Supporting information:

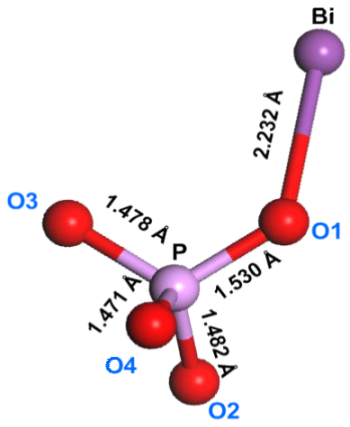

Figure S1. The ball-and-stick model of $BiPO_4$ coordination

As seen from **Figure S1**, the bond length between oxygen (O) atom and phosphorus (P) atom or bismuth (Bi)atom is not equal in $BiPO_4$. Based on the bond length (representing bond energy) between each two atoms, O atom maybe removed in turn, from O1, O2, O3 to O4, even the PO_4^{3-} is totally detached from $BiPO_4$, generating oxygen vacancies with different number and extent.

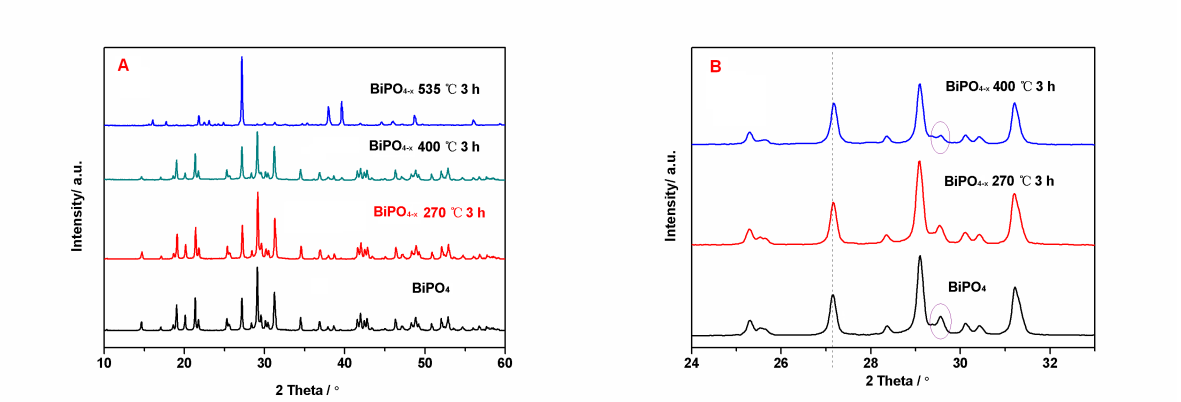

Figure S2. (A) XRD patterns of $BiPO_4$ and $BiPO_{4-x}$ nanorod treated at 270, 400 and 535 ℃ for 3 h; **(B)** The enlarged XRD patterns of $BiPO_4$ and $BiPO_{4-x}$ samples at local.

From the X-ray diffraction (XRD) patterns of pure $BiPO_4$ and $BiPO_{4-x}$ samples **Figure S2**, no phase transformation or any impurity is observed for $BiPO_4$ after H_2 reduction at 270 ºC for 3 h, so there most oxygen atoms are removed from $BiPO_4$ surface, generating surface oxygen vacancies. However, after H_2 reduction at 400 ºC for 3 h, the XRD peak of vacancy $BiPO_{4-x}$ decrease, indicating that crystallinity decreased, and the peak at 2θ = 27.1º (200) moves to big angle slightly, indicating that the lattice spacing *d* decreases, which may be resulted from the loss of lattice oxygen and the formation of bulk oxygen vacancy, and the peak intensity. And after 535 ºC 3 h H_2 reduction treated, $BiPO_4$ losses PO_4^{3-} totally becomes mental Bi (**Figure S2A**).

