Supporting Information

Investigation on kinetic and mechanism of Z-scheme Ag$_3$PO$_4$/ WO$_3$ p-n junction photocatalyst with enhanced removal efficiency of RhB

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Tel.: +86-371-67766660 (Office)
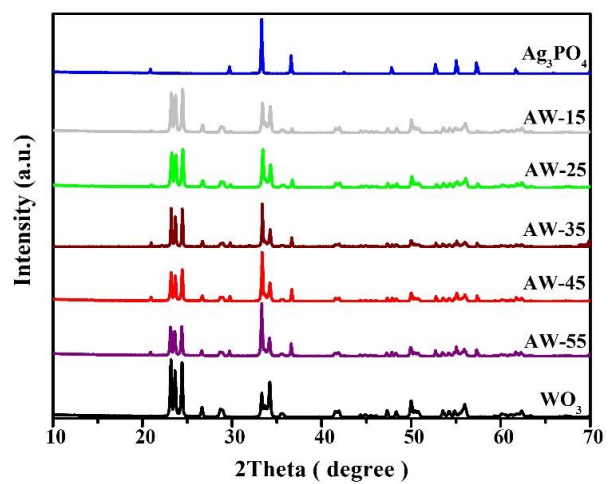
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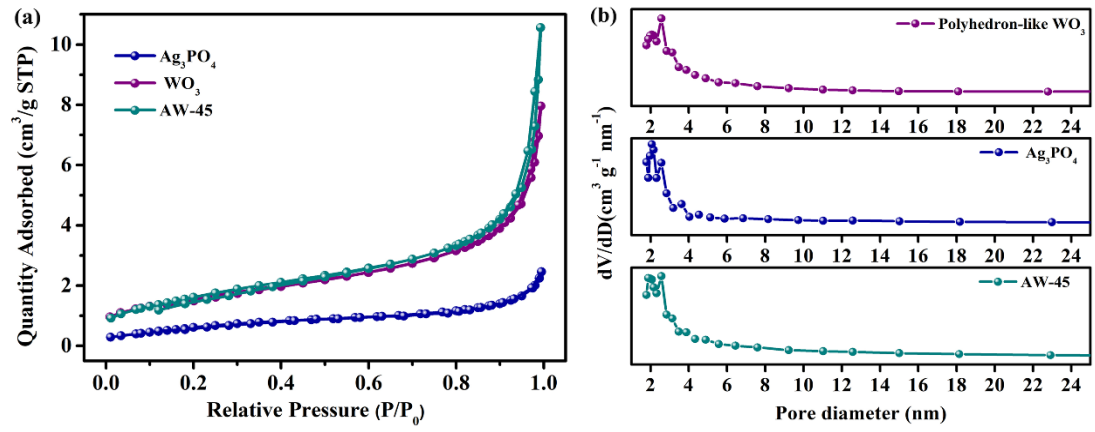**Figure S1.** XRD patterns of as-prepared WO_3, Ag_3PO_4, AW-15, AW-25, AW-35, AW-45 and AW-55.

Figure S2. (a) N_2 adsorption-desorption isotherm of Ag_3PO_4, WO_3, AW-45 at 77K, (b) the pore size distribution of the prepared samples, respectively.

Table. S1. BET surface areas, pore diameter and pore volumes of the as-prepared samples.

