Supporting Information

Highly active g-C_3N_4 photocatalysts modified with transition metal cobalt for hydrogen evolution

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Text S1 Materials

Boric acid (H_3BO_3), glycine ($C_2H_5NO_2$), citri acid anhydrous ($C_6H_8O_7$), sodium hydroxide (NaOH) and cobalt sulfate ($CoSO_4 \cdot 7H_2O$) were purchased from the Chengdu Kelong Chemical Reagent Ltd. Sodium hypophosphite (NaH_2PO_2) was obtained from Aladdin (Shanghai China). All the chemicals were used as received without any further purification. All the solutions were prepared with deionized water.

Text S2 Photoelectrochemical measurements

Photoelectrochemical measurements were performed using an IVIUM electrochemical analyzer (Holland). All the photoelectrochemical measurements were carried out in a three electrode system by using an electrochemical workstation under simulated solar light irradiation (LED Light，6 mW/cm^2). A glassy carbon electrode was utilized as a working electrode, platinum wire was used as the counter electrode, the reference electrode was Ag/AgCl. Typically, 2 mg catalysts, 100 μL isopropyl alcohol (IPA), 100 μL Nafion and 395 μL deionized water were mixed by sonicating for at least 30 min to form a homogeneous ink, which were then dip-coated onto the glassy carbon electrode and natural drying in air. Before testing, pure nitrogen gas was used to purge the 0.1 M Na_2SO_4 electrolyte for 30 min to keep the solution without air. The working electrodes were firstly activated for several times until the signals were stabilized and the polarization curves were recorded in 0.1 M Na_2SO_4. All measured potentials were converted to:

$$V \text{ vs. } RHE\ (E_{RHE} = E_{(Ag/AgCl)} + 0.2046 + 0.059 * pH \quad (1)$$

Fig. S1 a) photocatalytic H_2 evolution rate over Co/CN with different Co loading content, b) photocatalytic H_2 production of CNNs and Co/CN with different pH values in 6 h.

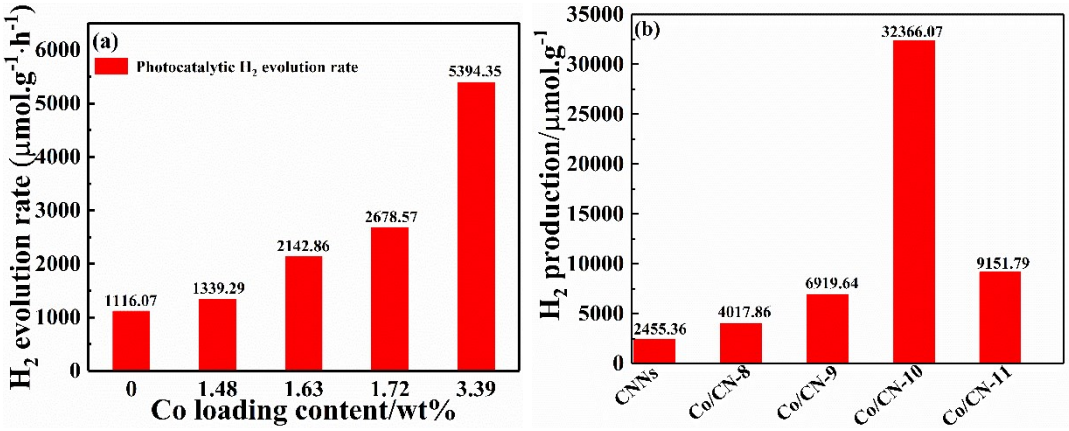

Fig. S2 (a) SEM image and (b-d) elemental mappings of Co/CN-10.

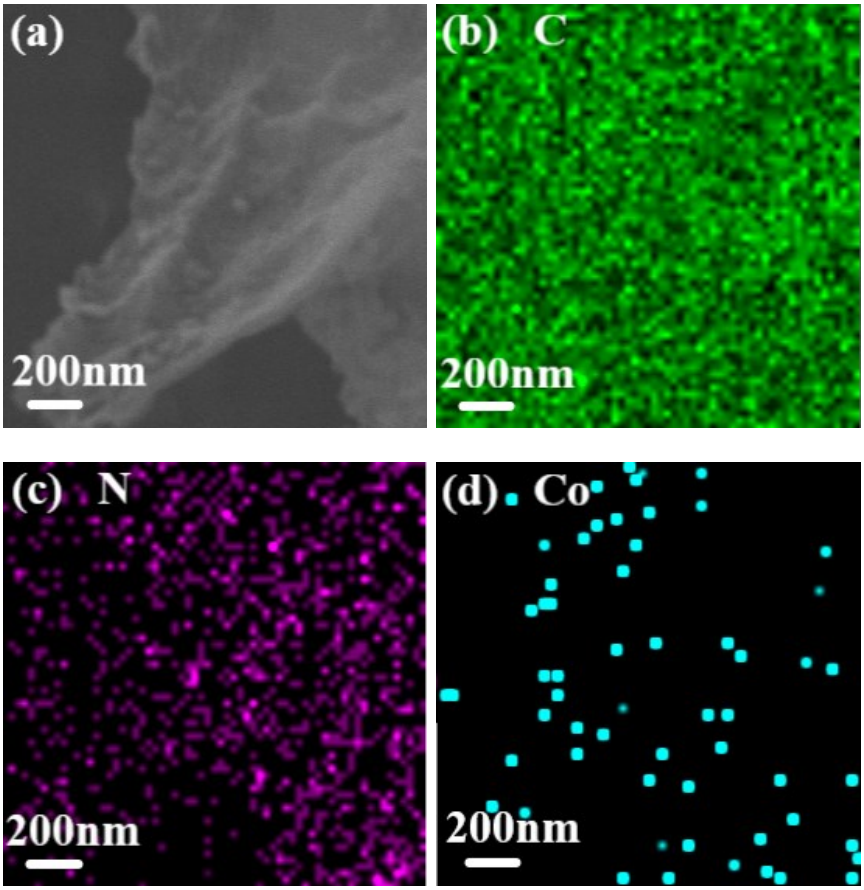

Fig. S3 SEM image of CNNs.

