Supplementary information

WC and Cobalt nanoparticles embedded nitrogen-doped carbon 3D nanocage derived from $H_3PW_{12}O_{40}$@ZIF-67 for photocatalytic nitrogen fixation

Libo Wang, Qiu Zhang, Tingting Wei, Fengyan Li,* Zhixia Sun, Lin Xu*

Materials. 2-methylimidazole and para-(dimethy-lamino) benzaldehyde were purchased from Aladdin. $Co(NO_3)_2 \cdot 6H_2O$, $H_3PW_{12}O_{40}$, sodium citrate, salicylic acid, sodium nitrosoferricyanide, NaClO, were acquired from Sinopharm Chemical Reagent. All the reagents were used without further purification.

Characterization. The composition of the synthetic samples were analyzed by X-ray diffraction (XRD) equipment (Siemens, D5005) from 15 to 80 ° under Cu Kα radiation at applied current 100mA and accelerating voltage 30kV, diffraction scan rate used 2 °·min^{-1}. The Fourier transform infrared (FT-IR) spectrum was testing using Nicolet Magna 560 FT-IR Spectrometer. Scanning electron microscope was measured on a Hitachi SU-8000 FE-SEM to determine the surface morphology of sample, the composition also analyzed by energy dispersion X-ray spectroscopy (EDX). The internal morphology of samples were detected utilized Transmission electron microscopy (TEM) instrument (JEM-2100 PLUS). The chemical states and elemental compositions were collected through X-ray photoelectron spectrometer (XPS, Model: USWHA150) under monochromatic Al Kα radiation excitation. BELSORPmax device was applied to perceive BET surface area and pore size distribution . Raman spectra were recorded on a Renishaw Raman spectrometer system. The electrochemical measurements were measured in a typical three-electrode system with a Pt foil as the counter electrode and Ag/AgCl as the reference electrode utilize CHI661D Electrochemical Workstation. Continous Flow Analytical System (CFA, Modle: Futura V3) was used to trace NH_3 and NH_4^+. The working electrodes were established by Co/NGC and WC-Co/NGC samples, all measurement were took place in a 0.5 M solution of Na_2SO_4 electrolyte with test area of 1 cm^2.

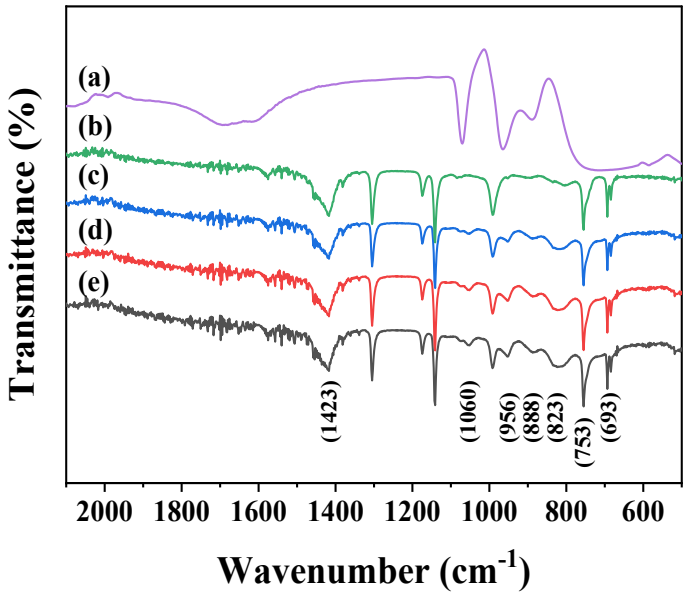

Fig. S1 FT-IR spectra of (a) PW_{12} (b) ZiF-67 (c) PW_{12}@ZIF-67-1 (d) PW_{12}@ZIF-67-2 (e) PW_{12}@ZIF-67-3

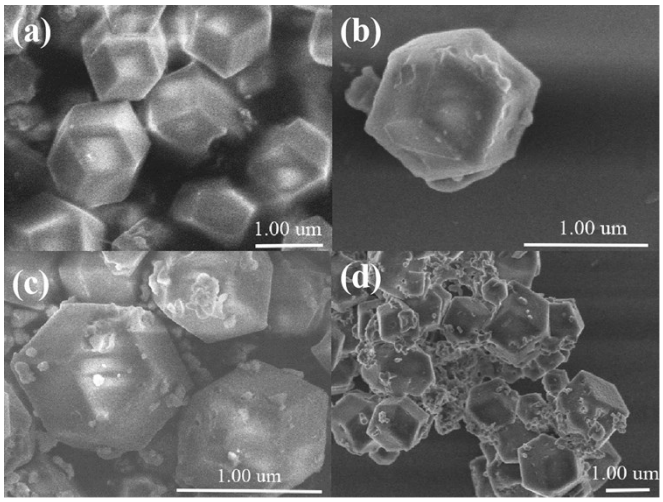

Fig. S2 SEM images of (a) ZiF-67, (b) PW_{12}@ZIF-67-1, (c) PW_{12}@ZIF-67-2 and (d) PW_{12}@ZIF-67-3.

