

Supplementary material

CoFe alloy nanoparticles encapsulated in 3D honeycomb-like N-doped graphitic carbon framework for photocatalytic CO₂ reduction

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Time-resolved transient PL measurement

Fluorescence lifetime and steady-state spectrometer (FLs980, Edinburgh Instruments, UK) was used to test the steady-state lifetime photoluminescence (PL) spectrum and time-resolved photoluminescence (TRPL) spectrum, and the excitation wavelength was 384 nm. The emission decay data were fitted to a double-exponential model and the emission decay behavior is deduced through Eq. (1)

$$\tau_{avg.} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (1)$$

Where τ and A are the decay time and the relative magnitude of components, respectively, and τ_{avg} is the intensity-averaged lifetime used for an overall comparison. The fitting results show the fast decay component (τ_1 and A_1) and the minority-slow component (τ_2 and A_2), decaying from the free excited states and the bound excited states, respectively.

Photoelectrochemistry measurement

The electrochemical measurements were performed on an electrochemical workstation (CHI760C, Chinstruments, China) using a three-electrode system. A Pt foil was used as counter electrode, the Ag/AgCl electrode was used as reference electrode, and the FTO conductive glass (1×1cm), whose conductive side was coated with thin sample film, was used as the working electrode. 0.5 M Na₂SO₄ solution was used as electrolyte.

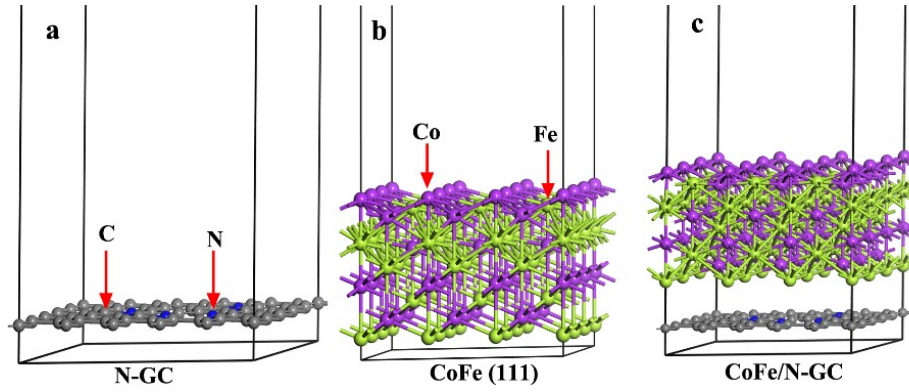


Fig. S1 Models for (a) N-GC, (b) CoFe (111) lattice plane and (c) Optimized CoFe/N-GC structure model.