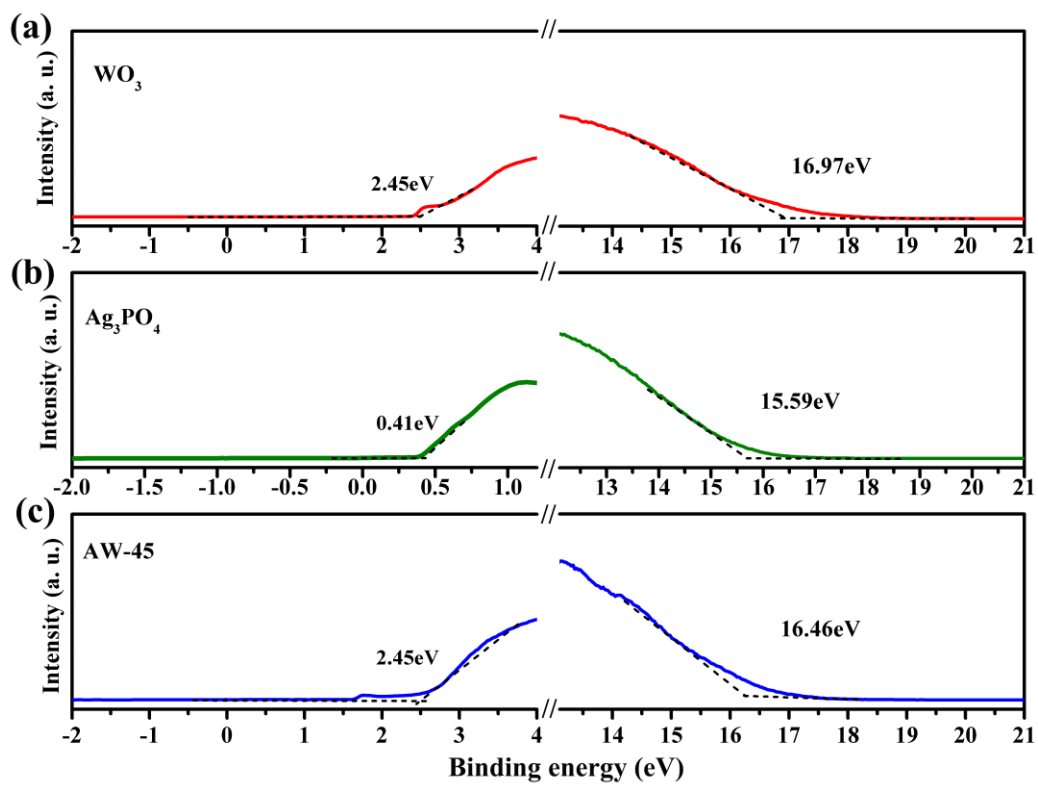| Photocatalysts	$S_{BET}(m^2g^{-1})$	Pore diameter (nm)	Pore volume $(cm^3\ g^{-1})$
WO$_3$	2.4734	22.2494	0.0137
Ag$_3$PO$_4$	2.4543	5.3808	0.0038
AW-15	1.0342	23.645	0.0061
AW-25	1.9529	15.8934	0.0077
AW-35	1.7432	15.7520	0.0055
AW-45	1.9458	19.6769	0.0093
AW-55	2.0271	21.1797	0.0107

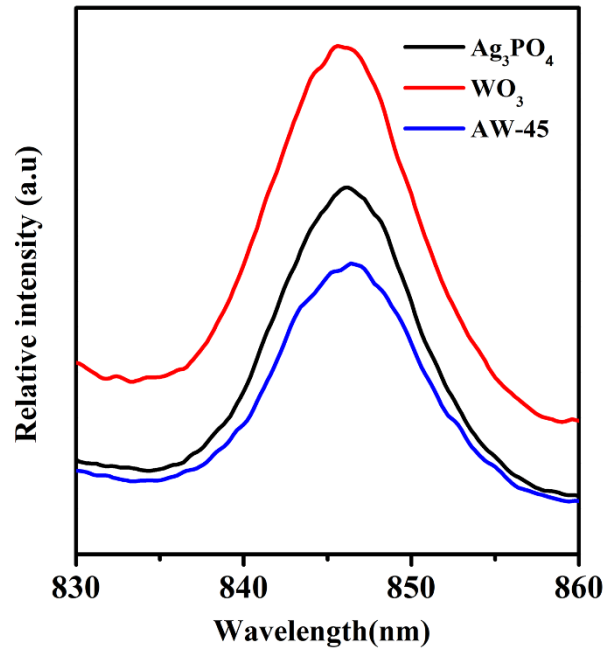Figure S3. Ultraviolet photoelectron spectrum as well as linear intersection for (a) WO_3, (b) Ag_3PO_4, and (c) AW-45.

