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Supporting Information

Direct Utilization of Air and Water as Feedstock in Photo-Driven

Nitrogen Reduction Reaction over Ternary Z-scheme

SiW₉Co₃/PDA/BWO Hetero-junction

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Experiment

Preparation of BWO microsphere.

All the chemicals in analytical grade were purchased without further treatment. The nanosheet-assembled BWO microspheres were prepared via hydrothermal process.¹ Typically, $Bi(NO_3)_3 \cdot 5H_2O$ (4.0 mmol) was first dissolved in of nitric solution (5 ml, 4.0 mol·L⁻¹), and Na₂WO₄·2H₂O solution (40 mL, 0.05 mol·L⁻¹) was introduced dropwise under vigorous stirring for 1 h at room temperature. Thereafter, the resulting precursor suspension was transferred into a 100 mL Teflon-lined autoclave and maintained at 190°C for 2 h hydrothermally. After cooling down, the light-green precipitate was filtrated, collected, washed by deionized water (DI H₂O) and absolute EtOH for several times, and finally dried under vacuum at 70°C for 6 h.

Preparation of SiW₉Co₃/PDA/BWO, PDA/BWO, SiW₉Co₃/BWO and SiW₉Co₃/PDA

 $K_6H_4[\alpha$ -SiW₉O₃₇Co₃(H₂O)₃]·17H₂O (SiW₉Co₃) was prepared according to literature.² Then, BWO (1.0 g) and SiW₉Co₃ (0.25 g) were dispersed in Tris-HCl buffer solution (100 mL, pH = 8.5) and treated by ultrasonic for 0.5 h. After adding dopamine hydrochloride (5.0 mg), the suspension was further stirred for 2.5 h at room temperature. The light grey precipitate was filtered, collected, washed by DI H₂O and EtOH several times, and dried under vacuum at 70°C for 5 h. The prepared sample were recorded as SiW₉Co₃/PDA/BWO. By changing the amount of BWO, dopamine hydrochloride and SiW₉Co₃, a series of samples with different proportions were prepared. For comparison, PDA/BWO, PDA/SiW₉Co₃ and SiW₉Co₃/BWO samples were also prepared by the similar method. Then, SiW₉Co₃-PDA-BWO-Mix was achieved by mechanical mixing SiW₉Co₃, PDA and BWO.

To prepare PDA/BWO composite, BWO (1.0 g) was dispersed in Tris-HCl buffer solution (100 mL, pH = 8.5) and treated by ultrasonic for 0.5 h. After adding dopamine hydrochloride (5.0 mg), the suspension was further stirred for 2.5 h at room temperature. The precipitate was filtered, collected, washed by DI H₂O and EtOH several times, and dried under vacuum at 70°C for 5 h. Then, the binary samples with

different PDA loading were achieved as well by changing the amount of dopamine hydrochloride.

In producing PDA/SiW₉Co₃ composite, SiW₉Co₃ (0.25 g) was dispersed in Tris-HCl buffer solution (100 mL, pH = 8.5) and treated by ultrasonic for 0.5 h. After adding dopamine hydrochloride (5.0 mg), the suspension was further stirred for 2.5 h at room temperature. The precipitate was filtered, collected, washed by DI H₂O and EtOH several times, and dried under vacuum at 70°C for 5 h.

When preparing SiW₉Co₃/BWO composite, BWO (1.0 g) and SiW₉Co₃ (0.25 g) were dispersed in Tris-HCl buffer solution (100 mL, pH = 8.5) and treated by ultrasonic for 0.5 h, and the suspension was further stirred for 2.5 h at room temperature. The precipitate was filtered, collected, washed by DI H₂O and EtOH several times, and dried under vacuum at 70°C for 5 h.

Characterization.