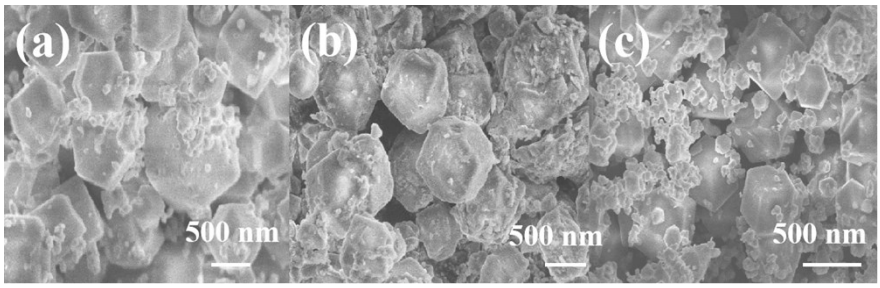

Fig. S3 SEM images of (a) PW_{12}/ZIF-67-1, (b) PW_{12}/ZIF-67-2 and (c) PW_{12}/ZIF-67-3.

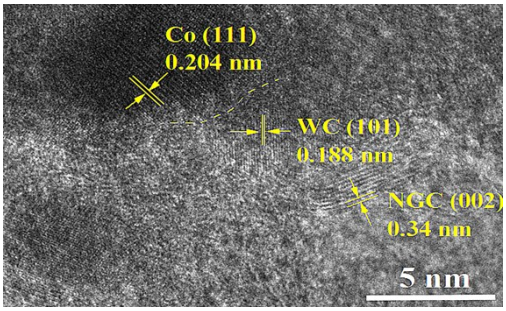

Fig. S4 High-resolution TEM images of WC-Co/NGC-2.

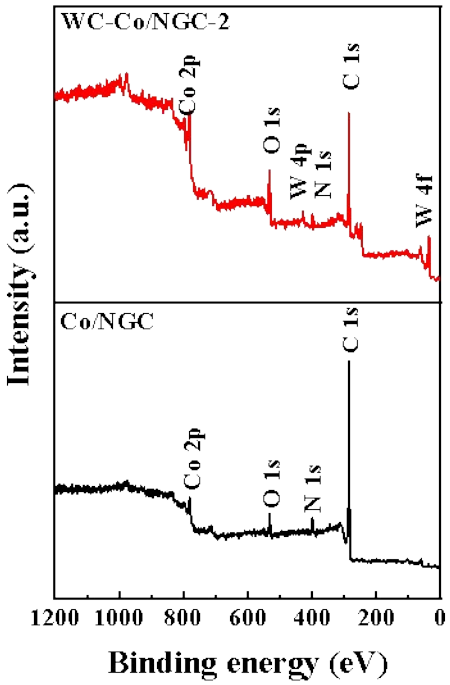

Fig. S5 XPS survey spectra of Co/NGC and WC-Co/NGC-2.

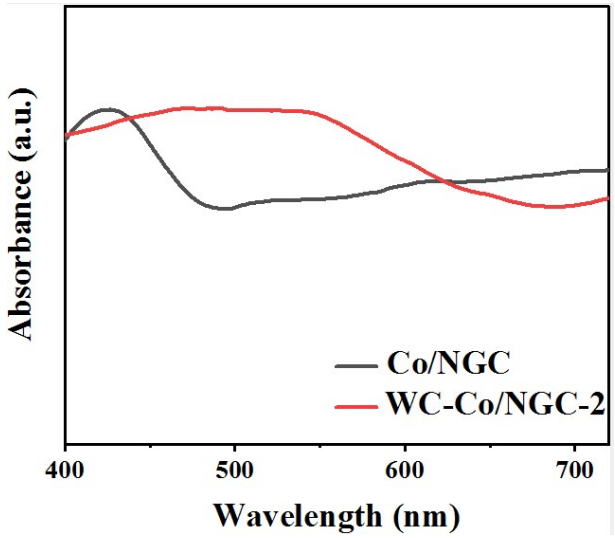

Fig. S6 UV-vis diffuse reflectance spectra of Co/NGC and WC-Co/NGC-2.

