Supporting Information

BiVO₄ quantum dots decorated BiPO₄ nanorods 0 D/1 D

heterojunction for enhanced Visible-Light-Driven photocatalysis Boyuan Li^{a†}, Zhenhua Cao^{b†}, Shixuan Wang^a, Qiang Wei^a*, Zhurui Shen*^a

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Fig. S1 (a) peak positions of the (101) (011) plane in the range of $\theta = 15.0-20.0^{\circ}$. (b) peak positions of the (120) plane in the range of $\theta = 28.0-30.0^{\circ}$.

With the increase of BiVO₄, it reached the most preferential crystallorgraphic orientation along the (101) direction. This was probably caused by the selective adsorption of Bi³⁺ on certain facet of BiPO₄. In addition to the preferential crystallographic orientation, a careful comparison of the (011) and (120) showed that the peak position of BiPO₄ with different BiVO₄ contents shifted slightly toward a lower 2-Theta (degree) value. According to Bragg' s Law: $n\lambda$ =2dsin θ , where d is the distance between crystal planes of (h k l), λ is the X-ray wavelength, and θ is the diffraction angle of the crystal plane (h k l). The decrease of 2 θ in BiPO₄ should result from the increase in lattice parameters (d (011) and (120) value), verifying that BiVO₄

has been successfully embedded into BiPO₄ and bonded with BiPO₄. The result could also be confirmed by FT-IR, XPS and TEM.



Fig. S2. SEM images of samples. (a) $BiPO_4$; (b) 3 wt% $BiVO_4/BiPO_4$; (c) 20 wt% $BiVO_4/BiPO_4$; (d) 30 wt% $BiVO_4/BiPO_4$.

The 3 wt% $BiVO_4/BiPO_4$ has almost no particles because the mass ratio of $BiVO_4$ is too low to find (Fig. S2 (b)). The amount of particles is apparently increased with $BiVO_4$ added.



Fig. S3 HRTEM images of (a) 3 wt% BiVO₄/BiPO₄, (c) 20 wt% BiVO₄/BiPO₄, (e) 30 wt% BiVO₄/BiPO₄ and (g) 50 wt% BiVO₄/BiPO₄. EDAX spectrum of (b) 3 wt% BiVO₄/BiPO₄, (d) 20 wt% BiVO₄/BiPO₄, (f) 30 wt% BiVO₄/BiPO₄ and (h) 50 wt% BiVO₄/BiPO₄.

In terms of BiVO₄ combined with BiPO₄ to form nanocomposite, the HRTEM and EDAX of 3 wt% BiVO₄/BiPO₄, 20 wt% BiVO₄/BiPO₄, 30 wt% BiVO₄/BiPO₄ and 50 wt% BiVO₄/BiPO₄ have been shown in Fig. S3. BiVO₄ formed quantum dots, dispersed on the surface of BiPO₄. From the Fig. S3a, c, e, g, it can be seen that a well interfacial contact between BiVO₄ and BiPO₄. The lattice fringes of the marked

particles can be assigned to the (112) (Fig. S1a), (114) (Fig. S1c), (112) (Fig. S1e) and (114) (101) (Fig. S1g) facets of BiVO₄. The heterojunction has well formed between BiVO₄ and BiPO₄. With the mass ratio of BiVO₄ increasing, the QDs on the surface of BiPO₄ have also been added. The EDAX shows the elements of Bi, P, V, O, indicating that the composite consisted of BiPO₄ and BiVO₄. From EDAX analysis, the mass ratio of V/P was approximately in correspondence with 3 wt%, 20wt% 30 wt% and 50 wt% (Fig. S3b, d, f, h). The results above proved that BiVO₄ formed a kind of nanocomposite with BiPO₄ rather than being present as a separate.



Fig. S4 Photo-degradation of Rh B of (a) 3 wt% BiVO₄/BiPO₄ by sonochemistry process and by mechanical mixture; (b) 20 wt% BiVO₄/BiPO₄ by sonochemistry process and by mechanical mixture; (c) 30 wt% BiVO₄/BiPO₄ by sonochemistry process and by mechanical mixture; (d) 50 wt% BiVO₄/BiPO₄ by sonochemistry process and by mechanical mixture; d) 50 wt% BiVO₄/BiPO₄ by sonochemistry process and by mechanical mixture.