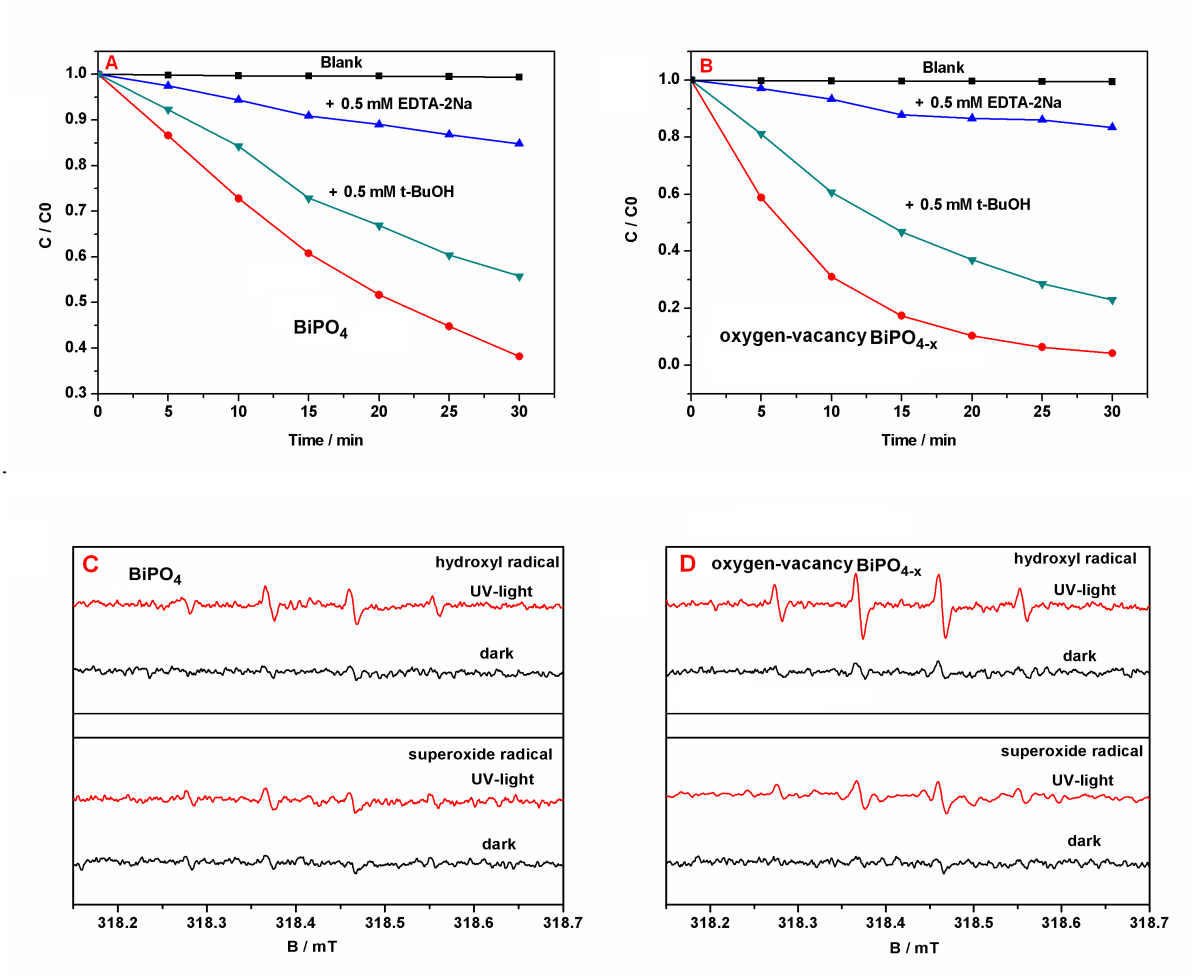

Figure S3 (A)(B) The plots of photoinduced carriers trapping in the system of photodegradation on MB over $BiPO_4$ and oxygen−vacancy $BiPO_{4-x}$, under UV light (λ = 254 nm), respectively; **(C)(D)** DMPO spin−trapping ESR spectra of $BiPO_4$ and oxygen−vacancy $BiPO_{4-x}$ photocatalysts.