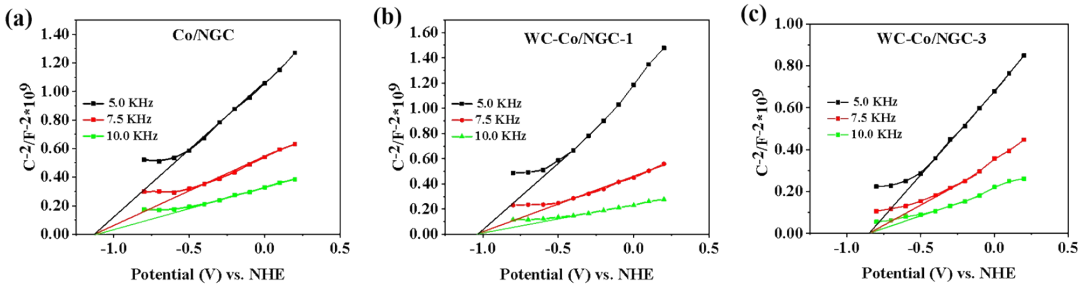

Fig. S7 Mott-Schottky curves of (a) Co/NGC, (b) WC-Co/NGC-1 and (c) WC-Co/NGC-3.

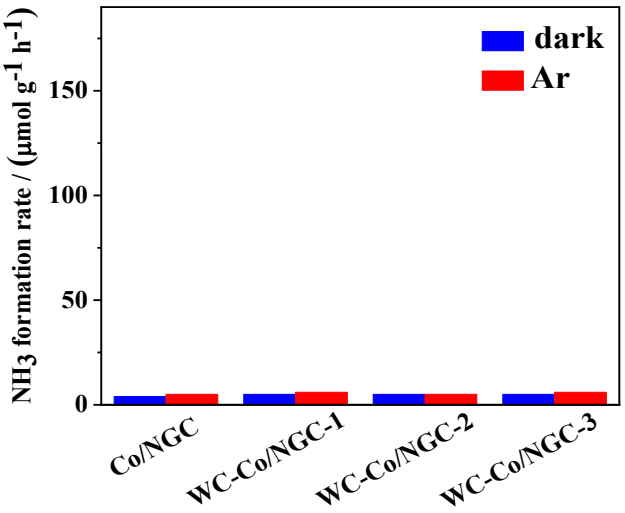

Fig. S8 NH_3 formation rate of WC-Co/NGC-2 in the atmospheres of N_2 without light and Ar under visible light.

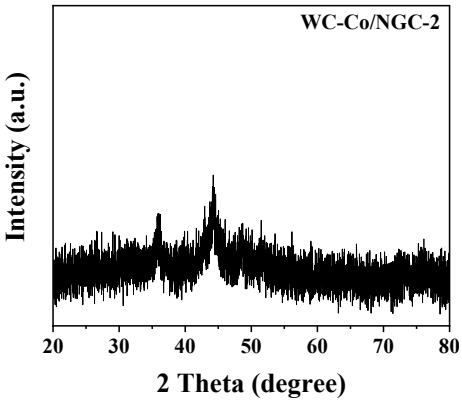

Fig. S9 XRD pattern of WC-Co/NGC-2 after the photocatalytic experiment.

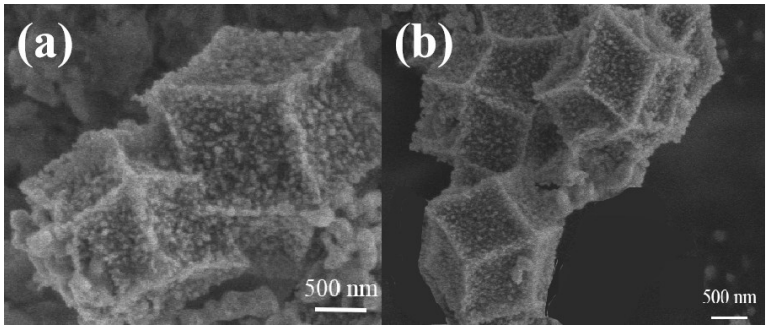

Fig. S10 SEM image of WC-Co/NGC-2 after the photocatalytic experiment.

Table S1 Analysis results of the molar percentage of W element in WC-Co/NGC-X obtained by EDS.

Catalyst	Molar percentage of W in compounds (mol %)
WC-Co/NGC-1	1.34
WC-Co/NGC-2	2.34
WC-Co/NGC-3	3.03

Table S2 Analysis results of the molar ratio of Co and W elements in WC-Co/NGC-X obtained by EDS and ICP.

Catalyst	Molar ratio of Co and W (mol %)	
	EDS	ICP
WC-Co/NGC-1	89.15 and 10.85	89.55 and 10.45
WC-Co/NGC-2	86.29 and 13.71	85.73 and 14.27
WC-Co/NGC-3	80.22 and 19.78	78.57 and 21.43

Table S3 The calculated ammonia production rates depended on different detection methods.

Catalyst	Ammonia production rate (μmol g^{-1} h^{-1})	
	Indiophenol blue	Continous Flow Analytical System
WC-Co/NGC-2	142	127