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Layered photocatalyst $Bi_2O_2[BO_2(OH)]$ with internal polar field enhanced photocatalytic activity

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Experimental Section

Chemicals

$Bi(NO_3)_3 \cdot 5H_2O$, H_3BO_3, NaOH, Polyvinylpyrrolidone (PVP), HNO_3 (65%), Rhodamine B (RhB) were analytical grade. All materials were used without further purification.

Synthesis of $Bi_2O_2[BO_2(OH)]$

In a typical procedure of synthesis of $Bi_2O_2[BO_2(OH)]$, 15 ml 1 mol L^{-1} HNO_3 and 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ were mixed in a 150 ml beaker and stirred until the $Bi(NO_3)_3$ dissolved completely. At the same time, 55 ml deionized water, 16 mmol H_3BO_3 and a certain amount of PVP were mixed in another 150 ml beaker and stirred until the H_3BO_3 and PVP dissolved completely. The usage of PVP was ranging from 0 g to 0.4 g. Then, these two solutions were mixed together and the pH value was adjusted to 2, 7 and 13 by using 5 mol L^{-1} NaOH with constant stirring. During the adjustment process, a white precipitate appeared gradually. Finally, the mixture was maintained stirring for 10 min. Then, the solution was transferred into a 100 ml Teflon-lined stainless vessel and heated at a certain temperature ranged from 120 ^{0}C to 230 ^{0}C for different hydrothermal reaction time in an autoclave. The vessels were cooled down to room temperature, and the white products were washed with ethanol and deionized water several times and dried at 60 ^{0}C for 12h.

The $Bi_2O_2CO_3$ sample as a reference was synthesized by a hydrothermal method.[1]

Photocatalytic Experiment

The degradation of organic dye Rhodamine B (RhB) was used to evaluate the photocatalytic activity of the prepared samples under UV light at room temperature. In a typical procedure, 0.1 g samples were dispersed in 100 ml 20 mg L^{-1} RhB solution with continuous stirring. The solutions were kept in the dark for 20 minutes to make the as-prepared samples' surface reach the dye absorption equilibrium. The photocatalytic reaction proceeded under UV light provided by a 300 W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd.). 5 ml RhB solution was taken out from the reaction beaker every 10 minutes and centrifuged to remove the suspension in the solution. The concentration of RhB was evaluated by measuring the absorption of aqueous Rhodamine B solution with a Shimadzu UV2550 recording spectrophotometer.

Characterization

The structures and morphologies of the as-prepare samples were measured by X-ray powder diffraction (XRD Bruker D8-advanced X-ray powder diffractometer with Cu-Ka radiation λ=1.5418 Å), scanning electron microscopy (SEM Hitachi S-4800 microscope) and high resolution transmission electron microscopy (HR-TEM JEOL JEM-2100 instrument) respectively. A Micromeritics ASAP 2020 apparatus was used to measure the BET surface areas and the pore-size distributions of the products. UV-Vis diffuse reflectance spectra were recorded on a Shimadzu UV 2550 spectrophotometer equipped with an integrating sphere.

Density Functional Calculations

Our spin-polarized DFT calculations employed the projector augmented wave method coded in the Vienna *ab initio* simulation package, and the generalized gradient approximation of Perdew, Burke and Ernzerhof for the exchange and correlation corrections with the plane wave cutoff energies of 400eV, a set of 7×2×9 k-points and the threshold of self-consistent-field energy convergence of 10^{-4} eV.

1 Y. Y. Liu, Z. Y. Wang, B. B. Huang, K. S. Yang, X. Y. Zhang, X. Y. Qin and Y. Dai, *Appl. Surf. Sci.*, 2010, **257**, 172.