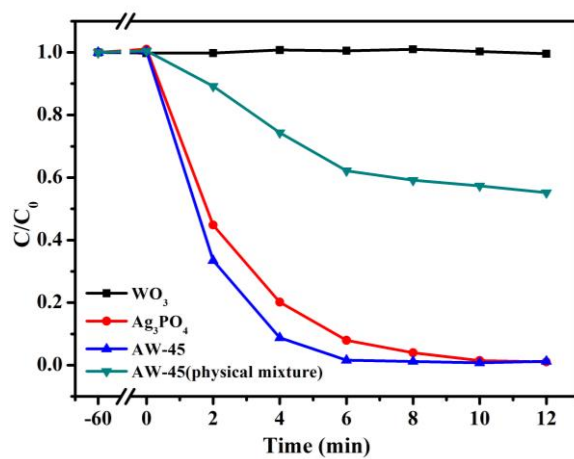**Figure S4.** PL spectra of Ag_3PO_4, WO_3, and **AW-45**.

Figure S5. The photocatalytic activity of spherical Ag_3PO_4, WO_3, AW-45 and AW-45 (physical mixture) samples on RhB (30 ppm) degradation under visible-light irradiation.
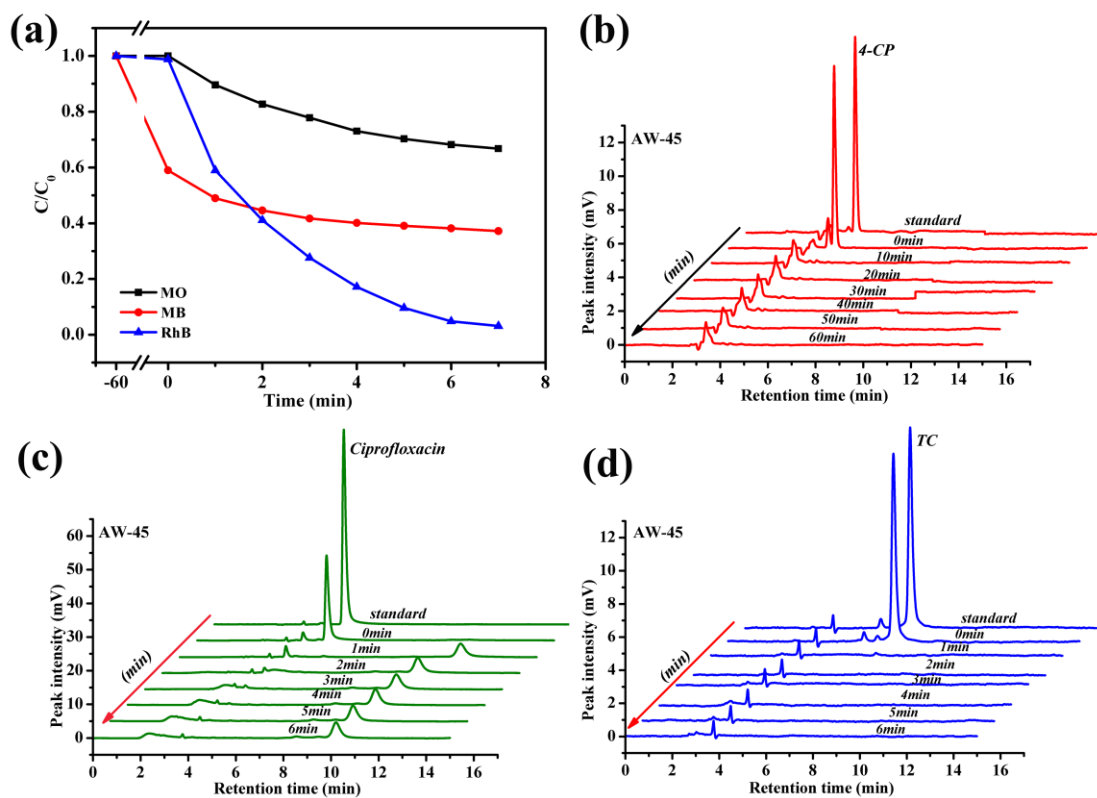
Figure S6. (a) The photocatalytic activities of AW-45 sample for the degradation of, MO, MB and RhB (30 ppm) (b, c, d) The comparison of HPLC degradation profiles of 4-CP(4-chlorophenol), Ciprofloxacin and TC (tetracycline) in visible-light irradiation.
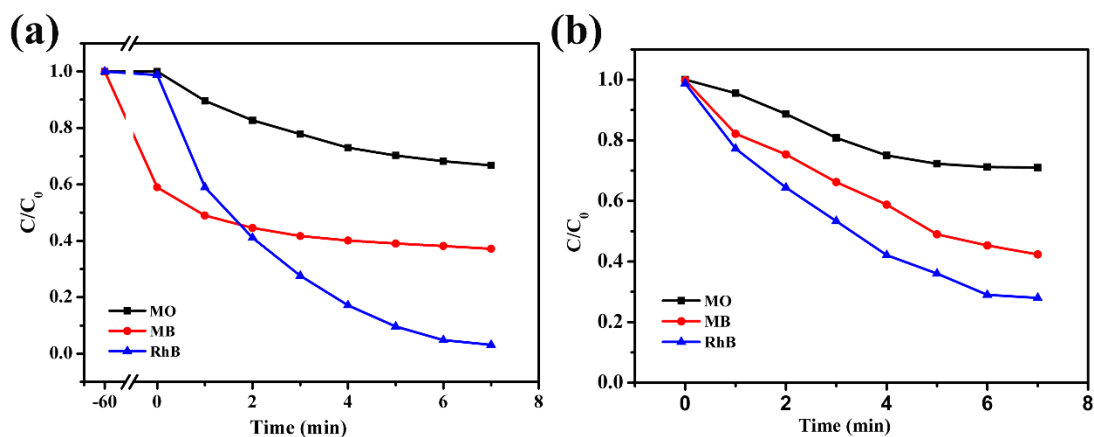
Fig. S7 (a) Adsorption and photocatalytic activity of AW-45 for MO, MB and RhB (30 ppm). (b) The photocatalytic activities of AW-45 for 30 ppm RhB degradation under visible-light irradiation;

