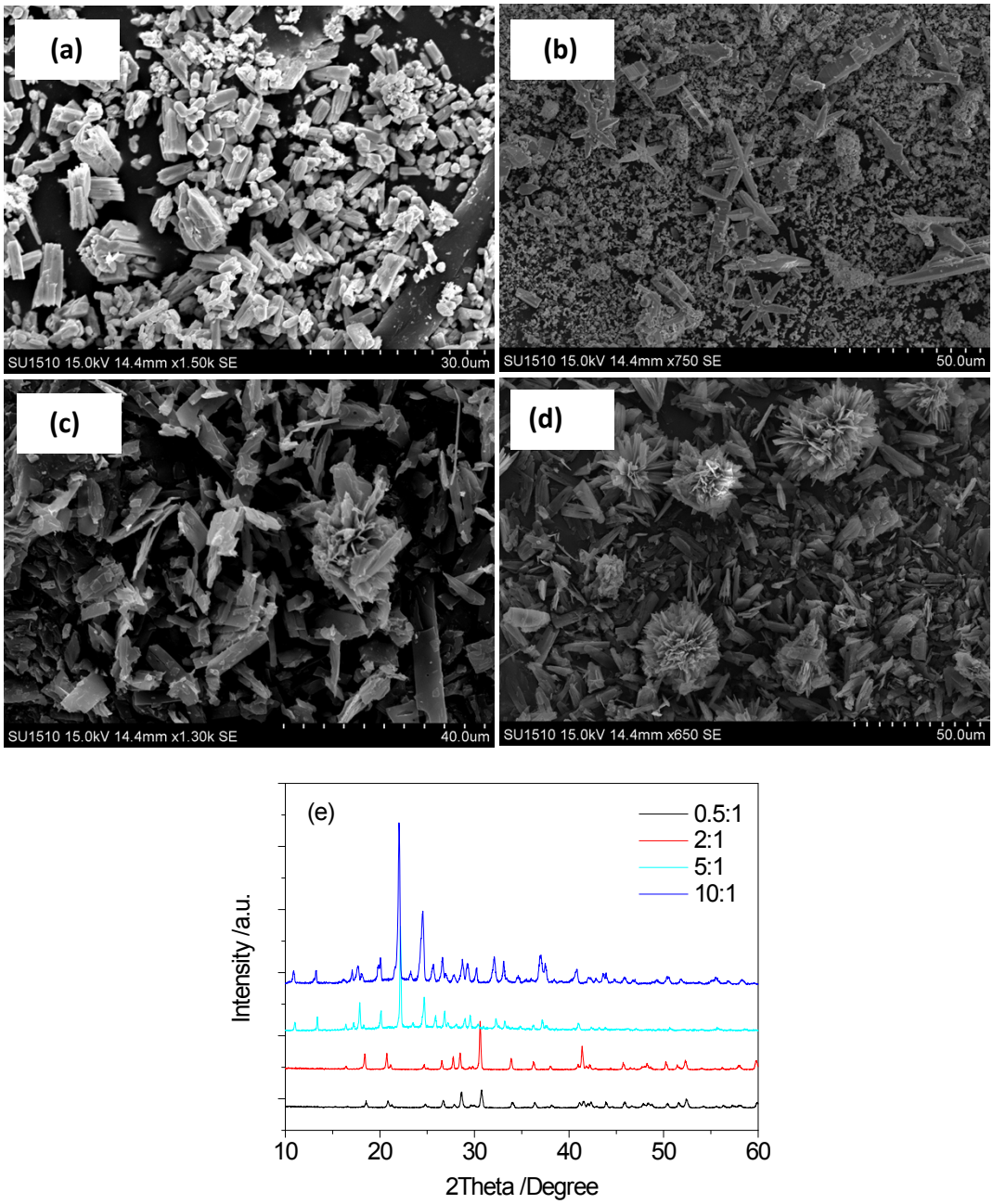


Figure S1 Effect of EDTA/Bi(III) molar ratio on the samples: (a) 0.5/1; (b) 2/1; (c) 5/1; (d) 10/1; (e) XRD