FT-IR spectra were recorded on a Bruker Tensor 27 spectrophotometer using KBr pellets in the range of 400-4000 cm⁻¹. The morphologies of these composites were characterized on a Hitachi SU-8010 SEM coupled with an energy-dispersive X-ray (EDX) spectrometer. Transmission electron microscopy (TEM) was performed on a JEM 2100F microscope operated at 200 kV. Powder X-Ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE, using Cu Ka radiation $(\lambda = 1.54056 \text{ Å})$. X-ray photoelectron spectrum (XPS) analyses were carried out on an PHI5000 Versa Probe III spectrometer with an Al-Kα (1486.6 eV) achromatic X-ray source. The UV-vis diffuse reflectance spectra (UV-vis-DRS) were obtained on a Shimadzu UV-3600Plus spectrophotometer using BaSO₄ as a reflectance standard. Room-temperature photoluminescence spectra (PL) and time-resolved photoluminescence spectra (time-resolved PL) were detected on an Edinburgh instruments Ltd. FLSP920 fluorescence spectrometer. The physical N2 adsorptiondesorption isotherms were recorded on Tristar 3020, and the surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation. Nitrogen temperatureprogrammed desorption (N₂-TPD) was conducted on a Micromeritics AutoChem II 2920 instrument. Electron paramagnetic resonance (EPR) spectroscopy was carried

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out using a Bruker A300. EPR spin-trapping experiments were performed on a Bruker E500-9.5/12 spectrometer under simulated sunlight irradiation. In a typical experiment, 20 mg of photocatalyst was dispersed in 5 mL of ultrapure water/methyl alcohol under ultrasonic for 30 min. Then, 10 μ L of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was added with ultrasonic dispersion for another 5 min. The sample was loaded in a capillary tube and further placed into a quartz nuclear magnetic tube before subjecting to EPR test. CHN elemental analyses were performed on a VarioEL III elemental analyzer. ICP-MS measurements were carried out on Thermo XSeries II.

Electrochemical analysis.

Electrochemical impedance spectra (EIS) and time-resolved photo-current behaviors were performed on an electrochemical workstation (CHI660E) using a standard threeelectrode configuration in 0.1 M Na₂SO₄ as electrolyte. Working electrode was prepared by spin-coating catalyst (20 mg) on ITO conductive glass (1 × 2 cm²). Pt slice and saturated calomel electrode (SCE, $E_{SHE} = E_{SCE} + 0.241$ V) were employed as counter electrode and reference electrode, respectively. To investigate their photocurrent behaviors, a 300W Xe lamp (PLS-SXE300D) with current of 13 A was employed as the light source (400 mW·cm⁻²).

Photo-driven nitrogen reduction reaction.

The photo-driven nitrogen reduction reaction was carried out under nitrogen atmosphere at room temperature and ambient pressure. Typically, 150 mg of sample was dispersed in 150 mL of ultrapure water in a quartz reactor (PQ 256). Initially, the suspension was stirred vigorously without illumination and bubbled with pure nitrogen (99.999%, 100 mL·min⁻¹) for 30 min. Afterwards, the suspension was irradiated by an Xe lamp (PLS-SXE300D) equipped with a wavelength cutoff filter (λ < 420 nm) at the intensity of 400 mW·cm⁻². Using similar protocol, Air was employed as feedstock instead of pure nitrogen. Then, simulated sunlight was employed irradiation source as well without using cutoff filter.

NH_3/NH_4^+ concentration analysis and determination of NH_3/NH_4^+ and ${}^{15}N_2$ isotope labeling experiment

The concentrations of ammonia were determined by spectrophotometry using

Nessler's reagent as color developer.³ During irradiation, reaction suspension (10 mL) was collected by a syringe every 30 minutes, and catalyst was removed by centrifugation. Then, clear reaction solution (5 mL) was transferred into the colorimetric tube followed by adding potassium sodium tartrate (KNaC₄H₄O₆, 0.1 mL, 0.5 g·mL⁻¹) and Nessler's reagent (0.1 mL). After color development for 10 minutes, the spectrum was recorded on SP-756P UV-Vis spectrometer. The concentration of NH₃/NH₄⁺ was calculated according to the absorbance at 420 nm. The calibration curve was obtained using NH₄Cl standard solutions with concentration of 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 mg·L⁻¹. Then, isotope labeling experiments were performed to clarify the source of NH₃/NH₄⁺ using ¹⁵N₂ as feeding gas, and solution NMR ¹H spectra and ¹⁵N spectra were recorded on JEOL JNM-ECZ400S. For comparison, ¹⁴N₂ (majority) and ¹⁵N₂ (minority) mixture was employed as feedstock. To determine the product of photo-driven nitrogen reduction using air and water as feedstock, ion-chromatography was carried out on a SHINE CIC-D120.