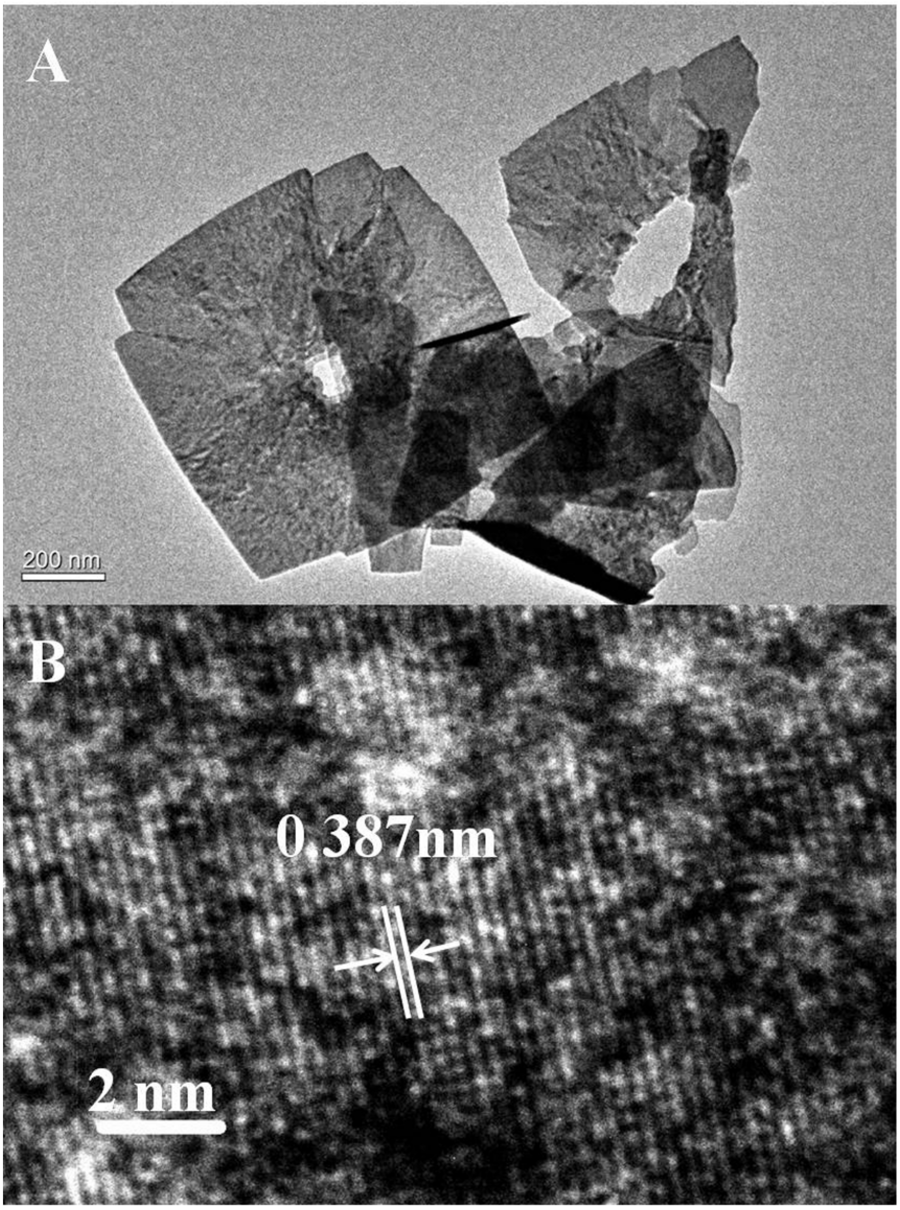

Fig. S1 A) TEM image of $Bi_2O_2[BO_2(OH)]$ nanosheets prepared at 120 ^{0}C with 0.3 g PVP for 12 hours, B) HR-TEM image of a single nanosheet in the corresponding magnified view.