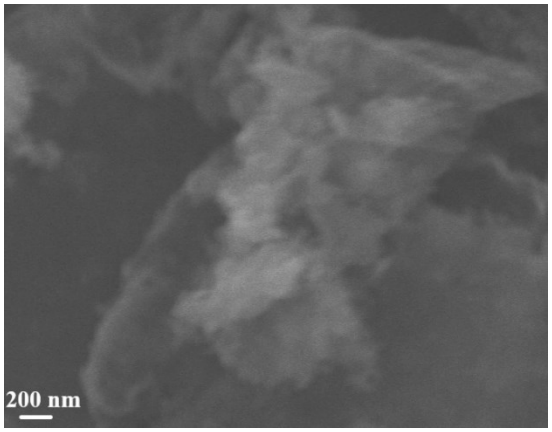

Fig. S4 XPS P 2p spectra of Co/CN with different pH values.

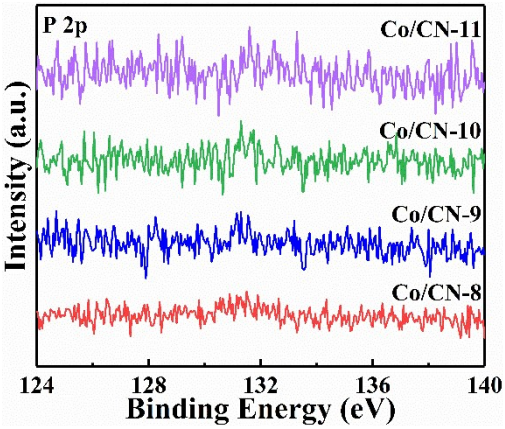

Fig. S5 The schematic diagram of the structures of Co/CN.

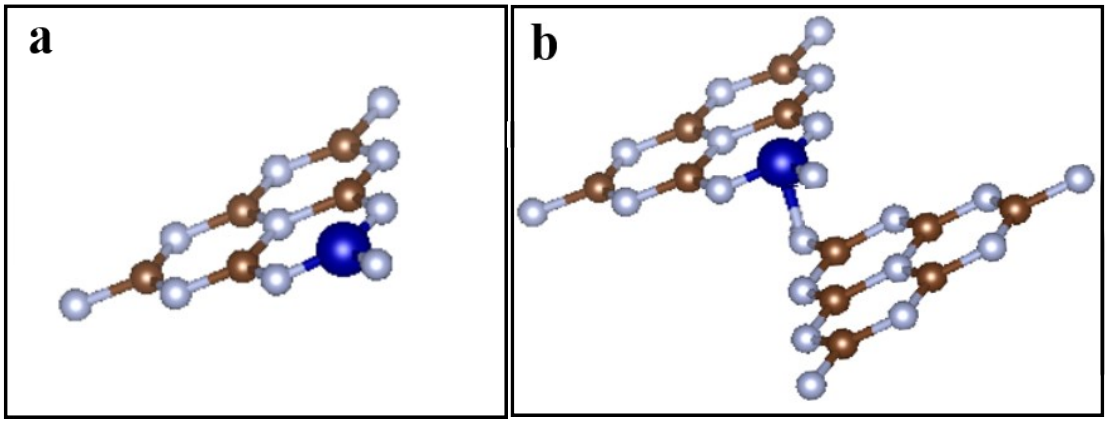

Table S1 Band gap, conduction band and valence band position of CNNs and Co/CN with different pH values.

Samples	CNNs	Co/CN-8	Co/CN-9	Co/CN-10	Co/CN-11
E_g (eV)	2.952	2.939	2.931	2.912	2.926
E_{FB} (eV)	-1.036	-1.078	-1.083	-1.112	-1.086
E_{CB} (eV)	-1.136	-1.178	-1.183	-1.212	-1.186
E_{VB} (eV)	1.816	1.761	1.748	1.700	1.740

Table S2 Fitting parameters of EXAFS spectra including coordination numbers (CN), atomic distance (R), Debye-Waller factors (σ^2), and the inner potential correction (ΔE_0).

Samples	Path	CN	R (Å)	σ^2 (10^{-3} Å^2)	ΔE_0 (eV)
Co/CN-8	Co-N	3.01	2.06 ± 0.05	0.01 ± 0.005	-1.13 ± 7.74
Co/CN-9	Co-N	1.77	2.02 ± 0.04	0.01 ± 0.007	-5.16 ± 7.71
Co/CN-10	Co-N	1.75	2.10 ± 0.02	0.002 ± 0.003	7.17 ± 6.82
Co/CN-11	Co-N	3.25	2.10 ± 0.02	0.002 ± 0.002	1.20 ± 5.05