Scheme S1. Schematic illustration for separation of photo-generation electron-hole pairs in four different types of heterojunction: (a) Type-II, (b) Type-II, (c) Type-III and (d) Z-scheme heterojunction. CB and VB stand for the conduction band and valence band, respectively

(b) Semiconductor A Semiconductor B



Fig. S1 SEM morphologies for (a) BWO, (b) PDA/BWO, (c) SiW₉Co₃/BWO and ternary (d) SiW₉Co₃/PDA/BWO composite, respectively



Fig. S2 (a) HR-TEM image, (b) TEM image, (c) EDX spectrum and (d) SAED pattern of SiW₉Co₃/PDA/BWO microsphere, and (e) EDX-Mapping for elements Bi, W, O, Si, Co, C and N

Element \ Loading of PDA	0.0625	0.125	0.25	0.5	1.0	2.0
C/wt%	0.616	0.772	0.706	0.717	1.292	1.107
N/wt%	0.129	0.104	0.118	.8 0.157 0.197		0.193
Element \ Loading of SiW9C03	6.25	12.5	25	25 3		50
C/wt%	0.795	0.776	0.694		0.757	0.738
N/wt%	0.150	0.142	0.143		0.139	0.143
Co(theoretical)/ wt%	0.450(0.450)	0.818(0.817)	1.434(1.439	9) 1.860(1.962)		2.400(2.498)

Table S1 C and N fractions in PDA/BWO samples with different PDA loadings, as well as C, N and Co fraction of SiW₉Co₃/PDA/BWO samples with different SiW₉Co₃ loadings



Fig. S3 Nitrogen adsorption-desorption isotherms of BWO and ternary SiW₉Co₃/PDA/BWO composite

Sample	BET Surface Area (m ² ·g ⁻¹)
BWO	34.5
SiW ₉ Co ₃ /PDA/BWO	29.4

Table S2 BET surface area (S_{BET}) of BWO and SiW₉Co₃/PDA/BWO



Fig. S4 FT-IR spectra of PDA, SiW₉Co₃, SiW₉Co₃/PDA/BWO and SiW₉Co₃-PDA-BWO-Mix



Fig. S5 High-resolution XPS spectra of Bi4*f* for BWO, PDA/BWO, SiW₉Co₃/PDA/BWO and SiW₉Co₃-PDA-BWO-Mix



Fig. S6 High-resolution XPS spectra of W4*f* for (a) BWO and PDA/BWO as well as (b) SiW₉Co₃ and SiW₉Co₃/PDA

In Fig. S6a, the W4*f* peaks for PDA/BWO shifted negatively when comparing with pristine BWO, which is an indication of strong interaction between PDA and BWO. This is in line with Bi4*f* outcomes. After deconvolution, both W(VI) and W(V) is obtained for PDA/BWO sample, with binding energies of 37.65 (W4*f*_{5/2}) and 35.50 eV (W4*f*_{5/2}) as well as 37.20 (W4*f*_{5/2}) and 35.20 eV (W4*f*_{5/2}), respectively. The obtained W(V) species are an indication of forming oxygen vacancies derived by polymerization of dopamine. Then, strong interaction between PDA and SiW₉Co₃ is as well observed in Fig. S6b, since negative shift (ca. -0.05 eV) of W4*f* binding energy is observed in SiW₉Co₃/PDA sample.