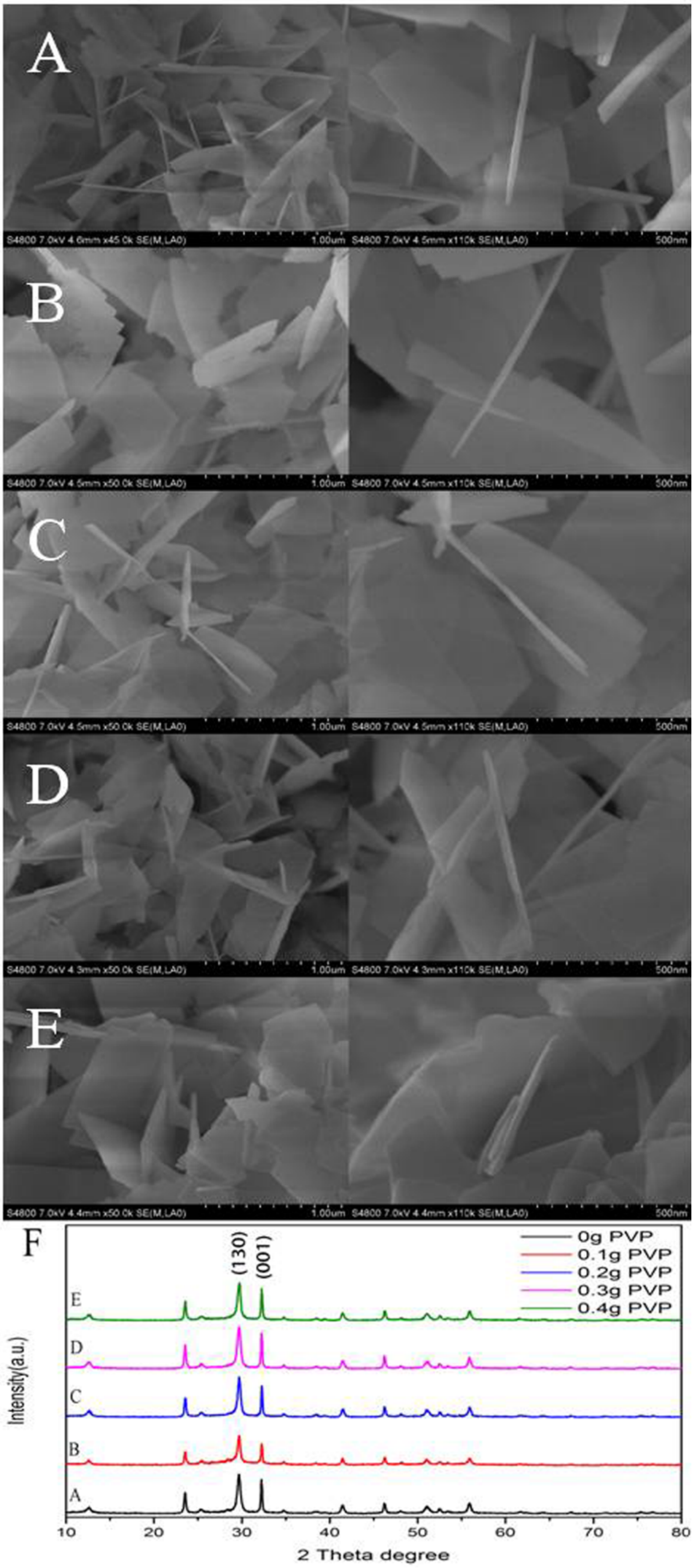

Fig. S2 SEM images of $Bi_2O_2[BO_2(OH)]$ prepared at 120 ^{0}C with different PVP for 12 hours, A) 0 g PVP, B) 0.1 g PVP, C) 0.2 g PVP, D) 0.3 g PVP and E) 0.4 g PVP; and F) XRD patterns of the as-prepared $Bi_2O_2[BO_2(OH)]$.