According to JCPDS 15-0767, it is obvious that $BiPO_4$ irregular polyhedrons and six-branch dendrites with more nanoparticles form at 0.5/1 and 2/1 (EDTA/Bi), respectively; but both samples have low XRD peaks intensities. At 5/1 and 10/1, EDTA samples, instead of $BiPO_4$ are acquired, which is attributed to the more and strong complexing effect of EDTA. It is noted that at high ratios (2/1, 5/1, 10/1), EDTA can not completely dissolve in the solution at room temperature. At too much

amounts of EDTA, Bi(III) ions can be released but are still remained in solution under our experiments. But EDTA has precipitated out through a dissolution – recrystallization process.

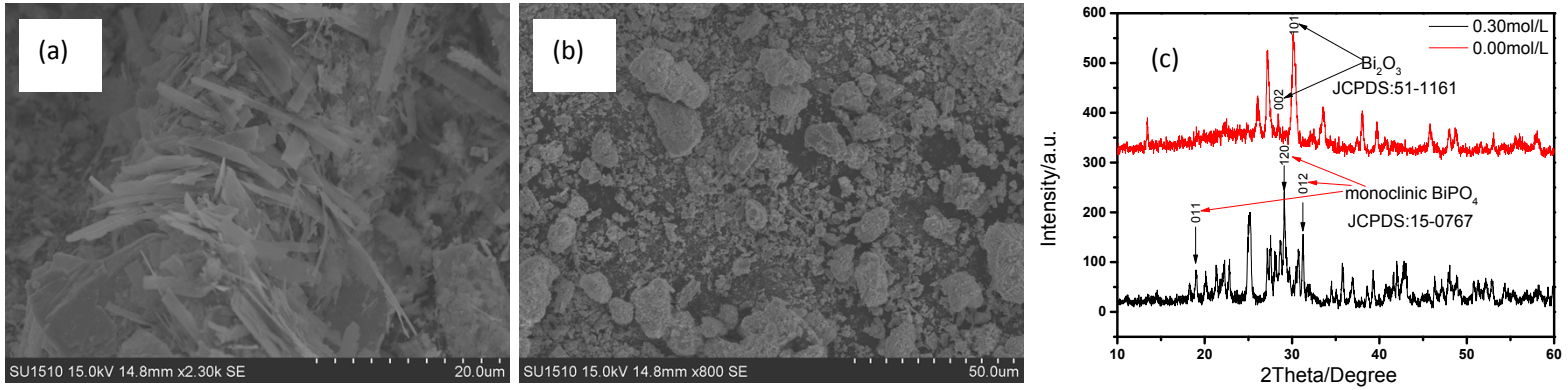


Figure S2 SEM images and XRD patterns of the samples prepared at different concentrations of hydrogen ions: (a) 0 mol/L; (b) 0.30 mol/L; (c) XRD

At 0.30 mol/L hydrogen ion (pH = 0.52), the as-prepared samples are NOT phase-pure $BiPO_4$, but with many unknown impurities phases. Therefore the concentrations of hydrogen ion are controlled in the range of 0.05 to 0.2 mole/L (pH=0.699~1.0), so as to obtain the phase-pure $BiPO_4$ sample. With further increasing pH value to or higher than 7, Bi_2O_3 form.

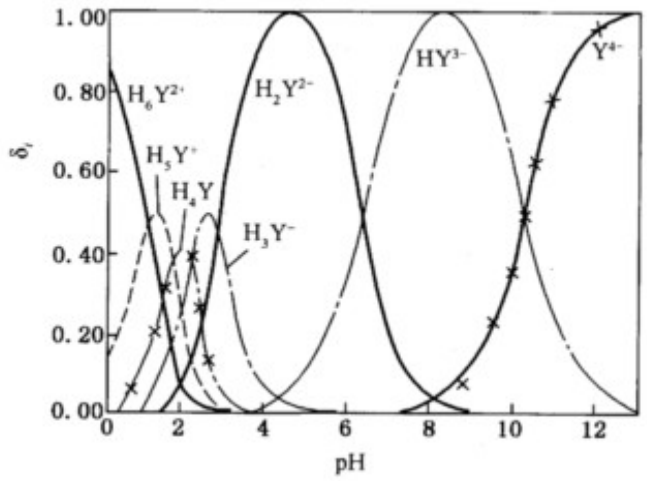
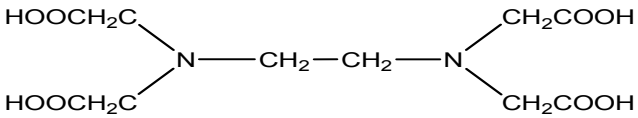