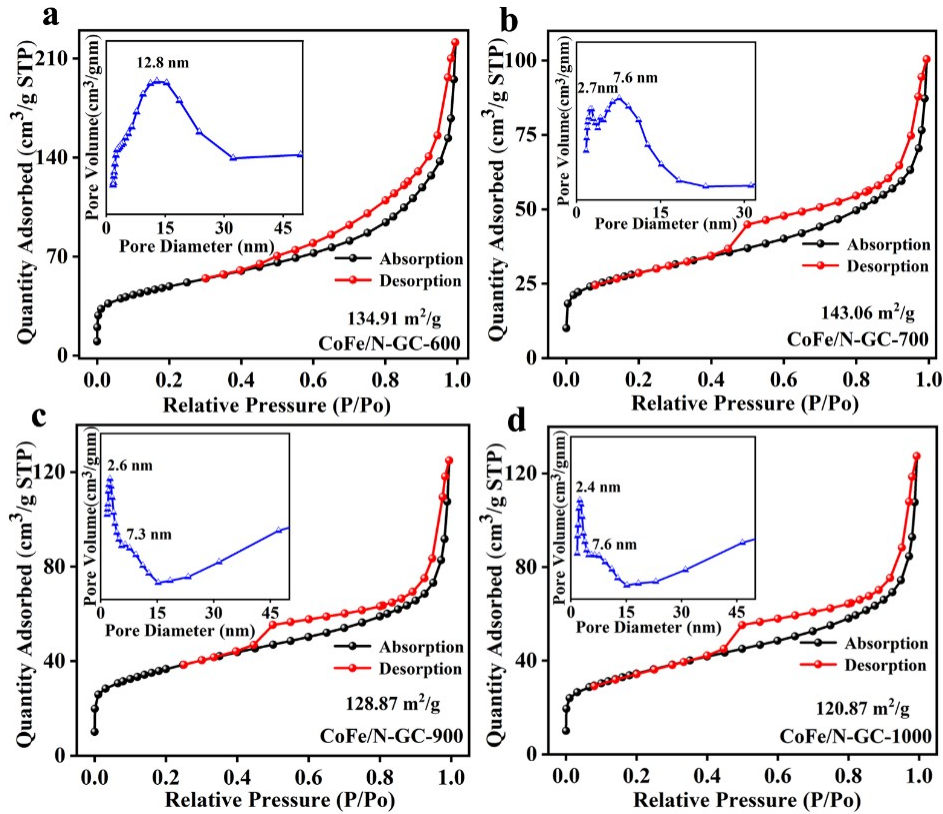


Fig. S2 (a-d) The N_2 adsorption desorption isotherms and pore size distribution (inset) of CoFe/N-GC-600, CoFe/N-GC-700 and CoFe/N-GC-900 and CoFe/N-GC-1000 respectively.