Fig. S7 shows that after 60 min of magnetic stirring in darkness, the AW-45 can adsorb MO (2.8%), MB (42%) and RhB (3.6%), respectively. Under visible-light irradiation, MO, MB and RhB were degraded approximately 44%, 63% and 99% after 7 min irradiation, respectively. However, Fig. S7b shows that both MO, MB and RhB were degraded approximately 30%, 55% and 70% after 7 min irradiation, respectively, without absorption-desorption equilibrium experiments, the catalytic activity in Fig. S7b is lower Fig. S7a. The reason for the above results may be that there is no insufficient contact between the substrate and the catalysts without absorption-desorption equilibrium experiments.
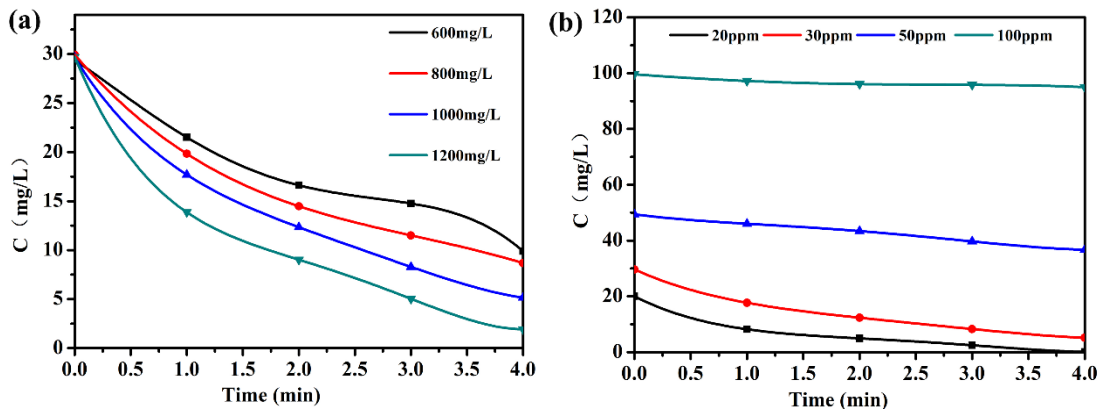
Figure S8. (a) RhB concentration curves at different times with the same initial catalyst concentration of and different RhB concentration. (b) RhB degradation concentration curve at different time with the same initial concentration of RhB and different catalyst concentration.
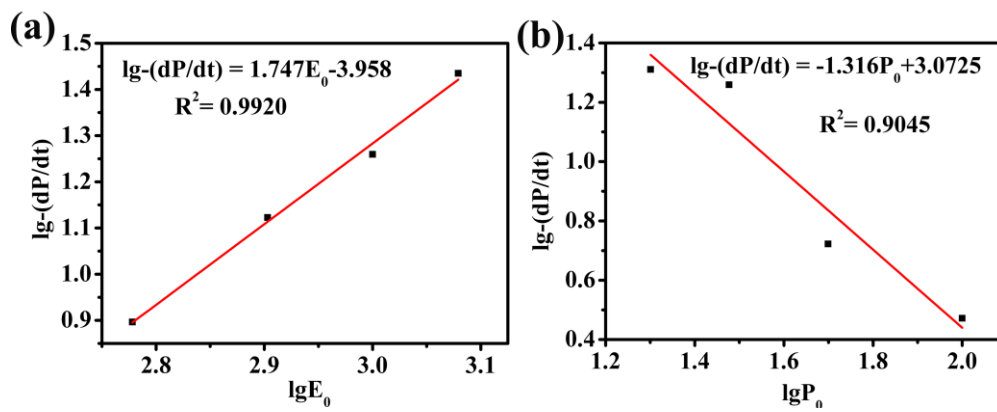