Figure S3 Distribution diagram of various existing forms of EDTA at different pH values ("*Analytical Chemistry*" (5th Edition), Wuhan University, Beijing, Higher Education Press, 2006.)

It is obvious that EDTA has seven existing forms at different pH values. At pH values low than 1.3, **EDTA** mainly exists as the three forms of $\mathbf{H_6Y^{2+}}$, $\mathbf{H_5Y^{+}}$ and $\mathbf{H_4Y}$ (Y=EDTA)

(a)



(b)

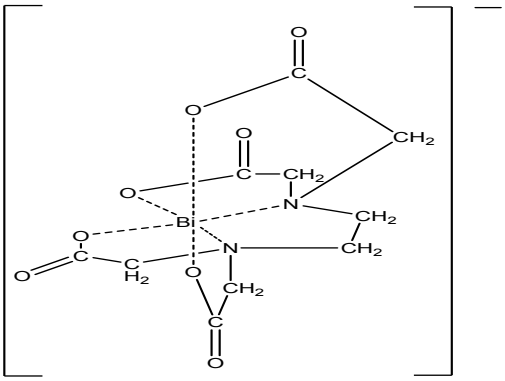


Figure 4 The chemical formula of EDTA (a) and Bi (III)-EDTA complex (b): EDTA, ethylene diamine tetraacetic acid

$$Bi^{3+} + Y \leftrightarrow BiY^{-} + 4H^{+} \quad (1)$$

$$BiY^{-} \leftrightarrow Bi^{3+} + Y^{4-} \quad (2)$$

$$Y^{4-} + H^{+} \leftrightarrow HY^{3-} \quad (3)$$

$$HY^{3-} + H^{+} \leftrightarrow H_2Y^{2-} \quad (4)$$

$$H_2Y^{2-} + H^{+} \leftrightarrow H_3Y^{-} \quad (5)$$

$$H_3Y^{-} + H^{+} \leftrightarrow H_4Y \quad (6)$$

$$H_4Y + H^{+} \leftrightarrow H_5Y^{+} \quad (7)$$

$$H_5Y^{+} + H^{+} \leftrightarrow H_6Y^{2+} \quad (8)$$

Equation S1 The chemical equations in the presence of both H^{+} and Bi^{3+}: (Y=EDTA)

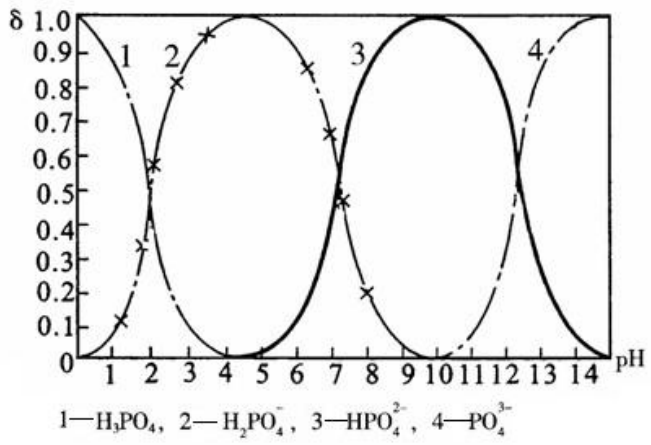


Figure S5 Distribution diagram of various existing forms of H_3PO_4 at different pH values ("*Analytical Chemistry*" (5th Edition), Wuhan University, Beijing, Higher Education Press, 2006.)