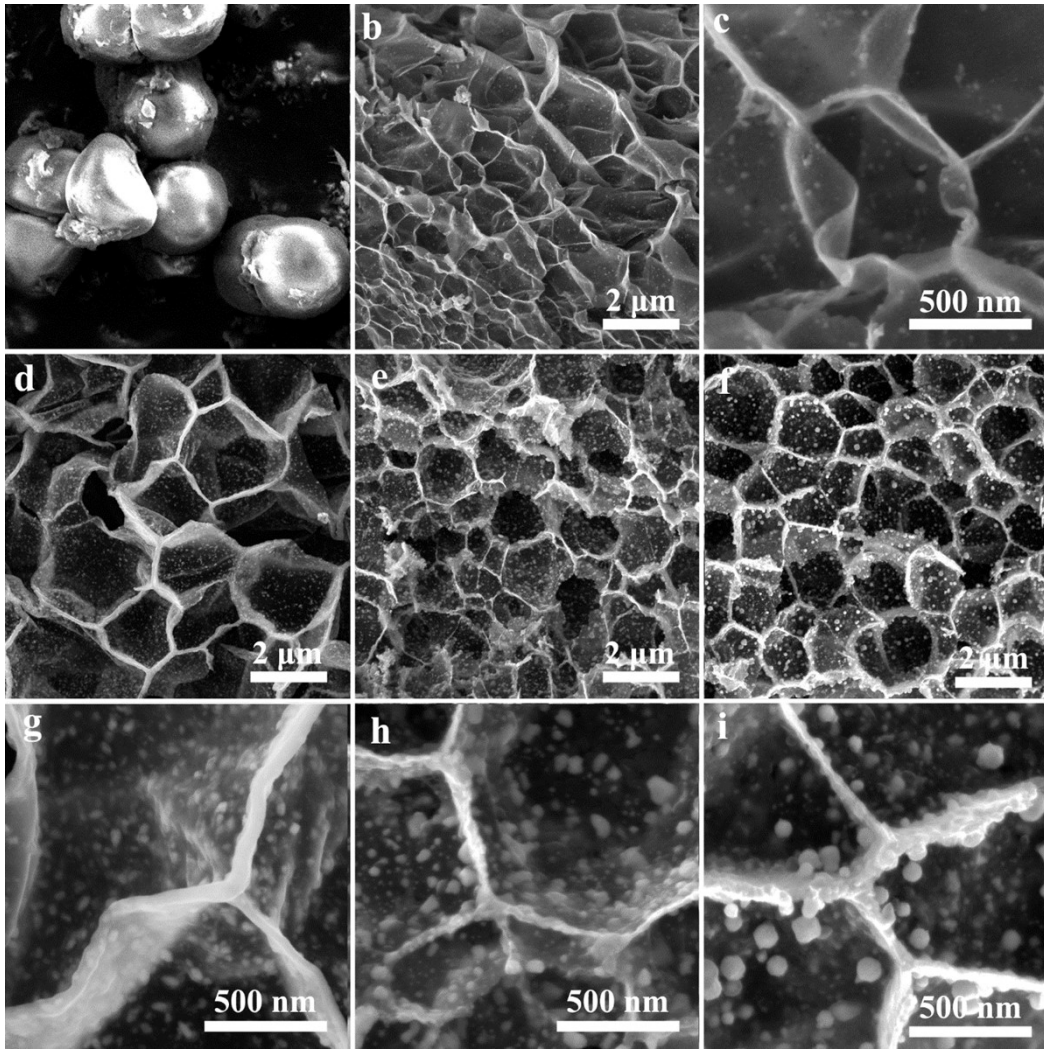


Fig. S3 The SEM images of Co^{2+} , Fe^{3+} -PVP precursor, CoFe/N-GC-600 (b, c), CoFe/N-GC-700 (d, g), CoFe/N-GC-900 (e, h) and CoFe/N-GC-1000 (f, i).