Fig. S7 High-resolution XPS spectra of N1*s* for SiW₉Co₃/PDA/BWO as well as Si2*p* and Co2*p* for SiW₉Co₃ and SiW₉Co₃/PDA/BWO

Note: High-resolution of Si2*p* and Co2*p* could confirm the coexistence of Si and Co in the SiW₉Co₃/PDA/BWO composite, even though poor resolution of the spectra were obtained. This is in line with the reported literature.⁴



Fig. S8 (a) Catalytic performance of PDA/BWO at different PDA loadings, and (b) that of SiW₉Co₃/PDA/BWO at different SiW₉Co₃ loadings



Fig. S9 Absorbance of reaction medium using (a) Nessler's reagent, (b) indophenol blue as color developer to determine NH_3/NH_4^+ in spectrophotometry, (c) ¹H NMR spectra for ¹⁵ NH_4^+ as well as ¹⁴ NH_4^+ and (d) ¹⁵N NMR spectra

Note: The photo-driven nitrogen reduction reaction was carried out over SiW₉Co₃/PDA/BWO as catalyst under visible light using pure nitrogen and water as feedstock. In the isotope experiment, pure ¹⁵N₂ was employed in as feedstock in photo-driven nitrogen reduction reaction and proton spectra was recorded (Fig. S9c). At chemical shift of 6.87 ppm, double peaks with coupling constant of 73.3 Hz was observed, owing to the spin quantum number I = 2 for ¹⁵N. For comparison, ¹⁴N₂ (majority) and ¹⁵N₂ (minority) mixture was employed as well. Apart from the weak doublet signal, a strong triplet signal with coupling constant of 52.3 Hz was obtained. Then, we performed ¹⁵N NMR to further confirm the existence of ¹⁵NH₄⁺ in the reaction medium (Fig. S9d).



Fig. S10 The calibration curve for NH₄Cl standard solution using Nessler's reagent as color developer in spectrophotometry



Fig. S11 (a) SEM morphologies, (b)HR-TEM image, (c) EDX mapping for elements Si, W, Co, C, N and O as well as (d) FT-IR spectra of SiW₉Co₃/PDA



Fig. S12 (a) Catalytic performance in photo-driven nitrogen reduction reaction, (b) EPR spectrum, (c) UV-vis diffuse reflectance spectrum, (d) N₂-TPD profile, (e) Transient photocurrent response under visible light irradiation, (f) EIS Nyquist plot, (g) PL spectra, and (h) Time-resolved PL decay spectra of SiW₉Co₃/PDA

SiW₉Co₃/PDA is chosen for comparison. It displays relative low activity in photo-driven nitrogen reduction (Fig. S12a). To understand its catalytic behavior, EPR spectrum is recorded and no obvious peaks is observed at g = 2.003 (Fig. S12b), similar to pristine SiW₉Co₃. Inheriting the PDA feature, SiW₉Co₃/PDA as well displays wide adsorption in UV-vis region (Fig. S12c). Then, weak nitrogen adsorption is revealed in N₂-TPD (Fig. S12d). The intensity transient photocurrent, charge transfer resistances (R_{ct}) and average lifetime are determined to be 3.2 μ A, 79.6 Ω , 5.5002 ns (Table S3-S5, Fig. S12e-h). Although it shows good features in utilization of sunlight and charge separation when comparing with SiW₉Co₃, its weak adsorption of nitrogen molecule may account for low activity in photo-driven nitrogen reduction.



Fig. S13 (a) Photo-Fenton degradation of methyl orange over BWO, SiW₉Co₃, PDA/BWO, SiW₉Co₃/PDA and SiW₉Co₃/PDA/BWO under visible light illumination, (b) Photo-Fenton degradation of methyl orange over SiW₉Co₃/PDA/BWO under different reaction conditions and (c) Schematic diagram illustrating the photo-Fenton catalysis mechanism over SiW₉Co₃/PDA/BWO photocatalysts under visible light irradiation