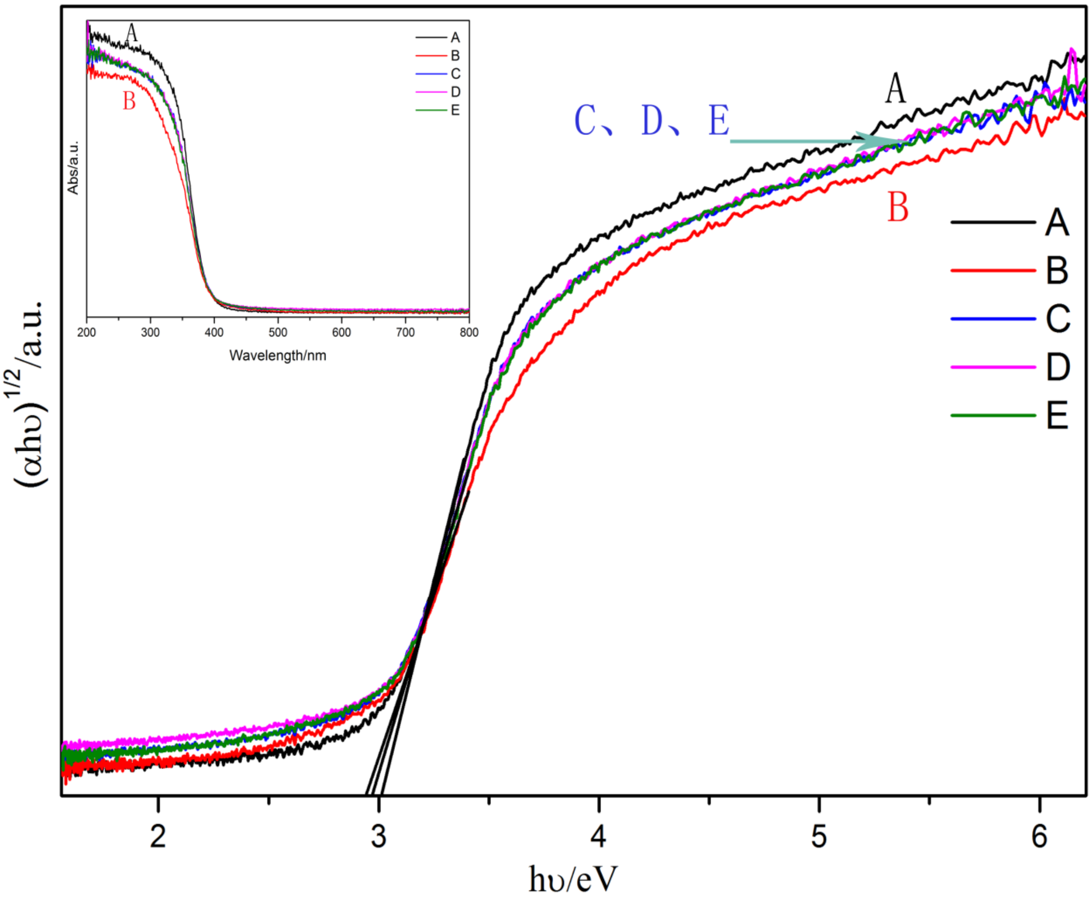

Fig. S3 UV-Vis diffuse reflectance spectra of $Bi_2O_2[BO_2(OH)]$ samples prepared with different PVP : A) 0 g, B) 0.1 g, C) 0.2 g, D) 0.3 g, E) 0.4 g.

$$E_{CB}^{0} \approx E_{CB} = \chi_{comp} - E^{e} - \frac{1}{2}E_{g} \qquad \text{(S1)}$$

$$\chi_{comp} = \sqrt[N]{\chi_1^{r}\chi_2^{s}\cdots\chi_{n-1}^{p}\chi_n^{q}} \qquad \text{(S2)}$$

$$N = r + s + \cdots + p + q \qquad \text{(S3)}$$

$$E_{g} = E_{VB} - E_{CB} \qquad \text{(S4)}$$

χ_{comp} is the absolute electronegativity of the semiconductors, which is related with the kind and number of the constituent atoms, geometric average of the absolute electronegativity of each atom and the tatal number of atoms (equation (S2) and (S3)); E^{e} is the energy of free electrons on the hydrogen scale that can be seen as a certain constant 4.5 eV. χ_{comp} is calculated to be 6.30 eV, thus the E_{CB} and E_{VB} are evaluated to be 0.32 eV and 3.28 eV, respectively.

