Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

Artificial Photosynthetic Hydrogen Evolution over g-C_3N_4 Nanosheets Coupled with Cobaloxime

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Experimental details

Sample preparation: $Co^{III}(dmgH)_2pyCl$ was purchased from Sigma Aldrich. The g-C_3N_4 nanosheets were synthesized according to a literature method.[1] Typically, melamine powder (6 g) was heated in an alumina crucible with a cover at 500 ºC in a muffle furnace for 2 h, and further heated to 520 ºC for another 2 h to generate g-C_3N_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.[2,3]

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

where I_t is intensity, A_i is the relative magnitude of the *i*th decay and τ_i is the *i*th decay time.

Photocatalytic hydrogen evolution from water reduction: Typically, 10 mg of g-C_3N_4 and 2 mg of $Co^{III}(dmgH)_2pyCl$ 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.

$$QE = \frac{2\times \ the \ \ number \ \ of \ \ evolved \ \ hydrogen \ \ molecules}{the \ \ number \ \ of \ \ incident \ \ photons} \times 100\%$$

Control photocatalytic experiments were done by using 10 mg $Co^{III}(dmgH)_2pyCl$ or 10 mg g-C_3N_4 without cobaloxime under the same condition.

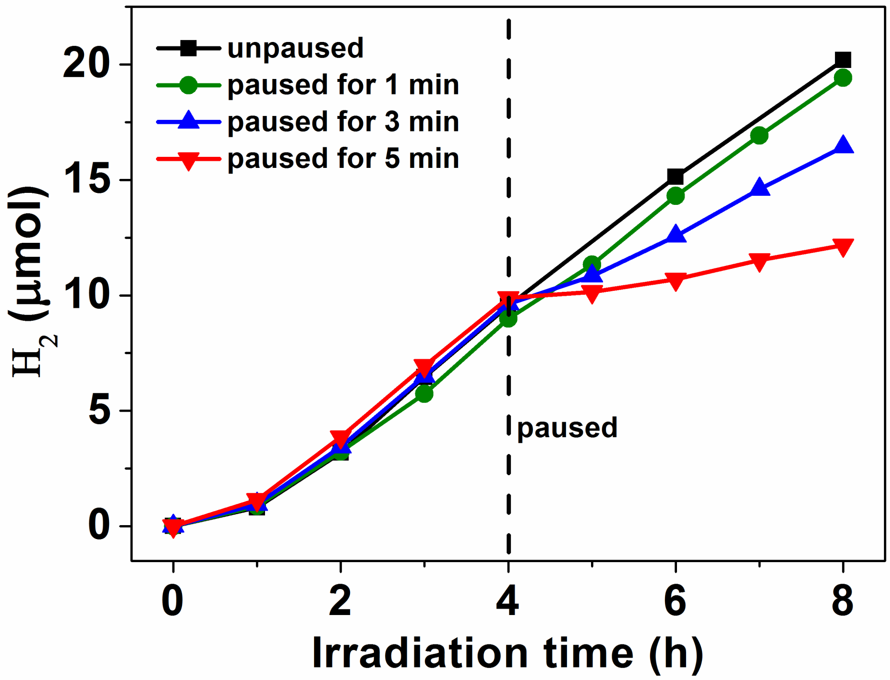

Fig. S1 H_2 evolution plot when continuing the photocatalytic reaction after paused for different time at 4 hours. When continuing the photocatalytic reaction after paused for 5 min, the H_2 evolution showed another 1-hour induction period with significantly decreased rate, suggesting that the Co(I) intermediates were not stable without light irradiation and degraded quickly during the 5-min dark period.

