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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References
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. Typically, Bi(NO$_3$)$_3$∙5H$_2$O (4.0 mmol) was first dissolved in of nitric solution (5 ml, 4.0 mol·L$^{-1}$), and Na$_2$WO$_4$·2H$_2$O solution (40 mL, 0.05 mol·L$^{-1}$) was introduced drop-wise 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 H$_2$O) and absolute EtOH for several times, and finally dried under vacuum at 70°C for 6 h.


K$_6$H$_4$[α-SiW$_9$O$_{37}$Co$_3$(H$_2$O)$_3$]·17H$_2$O (SiW$_9$Co$_3$) was prepared according to literature. Then, BWO (1.0 g) and SiW$_9$Co$_3$ (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 H$_2$O and EtOH several times, and dried under vacuum at 70°C for 5 h. The prepared sample were recorded as SiW$_9$Co$_3$/PDA/BWO. By changing the amount of BWO, dopamine hydrochloride and SiW$_9$Co$_3$, a series of samples with different proportions were prepared. For comparison, PDA/BWO, PDA/SiW$_9$Co$_3$ and SiW$_9$Co$_3$/BWO samples were also prepared by the similar method. Then, SiW$_9$Co$_3$-PDA-BWO-Mix was achieved by mechanical mixing SiW$_9$Co$_3$, 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 H$_2$O 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/SiW_9Co_3 composite, SiW_9Co_3 (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 H_2O and EtOH several times, and dried under vacuum at 70°C for 5 h.

When preparing SiW_9Co_3/BWO composite, BWO (1.0 g) and SiW_9Co_3 (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 H_2O 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 Kα radiation (λ=1.54056Å). 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 BaSO_4 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 N_2 adsorption-desorption isotherms were recorded on Tristar 3020, and the surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation. Nitrogen temperature-programmed desorption (N_2-TPD) was conducted on a Micromeritics AutoChem II 2920 instrument. Electron paramagnetic resonance (EPR) spectroscopy was carried
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 μL 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 three-electrode configuration in 0.1 M Na$_2$SO$_4$ as electrolyte. Working electrode was prepared by spin-coating catalyst (20 mg) on ITO conductive glass (1 × 2 cm$^2$). 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 photo-current 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 ($\lambda < 420$ 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$_3$/$\text{NH}_4^+$ concentration analysis and determination of NH$_3$/$\text{NH}_4^+$ 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 (KNaC\(_4\)H\(_4\)O\(_6\), 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 NH\(_3\)/NH\(_4^+\) was calculated according to the absorbance at 420 nm. The calibration curve was obtained using NH\(_4\)Cl 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 NH\(_3\)/NH\(_4^+\) using \(^{15}\)N\(_2\) as feeding gas, and solution NMR \(^1\)H spectra and \(^{15}\)N spectra were recorded on JEOL JNM-ECZ400S. For comparison, \(^{14}\)N\(_2\) (majority) and \(^{15}\)N\(_2\) (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-I, (b) Type-II, (c) Type-III and (d) Z-scheme heterojunction. CB and VB stand for the conduction band and valence band, respectively.
**Fig. S1** SEM morphologies for (a) BWO, (b) PDA/BWO, (c) SiW₅Co₃/BWO and ternary (d) SiW₅Co₃/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
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

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<td>2.400(2.498)</td>
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Fig. S3 Nitrogen adsorption-desorption isotherms of BWO and ternary Si$_9$Co$_3$/PDA/BWO composite
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<th>Sample</th>
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<td>Si₆W₆Co₃/PDA/BWO</td>
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Fig. S4 FT-IR spectra of PDA, SiW₉Co₃, SiW₉Co₃/PDA/BWO and SiW₉Co₃-PDA-BWO-Mix
Fig. S5 High-resolution XPS spectra of Bi4f for BWO, PDA/BWO, SiW₉Co₃/PDA/BWO and SiW₉Co₃-PDA-BWO-Mix
In Fig. S6a, the W4f 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 Bi4f outcomes. After deconvolution, both W(VI) and W(V) is obtained for PDA/BWO sample, with binding energies of 37.65 (W4f5/2) and 35.50 eV (W4f3/2) as well as 37.20 (W4f5/2) and 35.20 eV (W4f3/2), 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 W4f binding energy is observed in SiW9Co3/PDA sample.
**Fig. S7** High-resolution XPS spectra of N1s for SiW$_9$Co$_3$/PDA/BWO as well as Si2p and Co2p for SiW$_9$Co$_3$ and SiW$_9$Co$_3$/PDA/BWO