In the meantime, the performance of four composites prepared by sonochemistry process was compared with those by mechanical mixture (Fig. S4). We tested the photocatalytic activity of 3 wt% BiVO₄/BiPO₄ prepared by sonochemistry process and mechanical mixture, showing 17 % and 3.6 % degradation, respectively. The degradation of 20 wt% BiVO₄/BiPO₄, 30 wt% BiVO₄/BiPO₄ and 50 wt% BiVO₄/BiPO₄ was 3.8 %, 4.2 % and 5.3 %, respectively. The composites prepared by mechanical mixture almost showed the same degradation efficiency with pristine BiVO₄ (6 %). With BiVO₄ added, the degradation efficiency increased slightly from 3.6 % to 5. 3%, because BiPO₄ couldn't be excited under visible light. Therefore, BiVO₄ is present in the nanocomposite.



Fig. S5 HRTEM images of 50 wt% BiVO₄/BiPO₄ (a) before and (b) after sonochemical process.

As shown in Fig. S5, the heterojunction of $BiVO_4$ QDs/BiPO_4 nanorods before and after sonochemical process have similar morphology at low magnification. However, the HRTEM images show that the $BiVO_4$ QDs before sonication are amorphous, while the ones after sonication are crystalline. This result indicates that the sonochemical process promotes the crystallization of $BiVO_4$ QDs.

Samples	k(min ⁻¹)
BiVO ₄	0.000555
BiPO ₄	0.000417
3 wt% Com.	0.00181
20 wt% Com.	0.00217
30 wt% Com.	0.00346
50 wt% Com.	0.00217
Dark Control	0.0000927
Light Control	0.0000972

Table S1 k=-ln(C/C₀) of photocatalyst



Fig. S6 FT-IR spectra of 30 wt% BiVO₄/BiPO₄ photocatalyst before and after the photodegradation test.

In the Fig. S6, 1589 cm⁻¹, 1340 cm⁻¹, 1180 cm⁻¹ and 1079 cm⁻¹ represent the stretching vibrational peaks of the benzene ring molecular framework in Rh B molecules, which are the C-CH₃ symmetry bending vibration peak and the stretching vibration of the ether linkage bond C-O-C before degrading Rh B. It is clearly seen that there is only the stretching vibrational peak of 1630 cm⁻¹, indicating –OH is left in the solution which means there is no organic substance after degradation. The result of FT-IR consistent with TOC verifies again that 30 wt% BiVO₄/BiPO₄ has a wonderful mineralization process during the photodegradation.



Fig. S7 Specific surface area of BiPO₄ and 30 wt% BiVO₄/BiPO₄.

The specific surface area of 30 wt% $BiVO_4/BiPO_4$ is virtually almost the same as that of pure $BiPO_4$ (4.8 m² g⁻¹ for pure $BiPO_4$ and 10.2 m² g⁻¹ for 30 wt% $BiVO_4/BiPO_4$, Fig. S7). The inner left side of the Figure S3 is the pure $BiPO_4$ powder and the right one is the 30 wt% $BiVO_4/BiPO_4$.



Fig. S8 N₂ adsorption-desorption isotherms of BiPO₄ and 30 wt% BiVO₄/BiPO₄.

The N_2 adsorption-desorption isotherms of 30 wt% BiVO₄/BiPO₄ shows definitely higher quantity adsorb than pure BiPO₄ does, which means mesoporous increase after adding BiVO₄. However, none of the two curves are closed so that the composites are not composed of mesoporous at all.

Samples	R _s (ohm)	R _{ct} (ohm)	$C_{ct}(10^{-4})$
BiPO ₄	10.480	2713	1.433
BiVO ₄	9.335	2202	1.384
BiVO ₄ /BiPO ₄	10.150	1339	1.918

Table S2 The fitting parameters of the Randles equivalent circuit



Fig. S9 Mott-Schottky plot of BiVO₄.