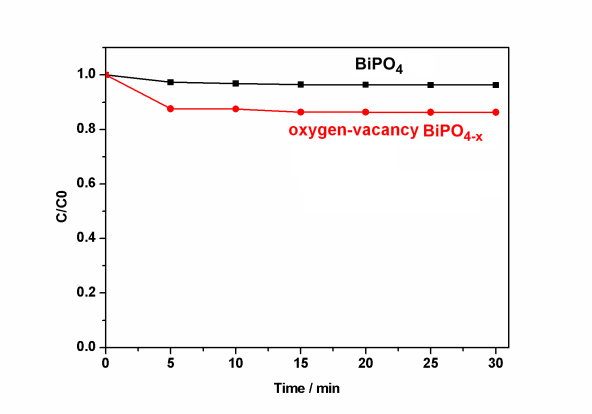

Figure S4. The adsorption of $BiPO_4$ and oxygen-vacancy $BiPO_{4-x}$ on the degradation of MB solution, in dark.

As can be seen from **Figure S4,** compared pure $BiPO_4$, the adsorption capacity of oxygen-vacancy $BiPO_{4-x}$ is slightly improved from about 3% for pure $BiPO_4$ to about 11% in dark. And after 10 min, the adsorption equilibrium achieved for both of them

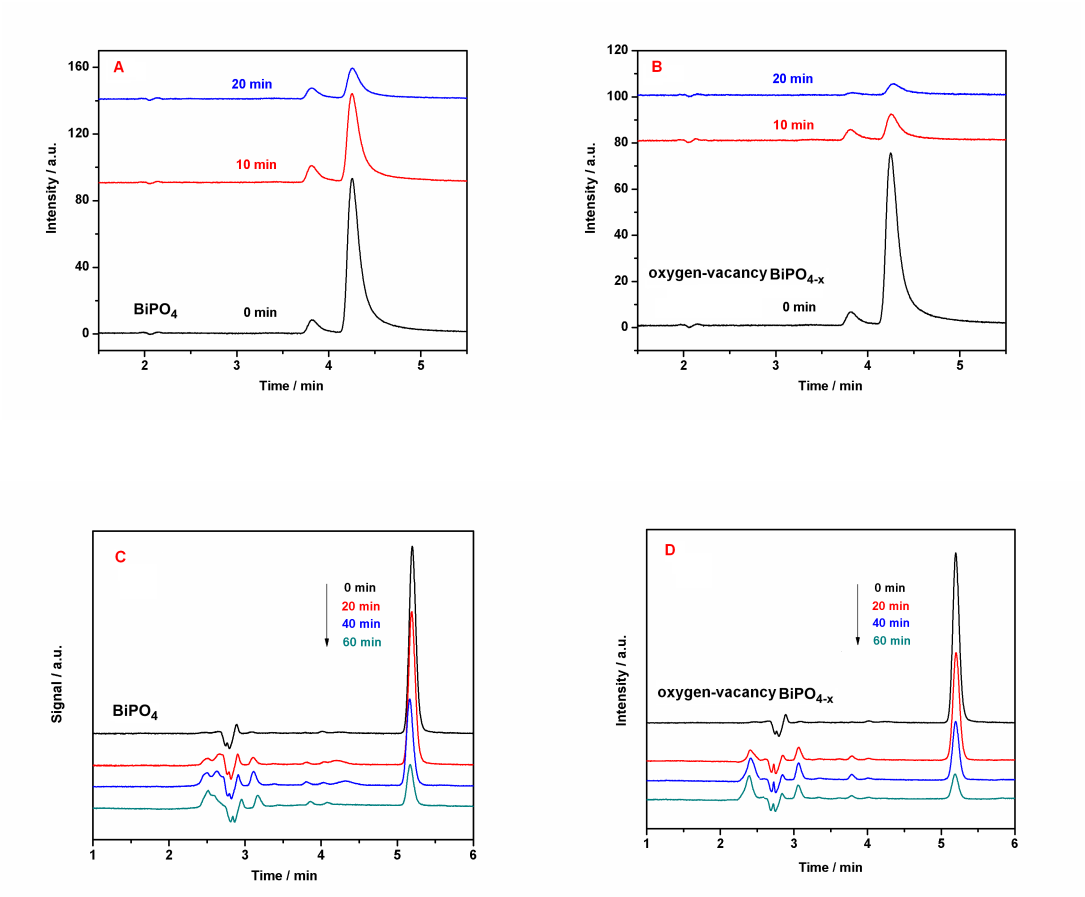

Figure S5. HPLC of intermediates at different irradiation intervals on MB **(A)(B)** and phenol **(C)(D)** by $BiPO_4$ and oxygen-vacancy $BiPO_{4-x}$, respectively.