Note: High-resolution of Si2p and Co2p could confirm the coexistence of Si and Co in the SiW$_9$Co$_3$/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) $^1$H NMR spectra for $^{15}$NH$_4^+$ as well as $^{14}$NH$_4^+$ and (d) $^{15}$N NMR spectra

Note: The photo-driven nitrogen reduction reaction was carried out over SiW$_9$Co$_3$/PDA/BWO as catalyst under visible light using pure nitrogen and water as feedstock. In the isotope experiment, pure $^{15}$N$_2$ was employed 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 $^{15}$N. For comparison, $^{14}$N$_2$ (majority) and $^{15}$N$_2$ (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 $^{15}$N NMR to further confirm the existence of $^{15}$NH$_4^+$ 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) N$_2$-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 SiW$_9$Co$_3$/PDA

SiW$_9$Co$_3$/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 SiW$_9$Co$_3$. Inheriting the PDA feature, SiW$_9$Co$_3$/PDA as well displays wide adsorption in UV-vis region (Fig. S12c). Then, weak nitrogen adsorption is revealed in N$_2$-TPD (Fig. S12d). The intensity transient photocurrent, charge transfer resistances ($R_{ct}$) and average lifetime are determined to be 3.2 $\mu$A, 79.6 $\Omega$, 5.5002 ns (Table S3-S5, Fig. S12e-h). Although it shows good features in utilization of sunlight and charge separation when comparing with SiW$_9$Co$_3$, 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, SiW₉Co₃/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 μL, 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 (λ = 507 nm). Under similar protocol, the control experiment proceeded either without irradiation or in the absence H₂O₂.
In the presence of H$_2$O$_2$, photo-Fenton degradation of methyl orange is carried out on BWO, SiW$_9$Co$_3$, PDA/BWO, SiW$_9$Co$_3$/BWO, SiW$_9$Co$_3$/PDA and SiW$_9$Co$_3$/PDA/BWO, respectively, under visible light illumination (Fig. S13a). Among these catalysts, ternary SiW$_9$Co$_3$/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 SiW$_9$Co$_3$/PDA/BWO, comparative experiments of light and H$_2$O$_2$ are carried out (Fig. S13b). In the absence of H$_2$O$_2$ 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 H$_2$O$_2$. In the absence of H$_2$O$_2$, the degradation ratio of methyl orange is less than 70% even under visible light irradiation after 60 min. In the presence of H$_2$O$_2$, the complete degradation of methyl orange is achieved within 20 min under visible light irradiation. This agrees with the photo-Fenton mechanism perfectly (Fig. S13c).
Table S3. Transient photocurrent intensity of BWO, SiW₉Co₃, PDA/BWO, SiW₉Co₃/BWO, SiW₉Co₃/PDA and SiW₉Co₃/PDA/BWO

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<th>I₁(μA)</th>
<th>I₂(μA)</th>
<th>I₃(μA)</th>
<th>I₄(μA)</th>
<th>I₅(μA)</th>
<th>Iᵣ(μA)</th>
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Table S4 The resistance of BWO, SiW₉Co₃, PDA/BWO, SiW₉Co₃/BWO, SiW₉Co₃/PDA and SiW₉Co₃/PDA/BWO obtained by EIS Nyquist plots