It is obvious that H_3PO_4 has four existing forms at different pH values. At pH values low than 2, $\mathbf{H_3PO_4}$ mainly exists as the two forms of $\mathbf{H_3PO_4}$ and $\mathbf{H_2PO_4^-}$. Under hydrothermal conditions, PO_4^{3-} is released, and the H^+ released by H_3PO_4 and H_2PO_4 will combine with $(edta^-)_4$ become H_6Y^{2+}. Since our experiments are mainly done under acidic conditions, phosphorous source mainly exists as the molecular form of H_3PO_4. After the Bi(III) ions are released from EDTA-Bi(III) complex, the hydrogen ions in H_3PO_4 can be released to produce PO_4^{3-} ions, resulting in the formation of $BiPO_4$.

Table S1 Equilibrium constants of EDTA and H_3PO_4

Chemicals	Equilibrium constants
EDTA	K_{a1}=1.0×10^{-2}, K_{a2}=2.1×10^{-3}, K_{a3}=6.9×10^{-7}, K_{a4}=5.9×10^{-11}
H_3PO_4	K_{a1}=6.7×10^{-3}, K_{a2}=6.2×10^{-8}, K_{a3}=4.5×10^{-13}
EDTA-Bi(III) complex	K_s=27.94
$BiPO_4$	K_{sp}=1.26×10^{-23}

Phosphorus source mainly exists as the form of H_3PO_4 and EDTA mainly exists as the molecular form, as shown in Figure S2.

("*Analytical Chemistry*" (5th Edition), Wuhan University, Beijing, Higher Education Press, 2006.)