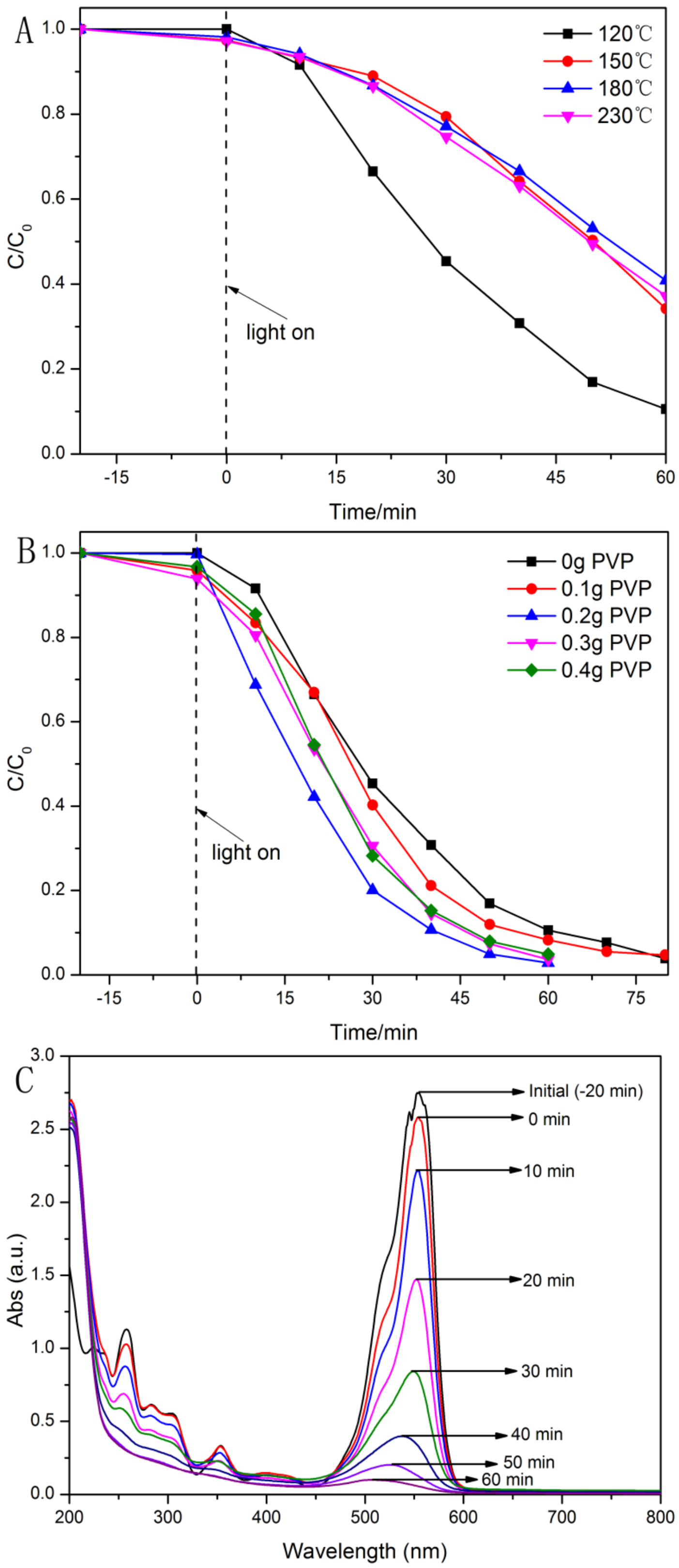

Fig. S4 A) The adsorption and photocatalytic degradation of RhB solution by different $Bi_2O_2[BO_2(OH)]$ samples (synthesized with no PVP at different temperature for 12 h) of the same weight under UV light irradiation, B) The adsorption and photocatalytic degradation of RhB solution by different $Bi_2O_2[BO_2(OH)]$ samples (synthesized with different PVP at 120 ^{0}C for 12 h) of the same weight under UV light irradiation, C) The temporal evolution of the absorption spectra of the RhB solution in the presence of $Bi_2O_2[BO_2(OH)]$ microflowers under UV light irradiation. ($C_0 = 20$ mg L^{-1}, 0.1 g $Bi_2O_2[BO_2(OH)]$)