Figure. S9 (a) Plots of lg (-dP/dt) versus $\lg E_0$. (b) Plots of lg (-dP/dt) versus $\lg P_0$.

Table. S2. The corresponding equations are obtained by fitting the four curves in the figure S1a respectively with the method of arbitrary approximation of higher-order polynomials, from top to bottom:

Concentration	Equation
600mg/L	$P_1 = -0.252t^4 + 1.518t^3 - 1.286t^2 - 7.877t + 29.412$
800mg/L	$P_2 = 0.005t^4 - 0.421t^3 + 3.593t^2 - 13.264t + 29.927$
1000mg/L	$P_3 = 0.201t^4 - 2.081t^3 + 8.118t^2 - 18.173t + 29.634$
1200mg/L	$P_4 = 0.422t^4 - 4.218t^3 + 15.192t^2 - 27.226t + 29.698$

The derivative of the above equations at time t is as follows:

$$\left(\frac{dP_1}{dt}\right)\bigg|_{t=0} = -7.877$$

$$\left(\frac{dP_2}{dt}\right)\bigg|_{t=0} = -13.264$$

$$\left(\frac{dP_3}{dt}\right)\bigg|_{t=0} = -18.173$$

$$\left(\frac{dP_4}{dt}\right)\bigg|_{t=0} = -27.226$$

Table. S3 The initial reaction rates corresponding to different initial concentrations of RhB.

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The initial concentration of catalyst:E_0	600mg/L	800mg/L	1000mg/L	1200mg/L
LgE_0	2.778	2.903	3	3.079
$-(\dfrac{dP}{dt})$	7.877	13.264	18.173	27.226
$lg-(\dfrac{dP}{dt})$	0.896	1.123	1.259	1.435

The common logarithm is taken to obtain a set of related data of lg-(dP/dt) and E_0, so we can get a linear correlation graph **Figure S9.a**

Table. S4. The corresponding equations are obtained by fitting the four curves in the figure S1b respectively with the method of arbitrary approximation of higher-order polynomials, from bottom to top:

Concentration	Equation
20ppm	$P_1=0.297t^4-3.079t^3+11.437t^2-20.464t+20.00$
30ppm	$P_2=0.211t^4-2.081t^3+8.118t^2-18.172t+29.643$
50ppm	$P_3=0.151t^4-1.221t^3+2.592t^2-2.276t+49.409$
100ppm	$P_4=-0.037t^4+0.146t^3+0.463t^2-2.963t+99.599$

The derivative of the above equations at time t is as follows:

$$\left(\frac{dP_1}{dt}\right)\bigg|_{t=0} = -20.464$$

$$\left(\frac{dP_2}{dt}\right)\bigg|_{t=0} = -18.172$$

$$\left(\frac{dP_3}{dt}\right)\bigg|_{t=0} = -5.276$$

$$\left(\frac{dP_4}{dt}\right)\bigg|_{t=0} = -2.963$$

Table. S5 The initial reaction rates corresponding to different initial concentrations of RhB.

