Supporting Information

Efficient photocatalytic hydrogen evolution with end-groupfunctionalized cobaloxime catalysts in combination with graphite-like C₃N₄

Xiao-Wei Song, ^a Hui-Min Wen, ^a Cheng-Bing Ma, ^a Hong-Hua Cui, ^a Hui Chen, ^a and Chang-Neng Chen*^a

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China;E-mail:

ccn@fjirsm.ac.cn



Fig. S1 XRD patterns of $g-C_3N_4$ before (a) and after (b) photocatalysis reaction



Fig. S2 TEM image of $g-C_3N_4$ before photocatalysis reaction



Fig. S3 TEM image of $g-C_3N_4$ after photocatalysis reaction following the conditions: C1 (1×10⁻⁴ M), $g-C_3N_4$ (4 mg), 5 vol% TEOA in CH₃CN-H₂O (9/1, v/v) solution (5 mL) at pH=9, irradiation light >400 nm in 12 h.



Fig. S4 the UV-vis DRS spectrum of $g-C_3N_4$



Fig. S5 Comparison of UV-vis absorption spectra between (a) C1 (1×10^{-4} M) in reaction solution and (b) the resulting clear solution after removing g-C₃N₄ from the C1/g-C₃N₄ system after photocatalysis



Fig. S6 Comparison of hydrogen production for (a) the original C1/g-C₃N₄ system containing C1 (1×10⁻⁴ M), g-C₃N₄ (4 mg) and TEOA (5 vol%) in CH₃CN-H₂O (9/1, v/v) solution at pH 10, (b) readdition of the fresh g-C₃N₄ (4 mg) to the filtrate of the original C1/g-C₃N₄ system, (c) readdition of the 5 vol% TEOA acetonitrile aqueous solution (9/1, v/v) to the g-C₃N₄ residue of the original C1/g-C₃N₄ system and (d) the bare g-C₃N₄ (4 mg) in CH₃CN-H₂O (9/1, v/v) solution at pH 10.



Fig. S7 Comparison of hydrogen production for (a) the original C2/g-C₃N₄ system containing C2 (1×10⁻⁴ M), g-C₃N₄ (4 mg) and TEOA (5 vol%) in CH₃CN-H₂O (9/1, v/v) solution at pH 10, (b) readdition of the fresh g-C₃N₄ (4 mg) to the filtrate of the original C2/g-C₃N₄ system, (c) readdition of the 5 vol% TEOA acetonitrile aqueous solution (9/1, v/v) to the g-C₃N₄ residue of the original C2/g-C₃N₄ system and (d) the bare g-C₃N₄ (4 mg) in CH₃CN-H₂O (9/1, v/v) solution at pH 10.



Fig. S8 Comparison of hydrogen production for (a) the original C3/g-C₃N₄ system containing C3 (1×10⁻⁴ M), g-C₃N₄ (4 mg) and TEOA (5 vol%) in CH₃CN-H₂O (9/1, v/v) solution at pH 10, (b) readdition of the fresh g-C₃N₄ (4 mg) to the filtrate of the original C3/g-C₃N₄ system, (c) readdition of the 5 vol% TEOA acetonitrile aqueous solution (9/1, v/v) to the g-C₃N₄ residue of the original C3/g-C₃N₄ system and (d) the bare g-C₃N₄ (4 mg) in CH₃CN-H₂O (9/1, v/v) solution at pH 10.



Fig. S9 the dependence of H_2 evolution on the concentration of TEOA from 2.5 vol % to 10 vol % under the following conditions: C1 (1×10⁻⁴ M) and g-C₃N₄ (4 mg) in CH₃CN-H₂O (9/1) solution (5 mL) at pH=9.



Fig. S10 (a) H₂ production from the system containing $g-C_3N_4$ (4 mg) and C1 (1×10⁻⁴ M) in a 5 vol% TEOA acetonitrile aqueous solution at pH 9; (b) readdition of C1 (0.5 µmol) to the solution after 12 h of irradiation.



Fig. S11 Time dependence of hydrogen production using C1 and $CoCl_2$ (1×10⁻⁴ M) under the following conditions: g-C₃N₄ (4 mg) and 5 vol% TEOA in CH₃CN-H₂O (9/1) solution (5 mL) at pH=9.



Fig. S12 Cyclic voltammograms of C1 (0.5 mM), C2 (0.5 mM) and C3 (0.5 mM) in CH₃CN (0.1 M NBu₄PF₆, v = 100 mV s⁻¹)



Fig. S13 Electrochemical response of 0.5 mM C1 to addition of acetic acid in CH₃CN (0.1 M NBu₄PF₆, v = 100 mV s⁻¹)



Fig. S14 Electrochemical response of 0.5 mM C2 to addition of acetic acid in CH₃CN (0.1 M NBu₄PF₆, v = 100 mV s⁻¹)