Photo-Fenton degradation of typical organic pollutants methyl orange was evaluated. In the typical procedure, catalyst (0.02 g) was dispersed into methyl orange aqueous solution (20 mL, 20 mg·L⁻¹, pH = 2, adjusted by using 1.0 M HNO₃). After achieving adsorption-absorption equilibrium in the dark for 30 min, H₂O₂ aqueous solution (50 μ L, 30 wt%) was added and reaction preceded under visible light irradiation. At every 10-minute intervals, 2 mL of supernatant was taken out and centrifuged to remove catalyst. Then the concentration of methyl orange in the clear solution was monitored by UV-Vis spectroscopy at its maximum characteristic absorption ($\lambda = 507$ nm). Under similar protocol, the control experiment proceeded either without irradiation or in the absence H₂O₂.

In the presence of H_2O_2 , photo-Fenton degradation of methyl orange is carried out on BWO, SiW₉Co₃, PDA/BWO, SiW₉Co₃/BWO, SiW₉Co₃/PDA and SiW₉Co₃/PDA/BWO, respectively, under visible light illumination (Fig. S13a). Among these catalysts, ternary SiW₉Co₃/PDA/BWO composite displays highest activity, where methyl orange is completely degraded within 20 min. In order to elucidate the photo-Fenton degradation of methyl orange activity over SiW₉Co₃/PDA/BWO, comparative experiments of light and H₂O₂ are carried out (Fig. S13b). In the absence of H₂O₂ and without illumination, methyl orange is hardly degraded. Thanks to the traditional Fenton mechanism, methyl orange is almost completely degraded within 40 min after the addition of H₂O₂. In the absence of H₂O₂, the degradation ratio of methyl orange is less than 70% even under visible light irradiation after 60 min. In the presence of H₂O₂, the complete within 20min under visible light irradiation. This agrees with the photo-Fenton mechanism perfectly (Fig. S13c).

Samples	I ₁ (μA)	I ₂ (µA)	I ₃ (µA)	I₄(μA)	I ₅ (μA)	I _{av} (µA)
BWO	1.2	1.2	1.1	1.2	1.2	1.2
SiW ₉ Co ₃	1.2	1.2	1.2	1.1	1.1	1.1
PDA/BWO	4.0	4.1	4.1	4.2	4.2	4.1
SiW ₉ Co ₃ /BWO	4.7	4.4	4.2	4.0	3.7	4.3
SiW ₉ Co ₃ /PDA	3.2	3.1	3.3	3.2	3.4	3.2
SiW ₉ Co ₃ /PDA/BWO	7.4	7.4	7.4	7.4	7.4	7.4

Table S3. Transient photocurrent intensity of BWO, SiW₉Co₃, PDA/BWO, SiW₉Co₃/BWO, SiW₉Co₃/PDA and SiW₉Co₃/PDA/BWO

Samples	$R_e(\Omega)$	$R_{ct}(\Omega)$
BWO	3.7	88.0
SiW ₉ Co ₃	2.6	83.1
PDA/BWO	3.1	77.7
SiW ₉ Co ₃ /BWO	3.2	75.3
SiW ₉ Co ₃ /PDA	3.3	79.6
SiW ₉ Co ₃ /PDA/BWO	3.2	74.2

Table S4 The resistance of BWO, SiW_9Co_3 , PDA/BWO, SiW_9Co_3/BWO , SiW_9Co_3/PDA and $SiW_9Co_3/PDA/BWO$ obtained by EIS Nyquist plots

Samples	$\tau_1(ns)$	$\tau_2(ns)$	A ₁ (%)	A ₂ (%)	τ _{av} (ns)
BWO	0.8612	4.0389	34.15	65.85	3.7217
SiW ₉ Co ₃	1.0200	5.5705	64.84	35.16	4.4218
PDA/BWO	0.9894	5.0249	58.43	41.57	4.1501
SiW ₉ Co ₃ /BWO	1.1319	6.3416	51.00	49.00	5.5254
SiW ₉ Co ₃ /PDA	1.1480	6.0641	40.63	59.37	5.5002
SiW ₉ Co ₃ /PDA/BWO	1.7500	6.7528	32.46	67.54	6.1987