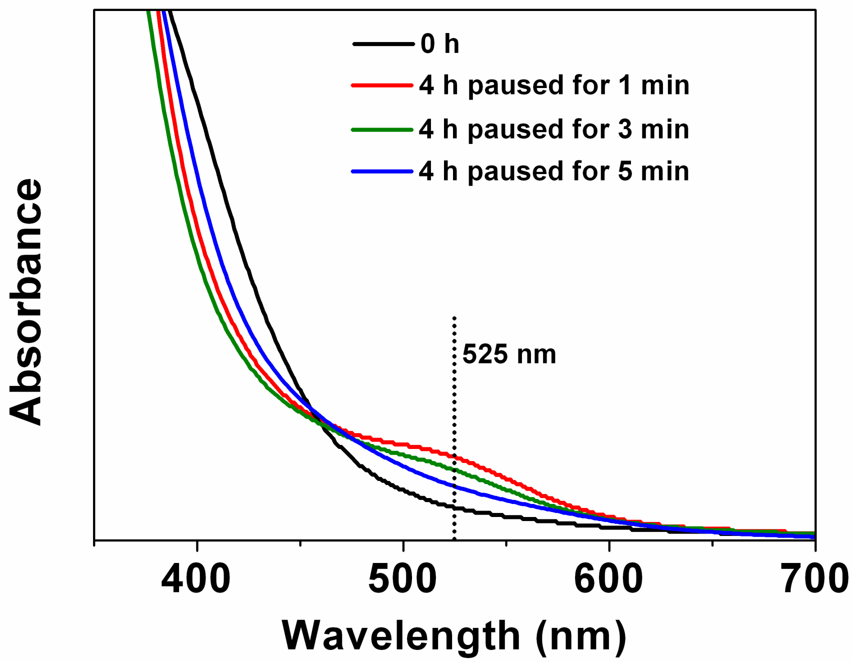

Fig. S2 Zoom-in UV-vis absorption spectra of the solution centrifuged from the photocatalytic system during irradiation.

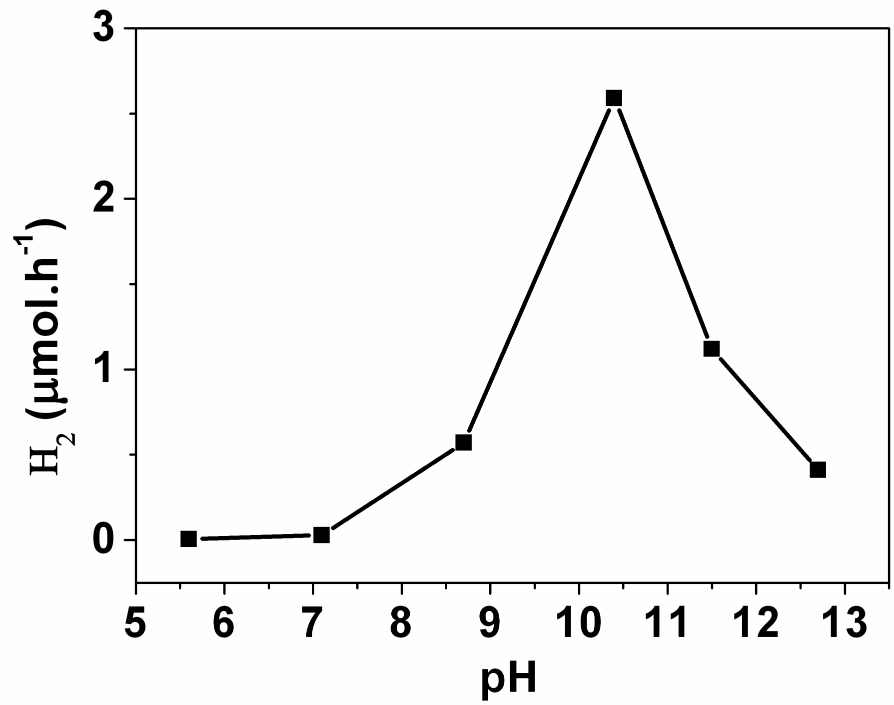

Fig. S3 pH effect on photocatalytic H_2 evolution (comparing by stable rate) from the system comprising g-C_3N_4 (10 mg) and $Co^{III}(dmgH)_2pyCl$ (2 mg) in a 15 vol% TEOA aqueous solution.