chemical reaction equations:

$$Bi^{3+} + NO_3^- + 2OH^- \longrightarrow BiONO_3\downarrow + H_2O \qquad (S5)$$

$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+ \qquad (S6)$$

$$B(OH)_3 + 2OH^- \longrightarrow [BO_2(OH)]^{2-} + 2H_2O \qquad (S7)$$

$$2BiONO_3\downarrow + [BO_2(OH)]^{2-} \longrightarrow Bi_2O_2[BO_2(OH)]\downarrow + 2NO_3^- \qquad (S8)$$

$Bi(NO_3)_3$ can easily hydrolyze to generate $BiONO_3$ which is slightly soluble in water. To avoid the hydrolysis of Bi^{3+}, $Bi(NO_3)_3$ is initially dissolved in 1 mol/L dilute HNO_3. When the pH value is adjusted to 7 using NaOH solution, the Bi^{3+} hydrolyzes to generate $BiONO_3$, as shown in equation (S5). On the other way, H_3BO_3 is a weak monoacid whose structural formula can be written as $B(OH)_3$. When boric acid hydrolyzes, it can pillage a –OH from H_2O and form $B(OH)_4^-$. Meanwhile, the remainder H^+ combines with one H_2O molecule to form the H_3O^+. And this hydrolytic reaction is an invertible reaction, as is shown in equation (S6). At the beginning, since the existence of HNO_3, the concentration of H^+ is high so the balance moves to left side of equation (S6). After the pH value is adjusted to 7, there comes a new balance. After the reaction condition changes to high temperature and pressure, the formation of $[BO_2(OH)]^{2-}$ makes a lack of $B(OH)_3$ (equation (S7)), which makes the balance move back to left to form more $B(OH)_3$ (equation (S6)). And there also has an ion exchange process between $[BO_2(OH)]^{2-}$ and $BiONO_3$, as a result, the lower solubility products – $Bi_2O_2[BO_2(OH)]$ are formed (equation (S8)).

Table S1. Selected bond lengths of $BO_2(OH)$ pyramid in $Bi_2O_2[BO_2(OH)]$ and its atom sites

		$BO_2(OH)$ pyramid	
B – O (1)		1.37546	
B – O (2)		1.37546	
B – O (3)		1.40634	
	x	y	z
B	0.5420	0.5000	0.1140
O(1)	0.6005	0.5819	0.0107
O(2)	0.6005	0.4181	0.0107
O(3)	0.3406	0.5000	0.2139

H atom is not listed in the Table S1 because it is ignored which shows an extremely low influence in the whole $Bi_2O_2[BO_2(OH)]$ molecule.

$$n_i r_+ = n_j(R_{ij} - r_+),\ (n_i - V_i)r_- = (n_j + S_{ij})(R_{ij} - r_-) \qquad (S9)$$

$$R = r_+ + r_- \qquad (S10)$$

In equation (S9) and (S10), n_i and n_j are electron number of atom i and j, while r_+ and r_- are the positive and negative center of i-j perssad. Thus, we get R, the difference between the “centroids” of positive and negative charge.