Table S5 Fluorescence lifetimes of BWO, SiW₉Co₃, PDA/BWO, SiW₉Co₃/BWO, SiW₉Co₃/PDA and SiW₉Co₃/PDA/BWO derived from time-resolved PL curves

Note: A two-exponential function equation is used to fit the decay time, $\tau_{av} = (A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2)/(A_1 \cdot \tau_1 + A_2 \cdot \tau_2)$, where τ and A are decay time and the relative magnitude of components, respectively. The average lifetime τ_{av} is employed for comparison. The results show the fast decay component (τ_1 and A_1) and the slow component (τ_2 and A_2), decaying from the free excited states and the bound excited states, respectively.



Fig. S14 Electron paramagnetic resonance (EPR) spin-trapping spectra in methanol for (a) BWO DMPO-adducts, (b) SiW_9Co_3 DMPO- O_2^- , (c) $SiW_9Co_3/PDA/BWO$ DMPO- O_2^- , in ultrapure water for (d) BWO DMPO- O_4 , (e) SiW_9Co_3 DMPO- O_4 , (f) $SiW_9Co_3/PDA/BWO$ DMPO- O_4 , (g) Vertical schematic diagram of the EPR hyperfine splitting, (h) EPR hyperfine splitting constant for DMPO-free radical adducts and (i) Electron transfer mechanism of type-II heterojunction

To confirm the Z-scheme hetero-junction feature of SiW₉Co₃/PDA/BWO composite, EPR spintrapping experiments are performed to detect superoxide radicals (\cdot O₂^{-/·}OOH) and hydroxyl radicals (\cdot OH) in the presence of nitrone spin trap DMPO (5,5-dimethyl-1-pyrroline N-oxide, Fig. S14). Under irradiation for 4 to 12 min, characteristic resonances with six-fold peaks, ascribing to DMPO- \cdot O₂⁻ adducts, ⁵⁻⁷ are visible for SiW₉Co₃ and SiW₉Co₃/PDA/BWO in methanol dispersion.

This means the photo-generated electron in conduction band (CB) of SiW₉Co₃ could reduce O₂ to yield $\cdot O_2^-$ (i.e. $E_{CB} \le \varphi O_2 / \cdot O_2^-$).⁸ In the case of BWO, six-line resonance with poor resolution emerges after 8 min irradiation. Its profile and the values of $A_{\rm N}$ and $A_{{\rm H}\beta}$ for the adduct are different from these of DMPO- O_2^- adducts (Fig. S14h). Both of these might hint that the trapping radical adduct is different from DMPO- O_2 , and plausible ascribed to be DMPO- OCH_3 according to the literature, ⁵ though the details are beyond present work. In the aqueous medium, a four-line EPR signal of DMPO-OH adducts with intensity ratio of 1:2:2:1 is obtained for BWO (Fig. S14d), demonstrating the formation of ·OH. 9, 10 In contrast, there is no sign of forming ·OH radical over SiW₉Co₃ (Fig. S14e), owing to its relative weak oxidation capacity (i.e. $E_{VB} < \varphi OH^{-}/OH$). After forming ternary composite, SiW₉Co₃/PDA/BWO displays strong oxidation capability ($E_{VB} > \varphi OH^{-1}$ /·OH), together with enhanced charge transfer efficiency (Fig. S14f). Then, strong signal intensity of SiW₉Co₃/PDA/BWO in both spin-trapping experiments indicates efficient immigration of photo-generated charge carriers in the heterojunction in comparison with single components (SiW₉Co₃ and BWO).¹¹ All these outcomes suggest the forming Z-scheme heterojunction for ternary SiW₉Co₃/PDA/BWO composite, where photo-generated holes in the VB of SiW₉Co₃ would combine with the photo-generated electrons in CB of BWO, leaving photo-generated holes in the VB of BWO with strong oxidation capacity and photo-generated electrons in the CB of SiW₉Co₃ with strong reduction capacity. ^{12, 13} This process is achieved via $\pi \rightarrow \pi^*$ electronic delocalization of PDA, thanks to its superior conductivity.¹⁴⁻¹⁹

