Supplementary Information

Artificial Photosynthetic Hydrogen Evolution over \( g\text{-}C_3\text{N}_4 \) Nanosheets Coupled with Cobaloxime

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Experimental details

Sample preparation: Co^{III}(dmgH)_{2}pyCl was purchased from Sigma Aldrich. The g-C_{3}N_{4} nanosheets were synthesized according to a literature method. Typically, melamine powder (6 g) was heated in an alumina crucible with a cover at 500 °C in a muffle furnace for 2 h, and further heated to 520 °C for another 2 h to generate g-C_{3}N_{4}. Detailed characterization is show in Fig. S8.

Characterization: X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer (Cu Kα source) at a scan rate of 1 °/min with the 2θ range from 5 to 50°. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100F transmission electron microscope at an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) were recorded on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). The BET surface areas were measured on a Micromeritics ASAP 2020M+C system. The steady-state photoluminescence (PL) spectra were obtained by a Shimazu RF-5310PC fluorometer at an excitation wavelength of 325 nm.

Transient optical spectroscopy: For time-resolved PL measurements, the excitation pulse (325 nm) was generated from an optical parametric amplifier (TOPAS™, Light Conversion Ltd). The Time-resolved PL spectra were obtained using a streak camera (Optronics GmbH) with a time resolution of 10 ps. The PL decay profile is fitted by using multiexponential function.

\[ I_t = \sum_{i=1}^{n} A_i \exp \left( -\frac{t}{\tau_i} \right) \]

where \( I_t \) is intensity, \( A_i \) is the relative magnitude of the \( i \)th decay and \( \tau_i \) is the \( i \)th decay time.
**Photocatalytic hydrogen evolution from water reduction:** Typically, 10 mg of g-C$_3$N$_4$ and 2 mg of Co$^{III}$(dmgH)$_2$pyCl were suspended in 10 mL aqueous solution of 15 vol% TEOA. The suspension was then purged with nitrogen for 3 h to drive away the residual air before sealed in a quartz flask. The photocatalytic hydrogen evolution was carried out by irradiating the suspension with a 300-W xenon lamp (MAX-302, visible module, Asahi Spectra, USA) to provide irradiation at 350-740 nm. The gas product composition was analyzed every 60 min by an Agilent 7890A gas chromatograph (GC) with TCD detector. The apparent quantum efficiency (QE) was estimated by using the following equation.

\[
Q_E = \frac{2 \times \text{the number of evolved hydrogen molecules}}{\text{the number of incident photons}} \times 100\%
\]

Control photocatalytic experiments were done by using 10 mg Co$^{III}$(dmgH)$_2$pyCl or 10 mg g-C$_3$N$_4$ without cobaloxime under the same condition.
**Fig. S1** H$_2$ evolution plot when continuing the photocatalytic reaction after paused for different time at 4 hours. When continuing the photocatalytic reaction after paused for 5 min, the H$_2$ evolution showed another 1-hour induction period with significantly decreased rate, suggesting that the Co(I) intermediates were not stable without light irradiation and degraded quickly during the 5-min dark period.
**Fig. S2** Zoom-in UV-vis absorption spectra of the solution centrifuged from the photocatalytic system during irradiation.
**Fig. S3** pH effect on photocatalytic H₂ evolution (comparing by stable rate) from the system comprising g-C₃N₄ (10 mg) and Co⁺⁺⁺(dmgH)₂pyCl (2 mg) in a 15 vol% TEOA aqueous solution.
Fig. S4 Photocatalytic H\textsubscript{2} evolution in the presence of CoCl\textsubscript{2} in TEOA aqueous solution as compared to the g-C\textsubscript{3}N\textsubscript{4}/Co\textsuperscript{III}(dmgH)\textsubscript{2}pyCl/TEOA system based on equal mole amount of cobalt element (~ 5 µmol for both cobaloxime and CoCl\textsubscript{2}).
Fig. S5  Visible light ($\lambda > 420$ nm) induced photocatalytic $\text{H}_2$ evolution from the system comprising g-$\text{C}_3\text{N}_4$ (10 mg) and Co$^{\text{III}}$(dmgH)$_2$pyCl (2 mg) in a 15 vol% TEOA aqueous solution.
Fig. S6 (a) Photocatalytic H\textsubscript{2} evolution curve with prolonged irradiation time for the system comprising g-C\textsubscript{3}N\textsubscript{4} (10 mg) and Co\textsuperscript{III}(dmgH)\textsubscript{2}pyCl (2 mg) in a 15 vol\% TEOA aqueous solution; (b) TEM image of the sample from the above system after photoirradiation; (c) HRTEM image of the sample from the above system after photoirradiation. The lattice fringes mostly match with the crystal planes of Co\textsubscript{2}O\textsubscript{3}. 

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Fig. S7 Cycling test of photocatalytic H₂ evolution for the reused g-C₃N₄ in the presence of fresh Co⁺⁺⁺(dmgH)₂pyCl.
**Fig. S8** Characterization of g-C$_3$N$_4$: (a) XRD pattern; (b) TEM image; (c) UV-vis absorption spectrum. The XRD pattern with two pronounced diffraction peaks agrees well with that reported in the literature. UV-vis diffuse reflectance spectrum indicates that g-C$_3$N$_4$ exhibits an absorption edge at 451 nm, corresponding to the band gap of 2.75 eV. (d) UV-vis absorption spectrum of Co$^{III}$(dmgH)$_2$pyCl in a 15 vol% TEOA aqueous solution.
References