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The initial concentration of RhB:P_0	20ppm	30ppm	50ppm	100ppm
lgP_0	1.301	1.477	1.699	2
$-(\dfrac{dP}{dt})$	20.464	18.172	5.276	2.963
$lg - (\dfrac{dP}{dt})$	1.311	1.259	0.722	0.472

The common logarithm is taken to obtain a set of related data of lg-(dP/dt) and E_0, so we can get a linear correlation graph **Figure S9.b**
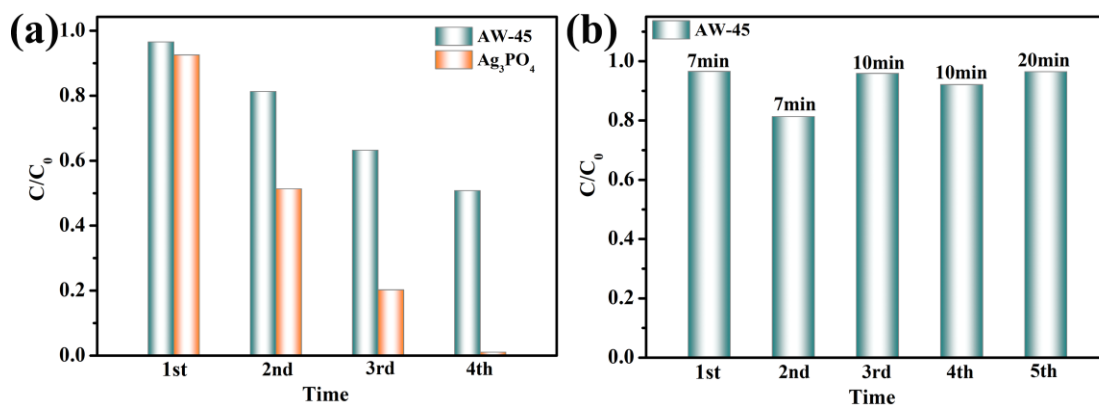
Figure. S10. (a) Cycling runs in photocatalytic degradation of RhB in the presence of AW-45 and Ag₃PO₄; (b) Cycling runs of the AW-45 sample for RhB degradation under different visible-light irradiation time;

Photo-corrosion is a common problem in silver phosphate materials. However, considering the practical application problem, the cycle experiment was re-ran and the exposure time was extended. It can be found that although the circulation capacity of **AW-45** is not ideal, it has slowed down the photo-corrosion of the catalyst to some extent compared to pure silver-based catalysts (Figure. S10a). When the irradiation time was extended to 10 minutes in the third and fourth cycles, it can be seen that the RhB could be degraded about 95% (Figure.S10b). After the sixth extension to 20 minutes, it can still exhibit superior degradation properties (Figure.S10b).
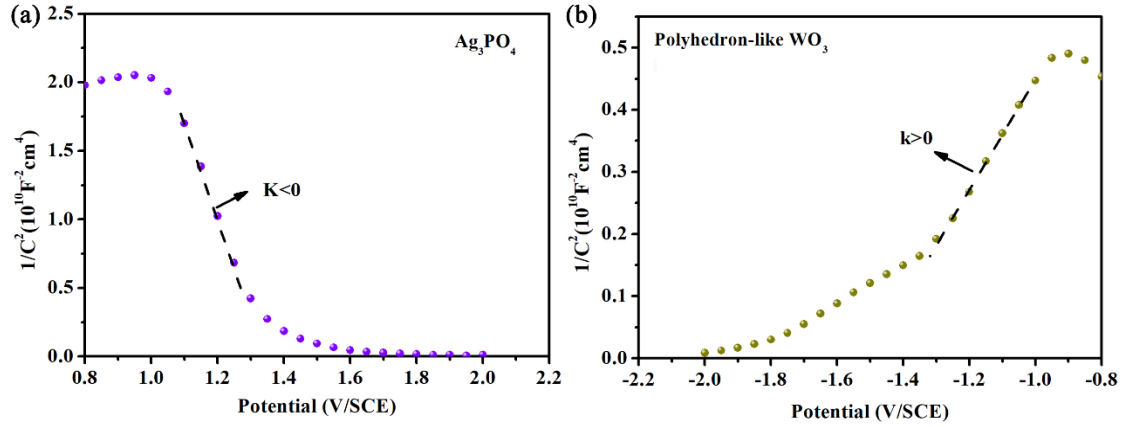
Fig. S11. Mott-Schottky cures of (a) Ag$_3$PO$_4$ and (b) WO$_3$