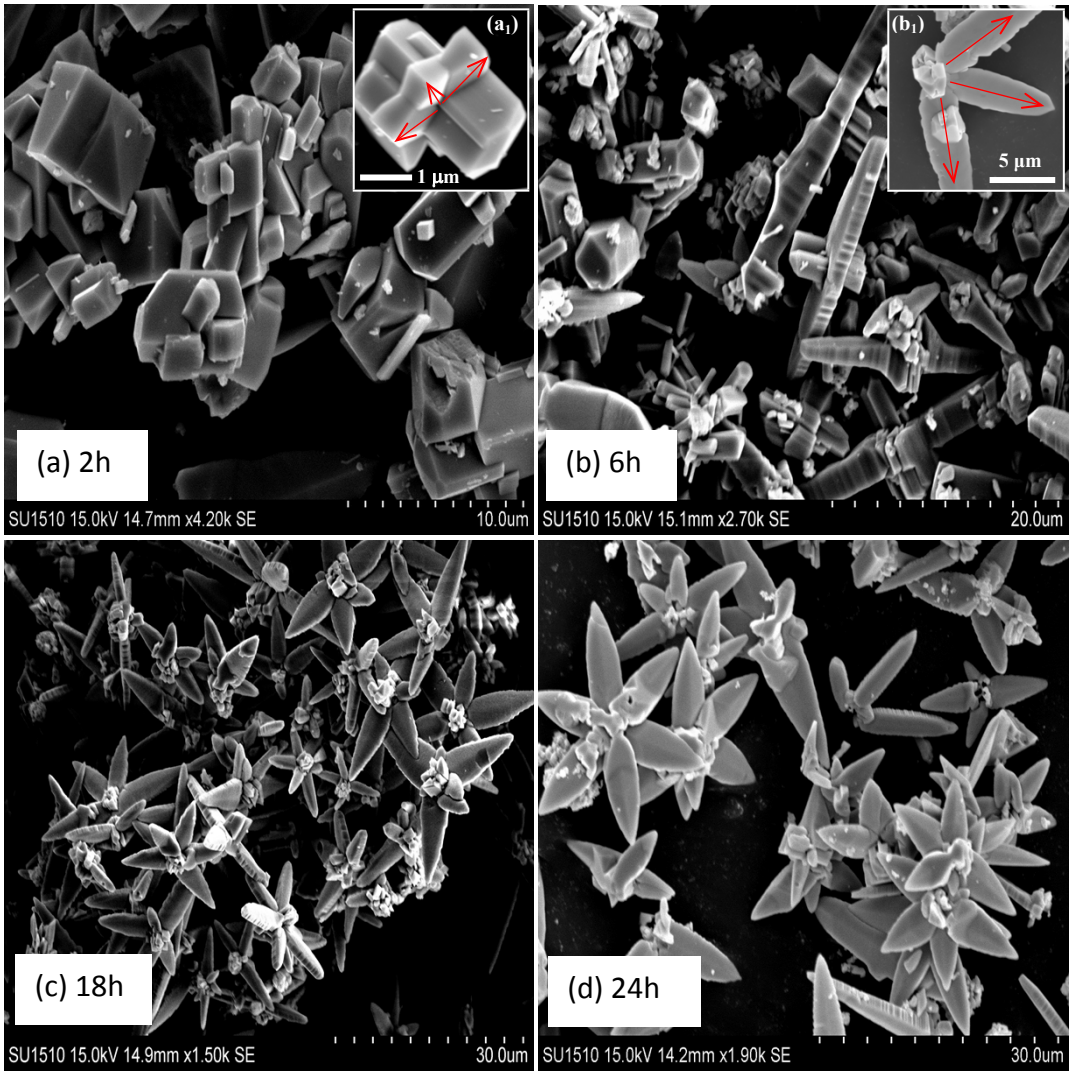


Figure S6 The time-dependent experiments for the six-branch $BiPO_4$ dendrites: (a-d) SEM; (e) XRD; using EDTA instead of EDTA-Na_2, pH= 1.0

At the initial time the polyhedrons have formed, and then they transform into the six-branch dendrites through the dissolution and recrystalization processes. The details mechnism is still unknown at the present time