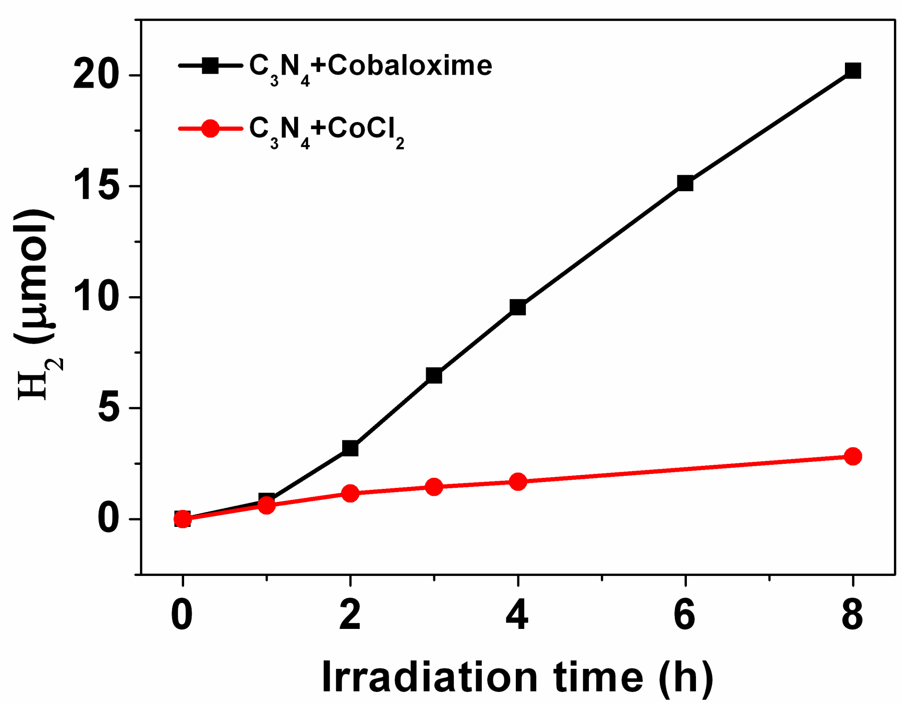

Fig. S4 Photocatalytic H_2 evolution in the presence of $CoCl_2$ in TEOA aqueous solution as compared to the g-C_3N_4/$Co^{III}$$(dmgH)_2$pyCl/TEOA system based on equal mole amount of cobalt element (~ 5 μmol for both cobaloxime and $CoCl_2$).