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<th>Samples</th>
<th>$R_e$ (Ω)</th>
<th>$R_d$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BWO</td>
<td>3.7</td>
<td>88.0</td>
</tr>
<tr>
<td>SiW₉Co₃</td>
<td>2.6</td>
<td>83.1</td>
</tr>
<tr>
<td>PDA/BWO</td>
<td>3.1</td>
<td>77.7</td>
</tr>
<tr>
<td>SiW₉Co₃/BWO</td>
<td>3.2</td>
<td>75.3</td>
</tr>
<tr>
<td>SiW₉Co₃/PDA</td>
<td>3.3</td>
<td>79.6</td>
</tr>
<tr>
<td>SiW₉Co₃/PDA/BWO</td>
<td>3.2</td>
<td>74.2</td>
</tr>
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Table S5 Fluorescence lifetimes of BWO, SiW₉Co₃, PDA/BWO, SiW₉Co₃/BWO, SiW₉Co₃/PDA and SiW₉Co₃/PDA/BWO derived from time-resolved PL curves

<table>
<thead>
<tr>
<th>Samples</th>
<th>(\tau_1) (ns)</th>
<th>(\tau_2) (ns)</th>
<th>(A_1) (%)</th>
<th>(A_2) (%)</th>
<th>(\tau_{av}) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BWO</td>
<td>0.8612</td>
<td>4.0389</td>
<td>34.15</td>
<td>65.85</td>
<td>3.7217</td>
</tr>
<tr>
<td>SiW₉Co₃</td>
<td>1.0200</td>
<td>5.5705</td>
<td>64.84</td>
<td>35.16</td>
<td>4.4218</td>
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<tr>
<td>PDA/BWO</td>
<td>0.9894</td>
<td>5.0249</td>
<td>58.43</td>
<td>41.57</td>
<td>4.1501</td>
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<tr>
<td>SiW₉Co₃/BWO</td>
<td>1.1319</td>
<td>6.3416</td>
<td>51.00</td>
<td>49.00</td>
<td>5.5254</td>
</tr>
<tr>
<td>SiW₉Co₃/PDA</td>
<td>1.1480</td>
<td>6.0641</td>
<td>40.63</td>
<td>59.37</td>
<td>5.5002</td>
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<tr>
<td>SiW₉Co₃/PDA/BWO</td>
<td>1.7500</td>
<td>6.7528</td>
<td>32.46</td>
<td>67.54</td>
<td>6.1987</td>
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</tbody>
</table>

Note: A two-exponential function equation is used to fit the decay time, \(\tau_{av} = \frac{A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2}{A_1 \cdot \tau_1 + A_2 \cdot \tau_2}\), where \(\tau\) and \(A\) are decay time and the relative magnitude of components, respectively. The average lifetime \(\tau_{av}\) is employed for comparison. The results show the fast decay component (\(\tau_1\) and \(A_1\)) and the slow component (\(\tau_2\) 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) SiW₉Co₃ DMPO-O₂-, (c) SiW₉Co₃/PDA/BWO DMPO-O₂-, in ultrapure water for (d) BWO DMPO-OH, (e) SiW₉Co₃ DMPO-OH, (f) SiW₉Co₃/PDA/BWO DMPO-OH, (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 spin-trapping experiments are performed to detect superoxide radicals (O₂-/∙OOH) and hydroxyl radicals (∙OH) in the presence of nitrore 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-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 ·O₂⁻ (i.e. $E_{CB} < \phi O_2^/-O_2^-$). In the case of BWO, six-line resonance with poor resolution emerges after 8 min irradiation. Its profile and the values of $\Lambda_N$ and $\Lambda_{H\beta}$ for the adduct are different from these of DMPO-·O₂⁻ adducts (Fig. S14h). Both of these might hint that the trapping radical adduct is different from DMPO-·O₂⁻, and plausible ascribed to be DMPO-·OCH₃ according to the literature, 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. In contrast, there is no sign of forming ·OH radical over SiW₉Co₃ (Fig. S14e), owing to its relative weak oxidation capacity (i.e. $E_{VB} < \phi OH^-/-OH$). After forming ternary composite, SiW₉Co₃/PDA/BWO displays strong oxidation capability ($E_{VB} > \phi OH^-/-OH$), 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). 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. This process is achieved via $\pi \rightarrow \pi^*$ electronic delocalization of PDA, thanks to its superior conductivity.