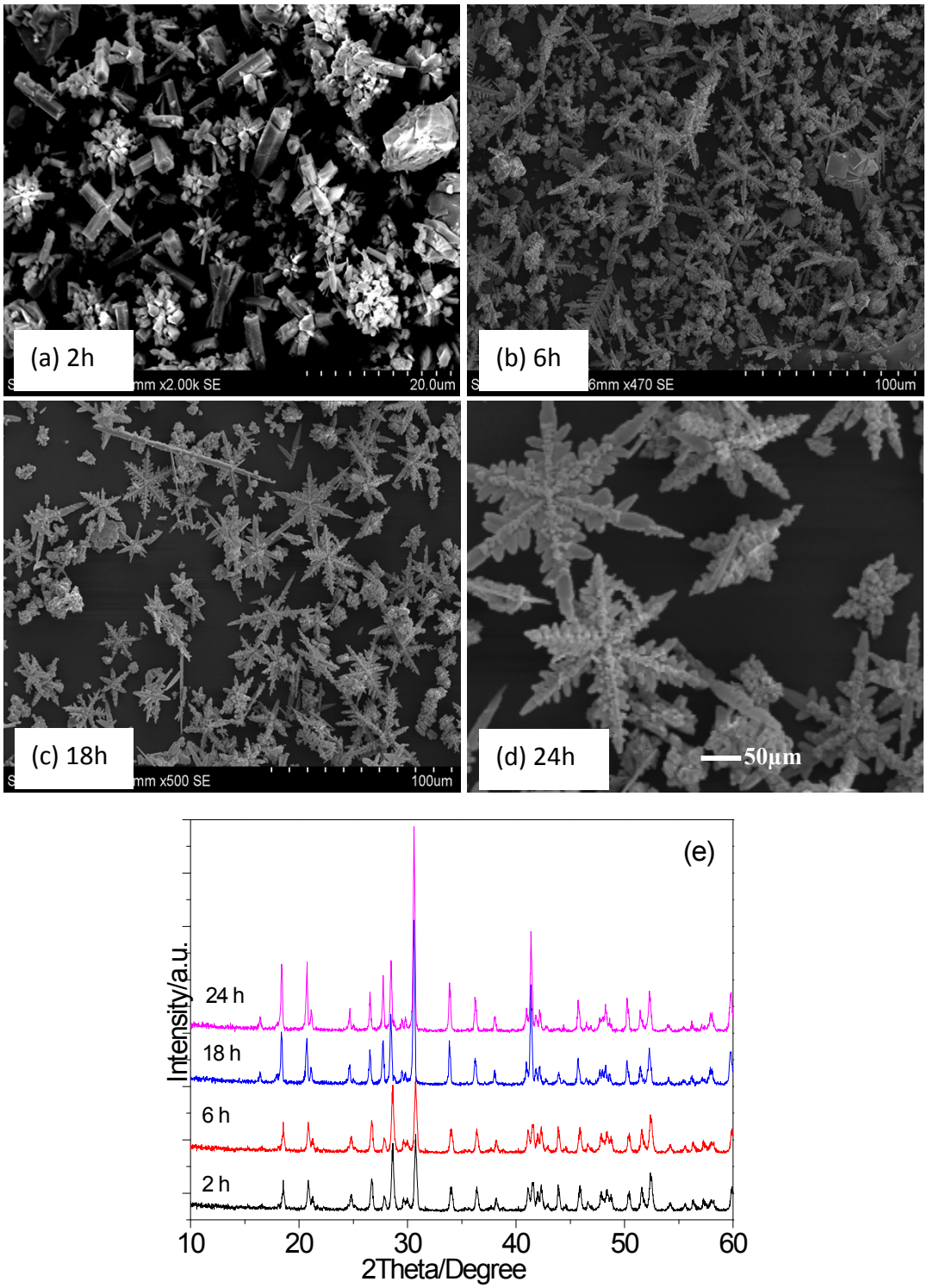


Figure S7 The time-dependent experiments for the snowflake-like $BiPO_4$ dendrites: (a-d) SEM; (e) XRD; using EDTA and adding 275 μL of 65wt.% HNO_3; pH =0.699 ([H+])=0.2mol/L)

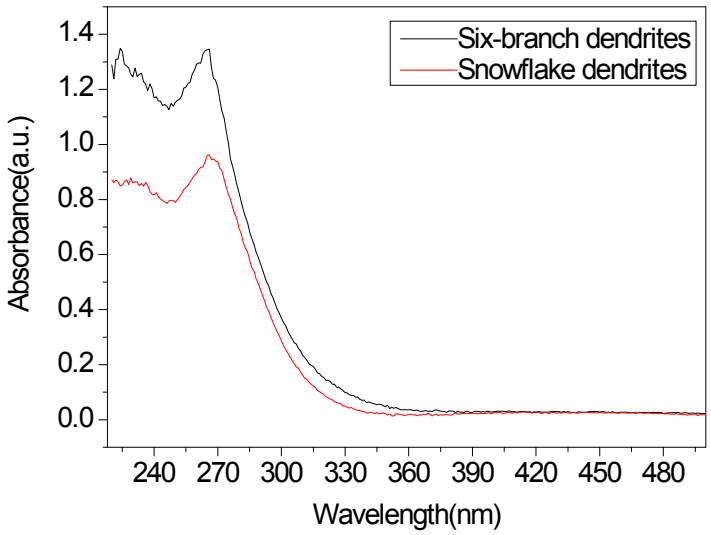


Figure S8 UV-vis diffuse reflection spectra (UV-DRS) of the snowflake dendrites and six-branch dendrites

Table S2 The crystal phases, particle sizes and texture properties of the $BiPO_4$ samples

Samples	Six-branch dendrites	Snowflake dendrites	Cubes
[1]Particle size	30 μm × 30 μm	40 μm × 40 μm	10 μm×10 μm
[2]S_{BET} (m^2 g^{-1})	6.5	3.2	7.9
[3]Pore volume (cm^3 g^{-1})	0.010	0.009	0.008
[3]Pore size (nm)	3.40	3.10	3.06

[1]Particle size, observed from SEM images; [2]S_{BET}, calculated by the Brunauer-Emmett-Teller (BET) method; [2]Pore volume and size, calculated by the Barrett-Joyner-Halenda (BJH) method.