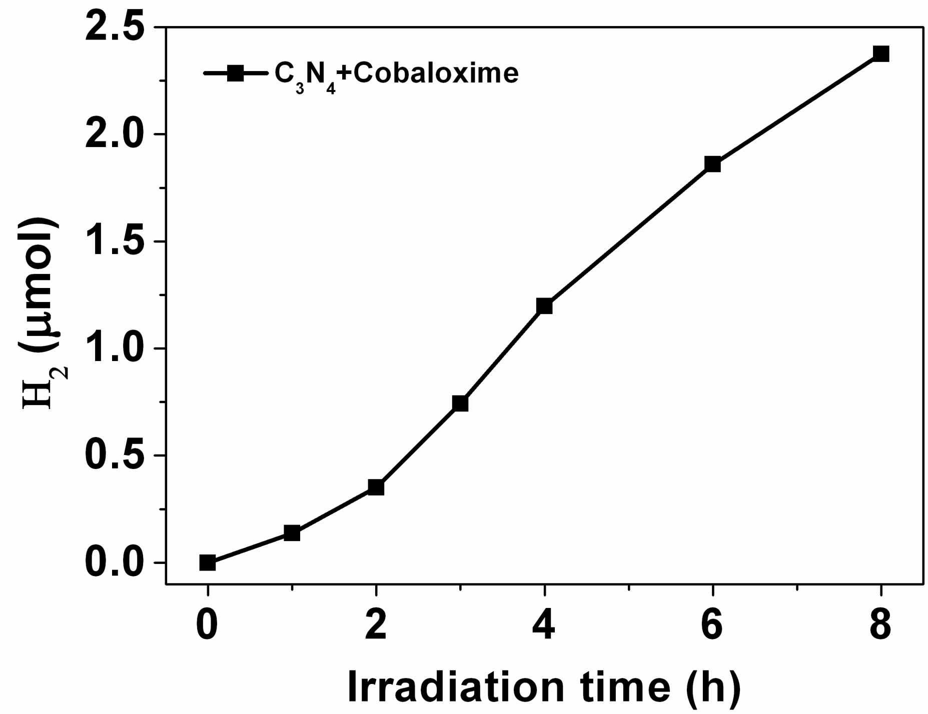

Fig. S5 Visible light (λ > 420 nm) induced photocatalytic H_2 evolution from the system comprising g-C_3N_4 (10 mg) and $Co^{III}(dmgH)_2pyCl$ (2 mg) in a 15 vol% TEOA aqueous solution.