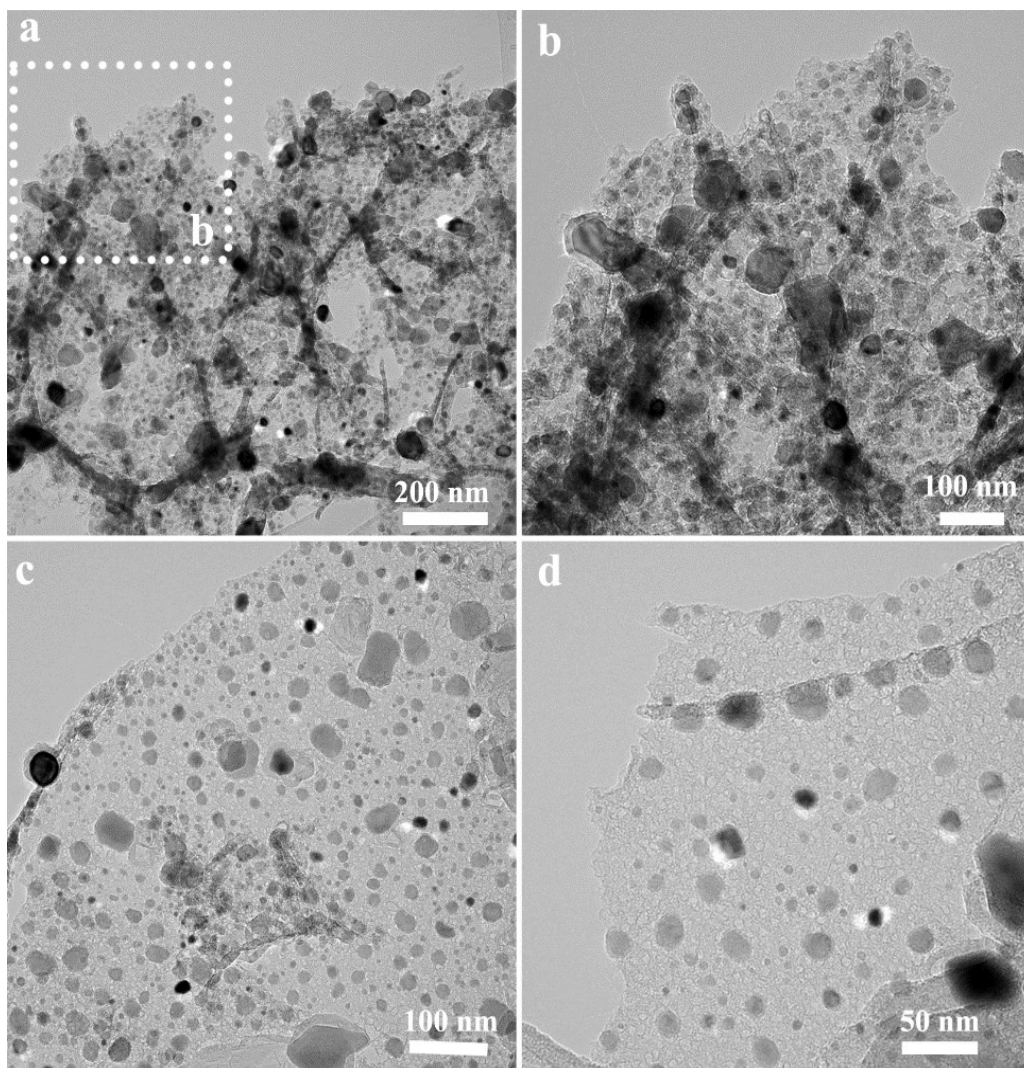


Fig. S4 (a-d) Low magnification TEM image of CoFe/N-GC-800

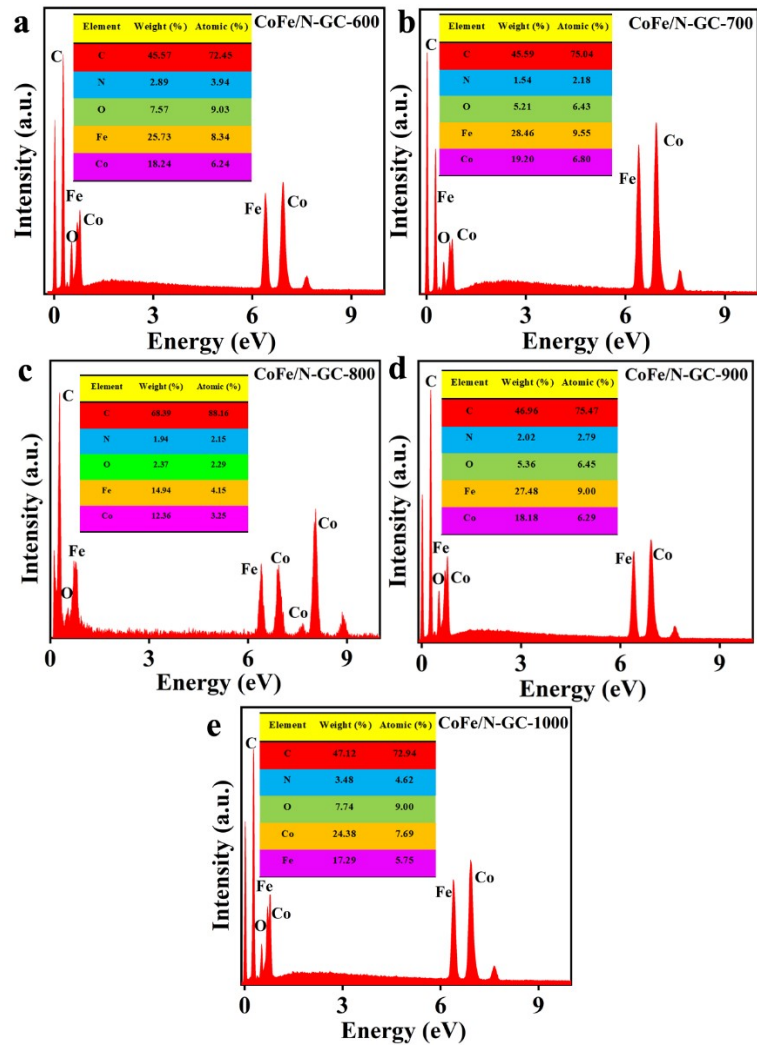


Fig. S5 EDS spectrum of CoFe/N-GC-600, CoFe/N-GC-700, CoFe/N-GC-800, CoFe/N-GC-900 and CoFe/N-GC-1000.

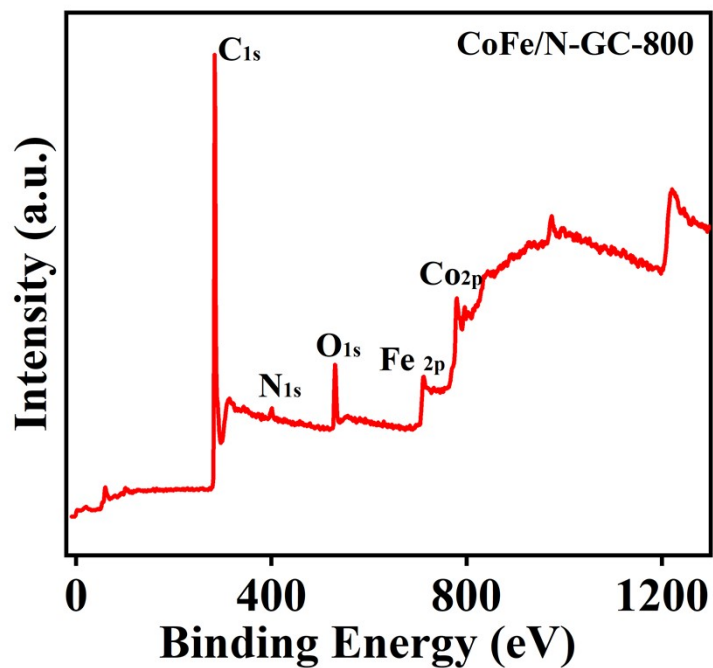


Fig. S6 The XPS survey spectra of CoFe/N-GC-800.