We have mentioned that Ag$_3$PO$_4$ material is always a p-type semiconductor [53, 54], and WO$_3$ material is most likely to be an n-type semiconductor [55, 56] in the chapter of introduction. Therefore, considering the particularity of as-obtained samples, we have also performed Mott-Schotty (M-S) methods to further detect the inherent electronic properties of pristine Ag$_3$PO$_4$ and WO$_3$. As shown in Fig. S6, the slope of $1/C^2$ vs potential curves (SCE) over Ag$_3$PO$_4$ material is negative, and that of WO$_3$ sample is positive. As is known to all, in Mott-Schottky test, the positive and negative slope represents p-type and n-type semiconductors, respectively [51]. Herein, by analyzing the results above, we have gained the ample evidences to verify that Ag$_3$PO$_4$ material is a p-type semiconductor, WO$_3$ is an n-type semiconductor, while the two type semiconductors combined with each other, there will be a p-n junction between the surfaces of two type semiconductors.
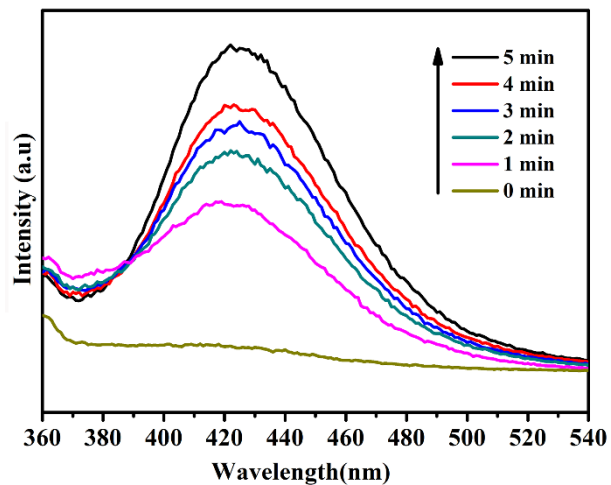
Figure. S12. •OH trapping FL spectral changes over AW-45 sample in a basic terephthalic acid solution (excitation wavelength is 315 nm) with different irradiation time.

Table. S6. Comparison of WO_3/ Ag_3PO_4 p-n junction photocatalyst degradation towards organic pollutants (RhB) under visible light. $C_{catalyst}$ is the concentration of photocatalyst in solution, while $C_{pollutants}$ is the concentration of photocatalyst in solution.

Photocatalysts	$C_{catalyst}$(mg/mL)	$C_{pollutants}$ (ppm)	Reaction Time (mins)	K_{app}	Refer
WO_3/Ag_3PO_4 p-n junction strcture	1	30	7	0.49439	This work
Ag_3PO_4/Ag/WO_{3-x} composite	1	10	3	Not given	[66]
Ag_3PO_4/Ag	1	20	40	Not given	[67]
Ag_3PO_4/Bi_2WO_6 nanocomposites	1	4.79	80	0.0595	[68]
CdS/WO_3	0.4	5	120	Not given	[69]
3DOM-WO_3/ Pt coated by mono-or few-layered WS_2	0.5	30	30	0.156	[70]
Heterojunction AgI/WO_3 Nanocomposite	0.5	10	21(98%)	Not given	[71]