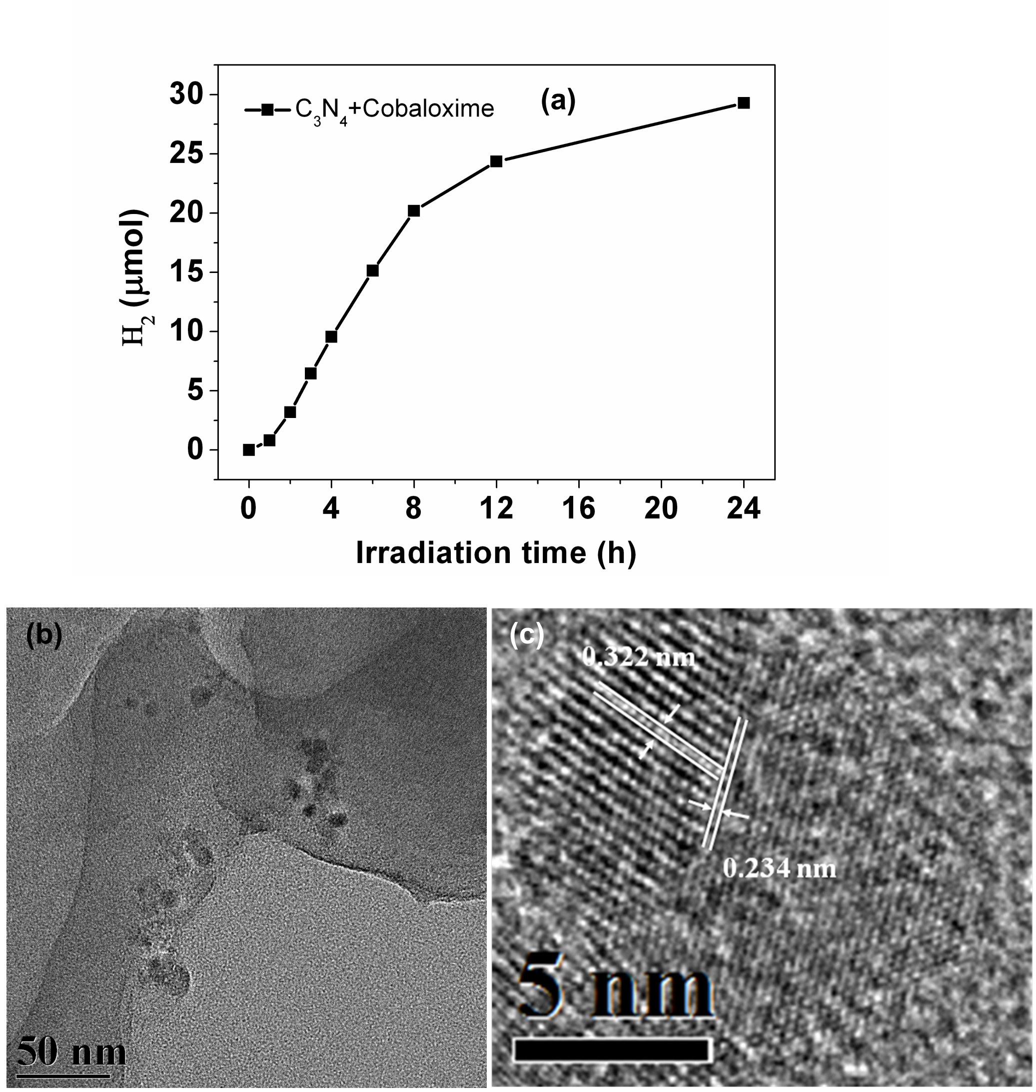

Fig. S6 (a) Photocatalytic H_2 evolution curve with prolonged irradiation time for the system comprising g-C_3N_4 (10 mg) and $Co^{III}(dmgH)_2pyCl$ (2 mg) in a 15 vol% TEOA aqueous solution; (b) TEM image of the sample from the above system after photoirradiation; (c) HRTEM image of the sample from the above system after photoirradiation. The lattice fringes mostly match with the crystal planes of Co_2O_3.

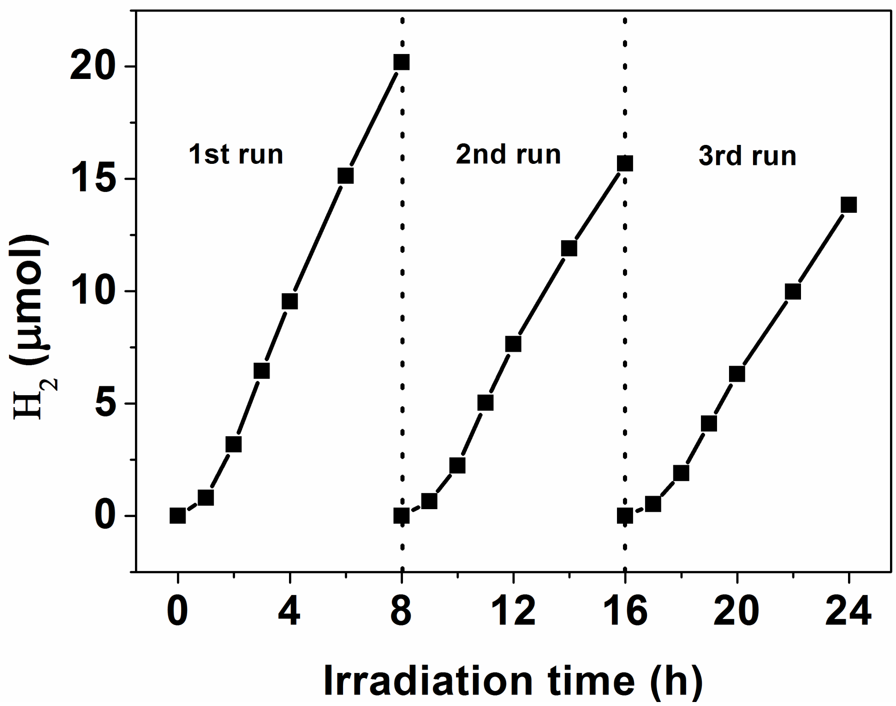

Fig. S7 Cycling test of photocatalytic H_2 evolution for the reused g-C_3N_4 in the presence of fresh $Co^{III}(dmgH)_2pyCl$.

