Supporting Information

Controlled synthesis of highly dispersed BiPO$_4$ photocatalyst with surface oxygen vacancy

Zhen Wei,$^a$ Yanfang Liu,$^a$ Jun Wang,$^a$ Ruilong Zong,$^a$ Wenqing Yao,$^a$ Juan Wang$^a$ and Yongfa Zhu$^a$

$^a$Department of Chemistry, Beijing Key Laboratory for Analytical Methods and Instrumentation, Tsinghua University, Beijing, 100084, China.

$^b$College of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, China

E-mail: zhuyf@tsinghua.edu.cn

Fig. S1A  XRD patterns of BiPO$_4$ synthesized at different reaction temperatures
Fig. S1B  TEM images of BiPO₄ synthesized at 140°C for different reaction time

Fig. S1C  TEM images of BiPO₄ synthesized at different reaction temperatures for 48 h
In order to test the adsorption capacity of the photocatalysts, the adsorption-desorption equilibrium experiments were conducted (results shown in the Fig.S2). As can be seen from Fig.S2, the adsorption percentages of MB on EG-140°C and cal.-140°C are almost identical, which are about 12%
and both are higher than that for SSR (about 4%). Therefore, the adsorption capacity of the highly dispersed photocatalysts are strong, which contributes to their efficient removal of the pollutants.

Fig. S3 Photos of EG-140°C and cal.-140°C dispersed in MB, RhB and MO $2 \times 10^{-5}$ mol/L solutions stand for 0h (upper) and 24h (lower)

As can be seen in Fig. S3, EG-140°C and cal.-140°C not only exhibit good dispersion performance in water, but also in the solution of MB, RhB and MO, since they are very small particles and do not agglomerate with these pollutants.
Fig. S4 (A) Degradation curves of MB ($1 \times 10^{-5}$ mol/L) by BiPO$_4$ prepared by different solvothermal time; (B) Apparent rate constants of degrading MO, RhB and phenol by SSR and cal.140°C; (C) and (D) are liquid chromatography of degrading phenol by cal.-140°C and SSR respectively.

Fig. S5 XRD patterns of cal.-140°C after 5 cycles of degradation of MB solution
Fig. S6 The photocatalytic activities of fresh and after storage 15 months cal.-140°C on the degradation of MB.

It is really difficult to recycle small particles. If the cal.-140°C disperses into water, it is difficult to subside completely for a week. With the reaction of photocatalysis, the hydrophilic organics on the surface is desorbed gradually and the absolute value of Zeta potential will decrease. This phenomenon becomes more and more obvious as the reaction of photocatalysis proceeds. The photocatalyst after 5 times recycle could be subsided completely after still standing for 30 min (shown in Fig. S7A). So it has solved the separation problem. The particles are aggregated after recycle for many times (shown in Fig. S7B).

Fig. S7 Optical photos and TEM images of catalysts cycled for 5 times without ultrasonication.
As shown in the DRS of cal.-140°C, the main absorption edge is about 298 nm, corresponding to the band gap of 4.16 eV. Besides, another absorption edge is 328 nm, corresponding to the band gap of 3.78 eV. According to the literature J. Mater. Chem. A, 2014, 2, 1174-1182 and J. Phys. Chem. C 2013, 117, 18520–18528, the band gap of pure monoclinic BiPO$_4$ is about 4.1 eV. Therefore, 4.16 eV is confirmed to be the intrinsic band gap of monoclinic BiPO$_4$, and 3.78 eV is the gap between the energy level induced by surface oxygen vacancy.