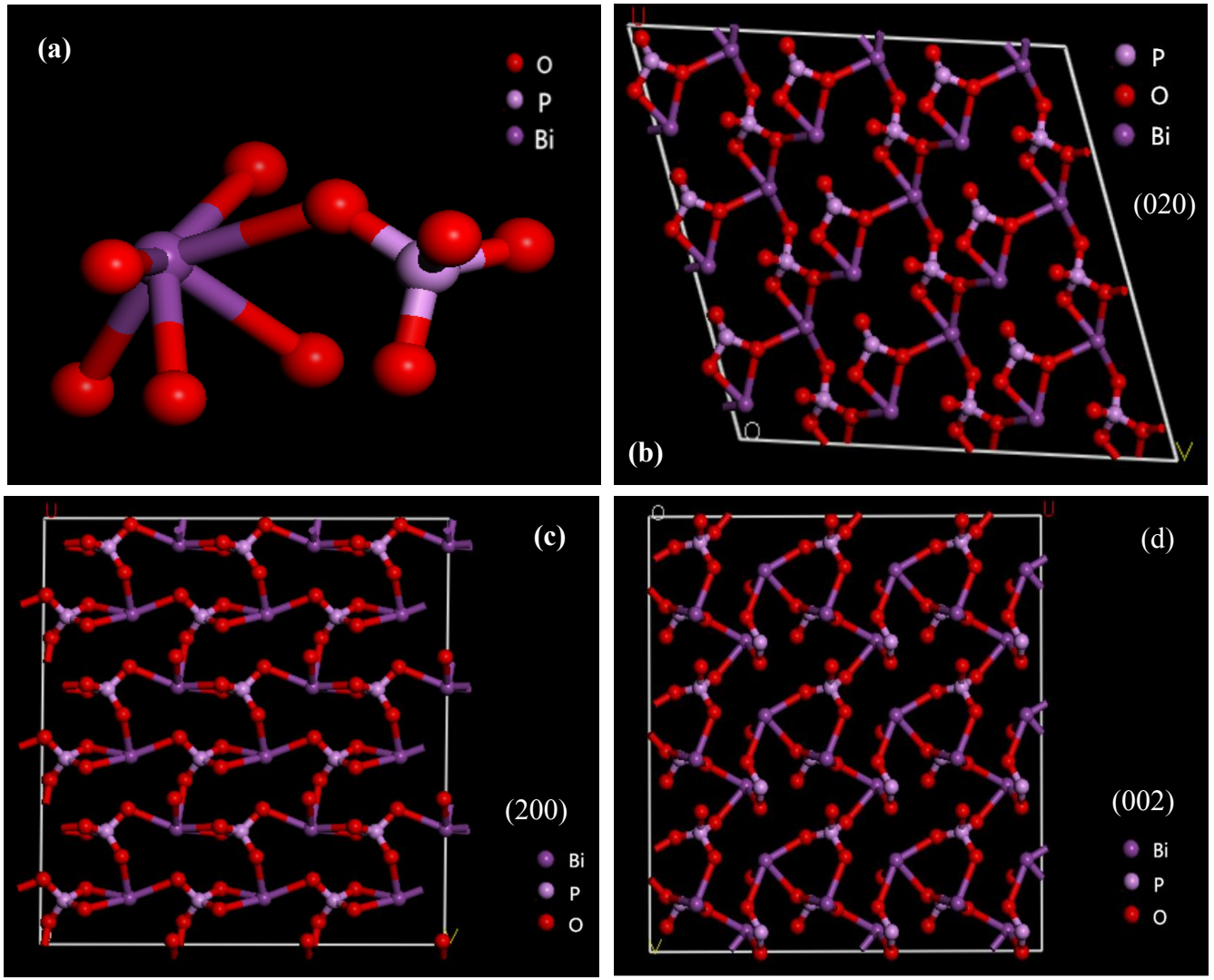


Figure S9 Molecular unit model (a) and atomic configurations of (020), (200) and (002) facets (b-d) of momoclinic $BiPO_4$