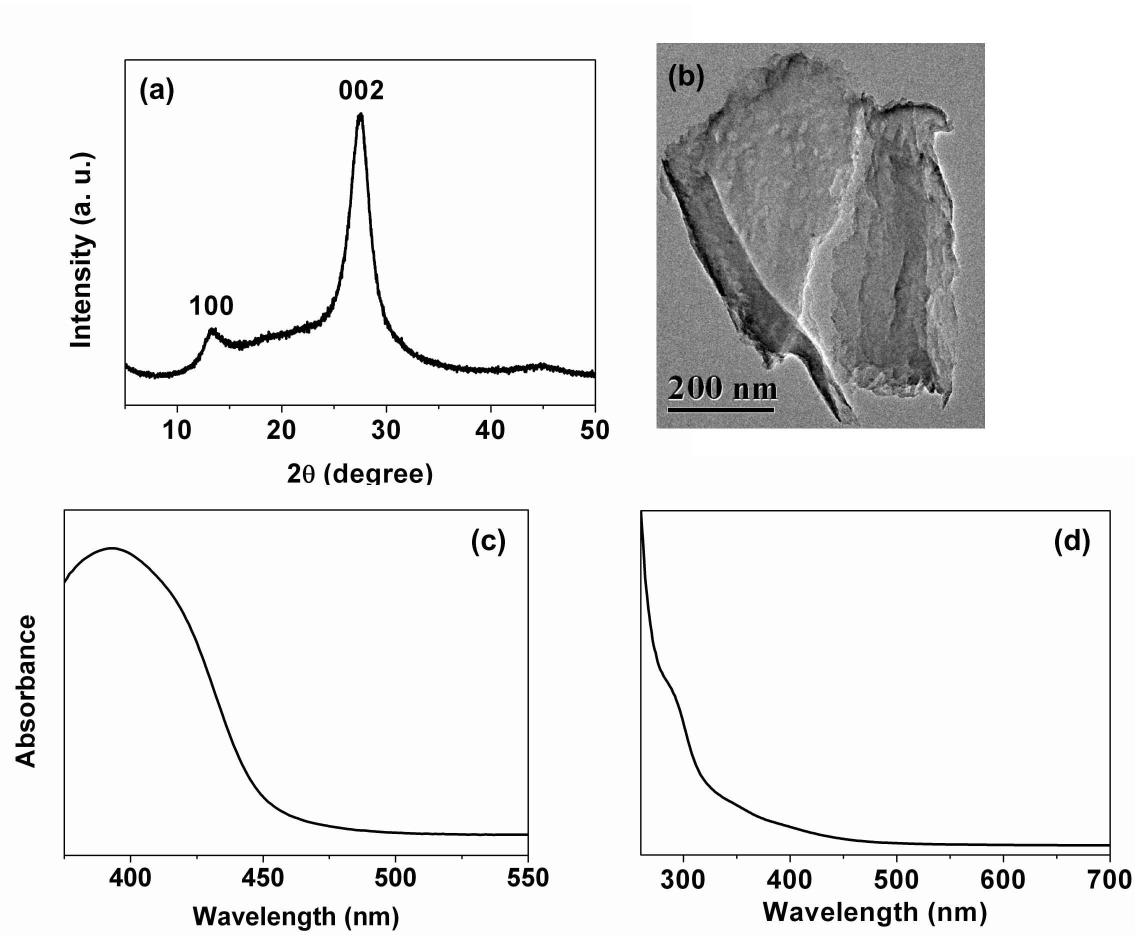

Fig. S8 Characterization of g-C_3N_4: (a) XRD pattern; (b) TEM image; (c) UV-vis absorption spectrum. The XRD pattern with two pronounced diffraction peaks agrees well with that reported in the literature. UV-vis diffuse reflectance spectrum indicates that g-C_3N_4 exhibits an absorption edge at 451 nm, corresponding to the band gap of 2.75 eV. (d) UV-vis absorption spectrum of $Co^{III}(dmgH)_2pyCl$ in a 15 vol% TEOA aqueous solution.

References

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