The intermediates of MB and phenol over $BiPO_4$ and oxygen-vacancy $BiPO_{4-x}$ were determined by HPLC (Lumtech) analysis with a UV detector at 663 nm and 270 nm, respectively.

To demonstrate the change and reveal some details of the reaction process of pure $BiPO_4$ and oxygen-vacancy $BiPO_{4-x}$, photodegradation intermediates distribution on MB and phenol at intervals during the photocatalytic process were monitored by HPLC, and the results are displayed in **Figure S5**. From **Figure S5A and B**, it can be found that the degradation intermediates on MB by oxygen-vacancy $BiPO_{4-x}$ hardly any changes but the extent and rate greatly increased, compared with that of pure $BiPO_4$. In addition, **Figure S5C**

and D shows that the degradation intermediates on phenol over two samples only little change in concentration, and the intermediates distribution is almost no different. Thses indicate that the photodegradation on MB or phenol by oxygen-vacancy $BiPO_{4-x}$ are both enhanced, compared with pure $BiPO_{4,}$ and photodegradation intermediates are not changed.

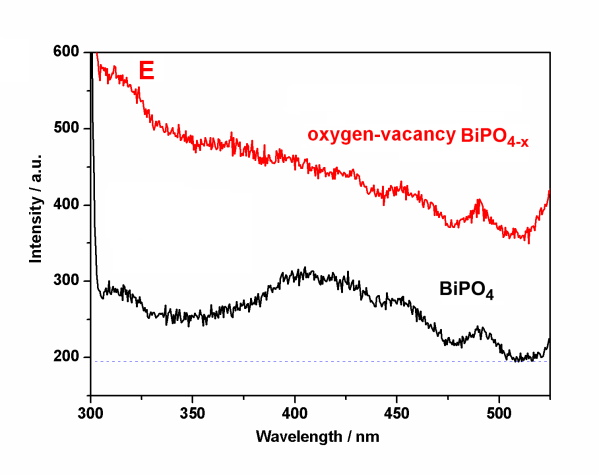

Figure S6. The PL (270 nm excitation) spectra of $BiPO_4$ and oxygen−vacancy $BiPO_{4-x}$.

The room temperature photoluminescence (PL) spectra of $BiPO_4$ and oxygen-vacancy $BiPO_{4-x}$ samples were investigated utilizing the PerkinElmer LS55 spectrophotometer equipped with xenon (Xe) lamp with an excitation wavelength of 277 nm.

Photoluminescence spectra (PL) can reveal surface structure characteristics of nanometer semiconductor materials, such as surface oxygen vacancies and defects etc., and surface oxygen vacancy is positively related with the PL signal.[1-3] The room temperature photoluminescence (PL) spectra of $BiPO_4$ and oxygen-vacancy $BiPO_{4-x}$ at wavelength 270 nm excitation were investigated, as shown in **Fig.S6**. Compared with pure $BiPO_4$, the PL peak of oxygen−vacancy $BiPO_{4-x}$ is obviously enhanced in the range of 300−520 nm, which is induced by oxygen vacancies. The larger the concentration of surface oxygen vacancy, the stronger the PL signal.[2,3] Therefore, more surface oxygen vacancies are produced on oxygen-vacancy $BiPO_{4-x}$ nanorod.

References

(1) Jing, L.Q.; Xin, B. F.; Yuan, F. L.; Xue, L. P.; Wang, B. Q.; Fu, H. G. *J. Phys. Chem. B* **2006**, *110*, 17860.

(2) Jing, L. Q.; Yuan, F. L.; Hou, H. G.; Xin, B. F.; Cai, W. M.; Fu, H. G. *Sci. in China Ser. B Chem.* **2005**, *48*, 25.

(3) Jing, L. Q.; Qu,Y. C.; Wang, B. Q.; Li, S. D.; Jiang, B. J.; Yang, L. B.; Fu,W.; Fu, H. G.; Sun, J. Z. *Sol. Energy Mater. Sol. Cells* 2006, **90**, 1773.