The obtained results could exclude the possibility of forming type-II hetero-junction. Supposing $SiW_9Co_3/PDA/BWO$ is type-II hetero-junction (Fig. S14i), photo-generated holes in the VB of BWO would transfer to the VB of SiW_9Co_3 , photo-generated electrons in the CB of SiW_9Co_3 would immigrate towards the CB of BWO. In this case, both oxidation and reduction capacity would be reduced, neither $\cdot O_2$ - nor $\cdot OH$ radicals would be visible in the spectra.^{12, 13}



Fig. S15 CV curves of BWO, SiW₉Co₃ and SiW₉Co₃/PDA/BWO in LiAc/HAc buffer solution (pH

= 6.0) under Ar atmosphere at room temperature



Fig. S16 EPR spin-trapping spectra in methanol for (a) PDA/BWO DMPO-adducts, (b) $SiW_9Co_3/PDA DMPO-O_2^-$, in ultrapure water for (c) PDA/BWO DMPO-OH, (d) $SiW_9Co_3/PDA DMPO-OH$, CV curves for (e) BWO, PDA/BWO and (f) SiW_9Co_3 , SiW_9Co_3/PDA in LiAc/HAc buffer solution (pH = 6.0) under Ar atmosphere at room temperature

To investigate the role of PDA in the composite, both EPR and CV experiments were carried out for PDA/BWO and SiW₉Co₃/PDA, respectively. For PDA/BWO, the intensity signals for spintrapping DMPO-adduct in methanol medium is enhanced (Fig. S16a, Fig. S14a for BWO), which might due to the efficient immigration of photo-generated charge carriers in PDA/BWO composite. Then, no visible resonance was obtained in the aqueous dispersion (Fig. S16c, Fig. S14d for BWO), which means the oxidation of OH⁻ might not occur on PDA/BWO composite, namely reduced oxidation capacity of PDA/BWO, though the reason and mechanism details are beyond our knowledge. This is in line with the CV outcomes (Fig. S16e). At present, the obtained result could not support the formation of Z-scheme hetero-junction between PDA and BWO. Then, the results for SiW₉Co₃/PDA (Fig. S16b, d) is similar to those of SiW₉Co₃ (Fig. S14b, e). Together with CV outcomes (Fig. S16f), there is no solid proof of forming Z-Scheme hetero-junction between PDA and SiW₉Co₃. According the above outcomes, there are no clear hints to form Z-scheme in the cases of PDA/BWO and SiW₉Co₃/PDA samples. Moreover, it further illustrating that Z-scheme is formed between BWO and SiW₉Co₃.



Fig. S17 Absorbance of reaction medium using (a) Nessler's reagent and (b) indophenol blue as color developer to determine NH₃/NH₄⁺ in spectrophotometry Note: The photo-driven nitrogen reduction reaction was carried out over SiW₉Co₃/PDA/BWO as

catalyst under visible light using air and water as feedstock.



Fig. S18 Ion-chromatography for produced NH_4^+ over $SiW_9Co_3/PDA/BWO$ using air and water as feedstock.



Fig. S19 (a) XRD patterns, (b) FT-IR spectra, (c) SEM morphologies, as well as (d) N, C and Co elemental concentration of SiW₉Co₃/PDA/BWO before and after photo-driven nitrogen reduction reaction under visible light irradiation



Fig. S20 Evaluation of durability of SiW₉Co₃/BWO (impregnation method), SiW₉Co₃/PDA/BWO in photo-driven nitrogen reduction reaction under visible light irradiation



Fig. S21 (a) Catalytic performance of $SiW_9Co_3/PDA/OVs$ -BWO in photo-driven nitrogen reduction reaction after 2 h visible light (or simulated sunlight) irradiation under pure N₂, air or Ar atmosphere