The obtained results could exclude the possibility of forming type-II hetero-junction. Supposing SiW₉Co₃/PDA/BWO is type-II hetero-junction (Fig. S14i), photo-generated holes in the VB of BWO would transfer to the VB of SiW₉Co₃, photo-generated electrons in the CB of SiW₉Co₃ would immigrate towards the CB of BWO. In this case, both oxidation and reduction capacity would be reduced, neither ·O₂⁻ nor ·OH radicals would be visible in the spectra.
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
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 spin-trapping 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 SiW$_9$Co$_3$/PDA (Fig. S16b, d) is similar to those of SiW$_9$Co$_3$ (Fig. S14b, e). Together with CV outcomes (Fig. S16f), there is no solid proof of forming Z-Scheme hetero-junction between PDA and SiW$_9$Co$_3$. According the above outcomes, there are no clear hints to form Z-scheme in the cases of PDA/BWO and SiW$_9$Co$_3$/PDA samples. Moreover, it further illustrating that Z-scheme is formed between BWO and SiW$_9$Co$_3$. 

Fig. S17 Absorbance of reaction medium using (a) Nessler’s reagent and (b) indophenol blue as color developer to determine NH$_3$/NH$_4^+$ in spectrophotometry.

Note: The photo-driven nitrogen reduction reaction was carried out over SiW$_6$Co$_3$/PDA/BWO as catalyst under visible light using air and water as feedstock.
Fig. S18 Ion-chromatography for produced NH$_4^+$ over SiW$_6$Co$_3$/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 SiW₉Co₃/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.
Table S6 The reported results for photo-driven nitrogen reduction reaction using water and pure nitrogen as feedstock

<table>
<thead>
<tr>
<th>Year</th>
<th>Catalyst</th>
<th>Feedstock</th>
<th>Light source</th>
<th>Ammonia yield</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>2019</td>
<td>defect-rich Bi$_3$O$_4$Br</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>12.06 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<tr>
<td>2019</td>
<td>OVs -TiO$_2$ nanosheets</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>31.54 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<td>2019</td>
<td>Or-Bi/Bi$_2$WO$_6$</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>11.77 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<tr>
<td>2019</td>
<td>Bi$_2$MoO$_6$/OV-BiBr</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>52.67 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<td>2019</td>
<td>AgCl/δ-Bi$_2$O$_3$</td>
<td>H$_2$O, N$_2$</td>
<td>visible light</td>
<td>&gt; 420 nm</td>
<td>50.8 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<td>2019</td>
<td>Bi$_4$O$_5$Br$_2$/ZIF-8</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 200 nm</td>
<td>78.9 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<tr>
<td>2019</td>
<td>V$_{\text{O}}$-BiOB</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>86 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<tr>
<td>2018</td>
<td>Mo-W$<em>{18}$O$</em>{49}$</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>90.7 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<td>2018</td>
<td>Bi$_2$WO$_6$/c-PAN</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>54.7 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<td>2018</td>
<td>O vacancy TiO$_2$</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>24 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<tr>
<td>2017</td>
<td>CuCr-LDH</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
<td>140 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<td>2017</td>
<td>Ultrathin MoS$_2$</td>
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<td>full spectrum</td>
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<td>1380 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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<td>2017</td>
<td>Ni$<em>2$P/Cd$</em>{0.5}$Zn$_{0.5}$S</td>
<td>H$_2$O, N$_2$</td>
<td>full spectrum</td>
<td>&gt; 420 nm</td>
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<td>2016</td>
<td>Fe-3D graphene</td>
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<td>UV</td>
<td>&gt; 420 nm</td>
<td>1380 µmol g$_{\text{cat}}^{-1}$ h$^{-1}$</td>
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</table>
References