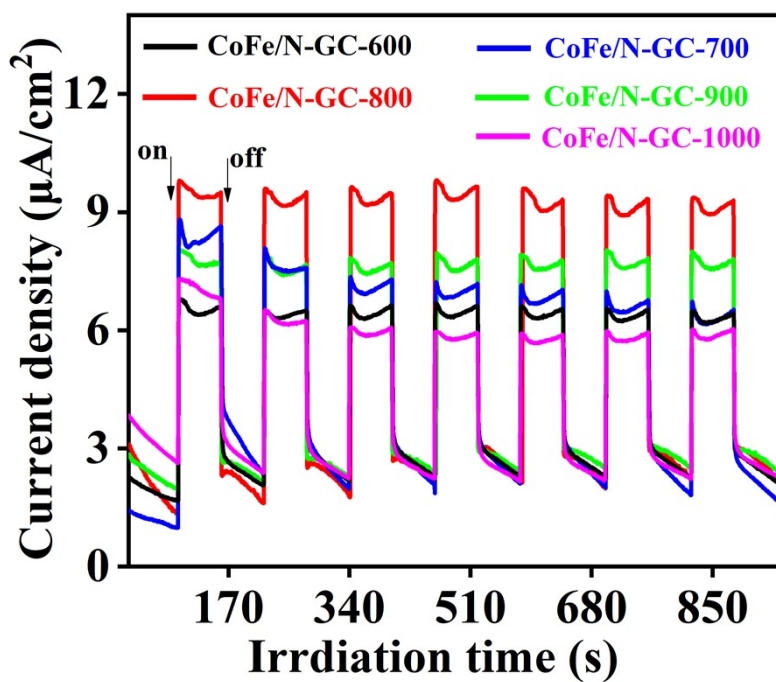


Fig. S7 Transient photocurrent responses of the obtained photocatalysts under 300 W simulated solar Xe arc lamp in 0.5 M Na_2SO_4 aqueous solution.

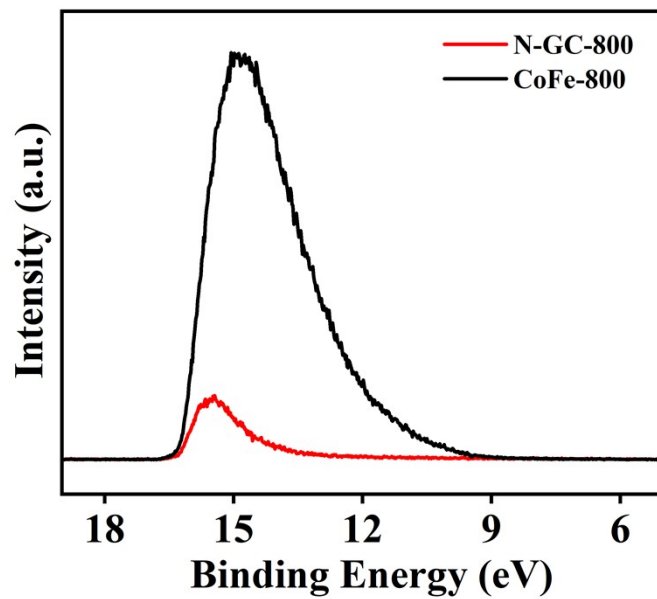


Fig. S8 UPS of N-GC-800 and CoFe-800 composite.

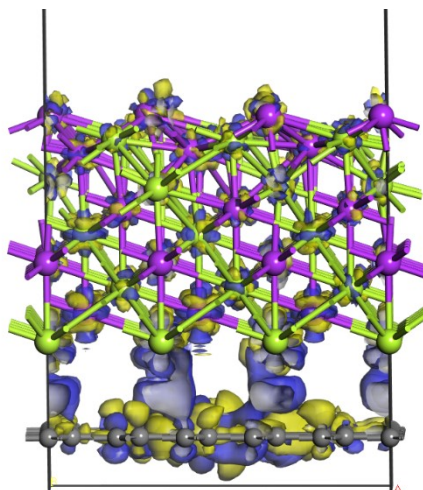


Fig. S9 The differential charge density of the N-GC and CoFe (111).