Year	Catalyst	Feedstock	Light source	Ammonia yield	Ref.
		U.O. N	> 420 nm	12.06 µmol g _{cat} ⁻¹ h ⁻¹	
SiW ₉ Co ₃ /PDA		H_2O, N_2	full spectrum	31.54 µmol g _{cat} ⁻¹ h ⁻¹	this
	S1W ₉ Co ₃ /PDA/BWO		> 420 nm	11.77 μ mol g _{cat} ⁻¹ h ⁻¹	work
		H_2O , Air	full spectrum	30.1 μmol g _{cat} ⁻¹ h ⁻¹	_
			> 420 nm	27.89 μ mol g _{cat} ⁻¹ h ⁻¹	
	SiW ₉ Co ₃ /PDA/OVs-	H_2O, N_2	full spectrum	52.67 μmol g _{cat} ⁻¹ h ⁻¹	this
	BWO		> 420 nm	25.07 μ mol g _{cat} ⁻¹ h ⁻¹	work
		H_2O , Air	full spectrum	44.21 μmol g _{cat} ⁻¹ h ⁻¹	-
2019	defect-rich Bi ₃ O ₄ Br	H ₂ O, N ₂	full spectrum	50.8 μ mol g _{cat} ⁻¹ h ⁻¹	20
2019	OVs -TiO ₂ nanosheets	H_2O, N_2	200 ~ 800 nm	78.9 μmol g _{cat} ⁻¹ h ⁻¹	21
2019	Or-Bi/Bi ₂ WO ₆	H ₂ O, N ₂	full spectrum	86 μ mol g _{cat} ⁻¹ h ⁻¹	22
			full spectrum	90.7 µmol g _{cat} ⁻¹ h ⁻¹	23
2019	B12MoO6/OV-B1OBr	H_2O, N_2	> 420 nm	81.0 μmol g _{cat} ⁻¹ h ⁻¹	25
2019	AgCl/δ-Bi ₂ O ₃	H ₂ O, N ₂	visible light	202 μ mol g _{cat} ⁻¹ h ⁻¹	24
2019	$Bi_4O_5Br_2/ZIF$ -8	H ₂ O, N ₂	$200 \sim 800 \ nm$	$327.34 \ \mu mol \ g_{cat}^{-1} \ h^{-1}$	25
2019	V DOD-	U.O. N	> 420 nm	49.04 μ mol g _{cat} ⁻¹ h ⁻¹	26
2018	v ₀ -BiOBi	H_2O, N_2	full spectrum	54.7 μmol g _{cat} ⁻¹ h ⁻¹	_ 20
2018	Mo-W ₁₈ O ₄₉	H ₂ O, N ₂	full spectrum	61.9 μmol g _{cat} ⁻¹ h ⁻¹	27
2018	Bi ₂ WO ₆ /c-PAN	H ₂ O, N ₂	\geq 400 nm	140 µmol g _{cat} -1 h-1	28
2017	O vacancy TiO ₂	H_2O, N_2	> 280 nm	$0.73 \ \mu mol \ g_{cat}^{-1} \ h^{-1}$	29
2017	CuCr-LDH	H ₂ O, N ₂	> 400 nm	57.1 μmol g _{cat} ⁻¹ h ⁻¹	30
2017	Ultrathin MoS ₂	H_2O, N_2	full spectrum	ca. 135 μ mol g _{cat} ⁻¹ h ⁻¹	31
2017	Ni2P/Cd0.5Zn0.5S	H ₂ O, N ₂	> 400 nm	254 µmol g _{cat} -1 h-1	32
2017	Bi ₅ O ₇ Br nanotubes	H ₂ O, N ₂	> 400 nm	1380 μ mol g _{cat} ⁻¹ h ⁻¹	33
2016	Fe-3D graphene	H_2O, N_2	UV	24 μ mol g _{cat} ⁻¹ h ⁻¹	34

Table S6 The reported results for photo-driven nitrogen reduction reaction using water and
 pure nitrogen as feedstock

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