Table S2. Bond valence sum (V_i) of $BO_2(OH)$ pyramid

		O(1)	O(2)	O(3)
B	R_{ij}	1.37546	1.37546	1.40634
	S_{ij}	0.98802	0.98802	0.90891
$V_j=\Sigma_j S_{ij}$			2.88495	

Table S3. Dipole moment calculation for the $BO_2(OH)$ pyramid and the total value in unit cell of $Bi_2O_2[BO_2(OH)]$

	μx	μy	μz
BO(1)	0.60521	0.84729	-1.06868
BO(2)	0.60521	-0.84729	-1.06868
BO(3)	-2.05422	0	1.01793
$\sum\boldsymbol{\mu}$	-0.84380	0	-1.11943

$\sum\boldsymbol{\mu}_{\mathbf{cell}} = 3\sum\boldsymbol{\mu} = (-2.53140, 0, -3.35829)$

$$\left|\sum\mu_{cell}\right| = \sqrt{\mu x_{cell}^{2} + \mu y_{cell}^{2} - 2\mu x_{cell}\mu y_{cell}\cos(\beta - 90)} = 2.40573$$

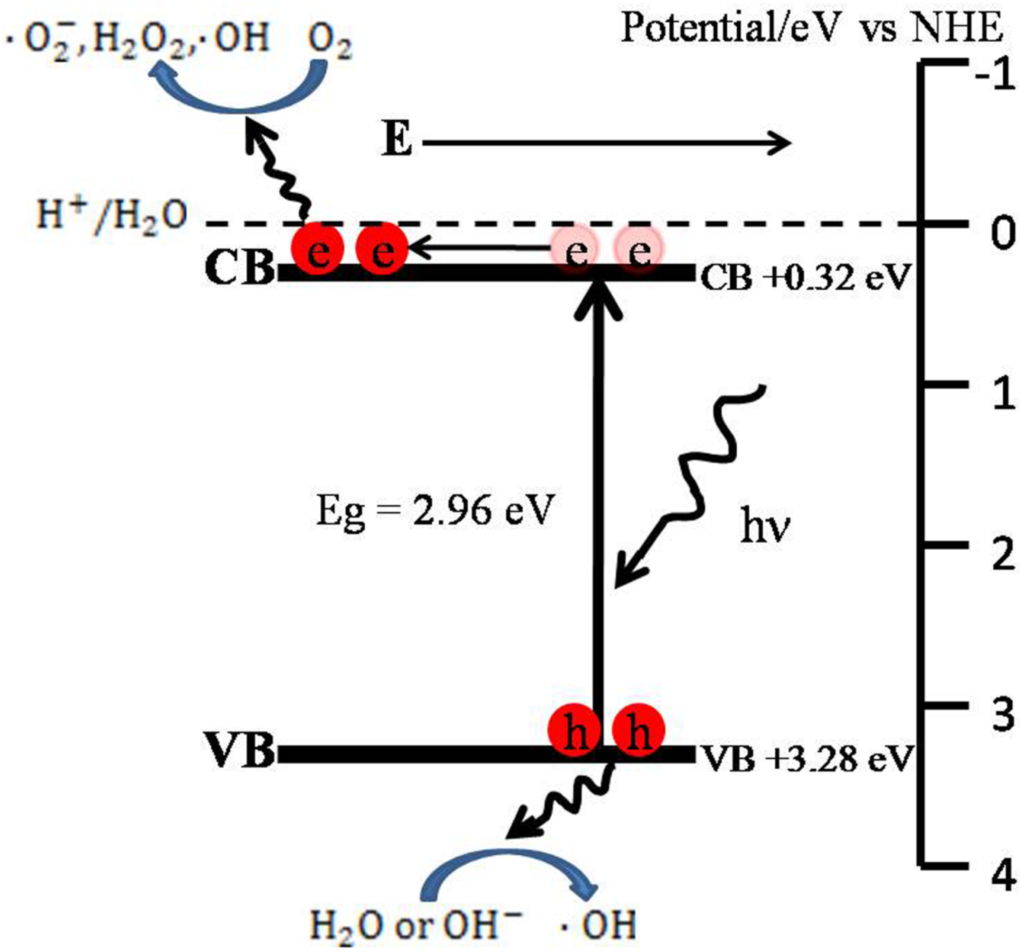

Fig. S5 A schematic diagram showing the band structure and how e – h pairs are separated and consumed in its internal polar field.