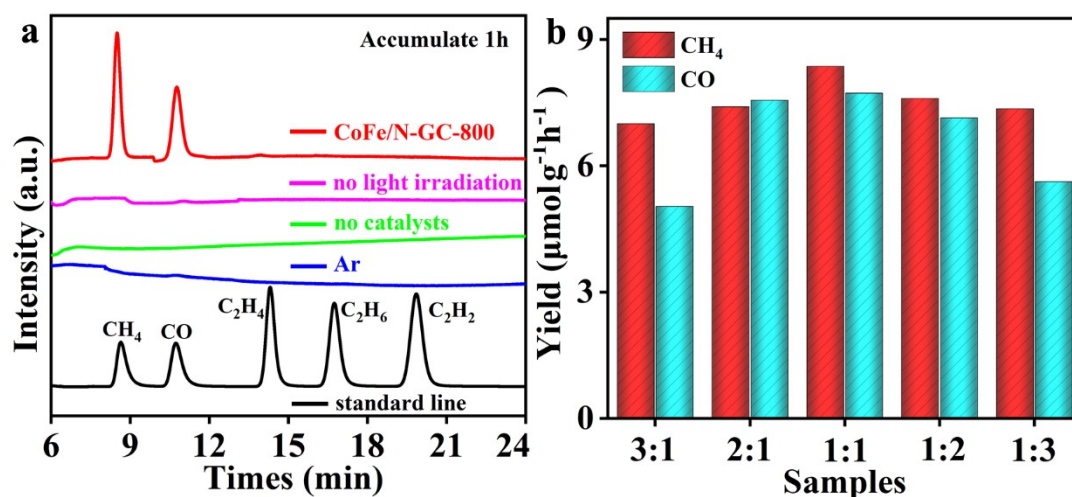


Fig. S10 (a) Comparison of gas chromatograms of the photocatalytic CO_2RR of gaseous products on the CoFe/N-GC-800 catalyst under different conditions under 1 h light irradiation. (b) Photocatalytic activity of photocatalysts with different mass ratios calcinated at $800\text{ }^\circ\text{C}$. ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : \text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O} = 3:1, 2:1, 1:1, 1:2$ and $1:3$)

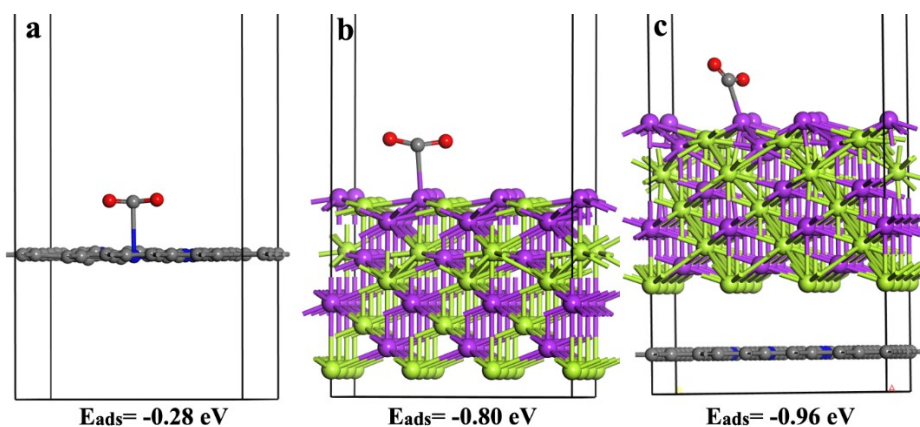


Fig. S11 Simulated CO_2 adsorption on the optimized structural (a) N-GC, (b) CoFe (111) lattice plane and (c) CoFe/N-GC.

Table S1 Fitting parameters for TRPL curves recorded for CoFe/N-GC samples.

Sample	τ_1 (ns)	% percentage	τ_2 (ns)	% percentage	τ_{avg} (ns)
CoFe/N-GC-600	0.42	0.63	0.42	0.37	0.42
CoFe/N-GC-700	0.43	0.63	0.43	0.37	0.43
CoFe/N-GC-800	0.32	0.68	0.34	0.32	0.32
CoFe/N-GC-900	0.46	0.63	0.46	0.37	0.46
CoFe/N-GC-1000	0.41	0.65	0.41	0.35	0.41