Supporting information for

Co$_4$N-WN$_x$ composite for efficient piezocatalytic hydrogen evolution

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I. Experimental section

Synthesis of CoWO$_4$ nanoparticles: 1 mmol of Co (NO$_3$)$_2$·6H$_2$O and 1 mmol of Na$_2$WO$_4$ were dissolved in 40 mL deionized water and stirred until dissolved and then transferred into a 50 mL Teflon-lined stainless-steel autoclave maintained at 180 °C for 8 h. After lowering of temperature, the CoWO$_4$ NPs are formed followed by washing with deionized water and absolute ethanol and dried at 60 °C for 6 h.

Characterization details: Piezoelectric force microscopy (PFM) images were recorded on a Dimension Icon atomic force microscope (Bruker Co., Germany) using a SCM-PIT probe with Pt/Ir coating with resonance frequency of ~75 kHz and spring constant of ~2.8 N·m^{-1}. Transmission electron microscopy (TEM) and scanning TEM (STEM) were performed using JEOL JEM-2100F TEM/STEM equipped Oxford INCA EDS detector for elemental maps. It was operated at 200 kV with a 13 mrad convergence semi-angle for the optimal probe condition. The collection inner semi-angle for HAADF detector was 46 mrad.

Piezocatalytic H$_2$ production measurements: Disperse 4 mg of the prepared sample in 10 mL of deionized water. After the sample was uniformly dispersed in water, the reaction vessel is closed. The reaction vessel was evacuated, and Ar was introduced for repeated evacuation to remove residual air. In an Ar atmosphere, the reaction vessel was sonicated with an ultrasonic cleaner (KS-100DE) with a power of 120 W and a frequency of 40 kHz. We change the water every half an hour to keep the water temperature at about 25 °C, since piezocatalysis is rather temperature sensitive.[1, 2] After 1 h of ultrasound, use a gas chromatograph (Scion GC7900, Ar as carrier gas) with a thermal conductivity detector (TCD) to detect the generated H$_2$.

Piezocatalytic degradation measurements: Disperse 4 mg of powder sample CWN-750 in an aqueous solution of RhB (10 mL, 5 mg L^{-1}), and continuously stir for 60 min before sonication to achieve adsorption and desorption equilibrium. Then transfer to the ultrasonic cleaner for ultrasonic treatment with 120 W power and 40 kHz frequency, and change the ultrasonic time for 15 min, 30 min, 45 min and 60 min. After the end of the ultrasound, a gas chromatograph (Scion GC7900, Ar as carrier gas) with a thermal conductivity detector (TCD) was used to detect the generated H$_2$. Take 5 mL of the suspension, centrifuge and take the supernatant, and use the ultraviolet-visible spectrophotometer (UV–vis DRS, Hitachi U-3900, Japan) to measure the absorbance of the RhB solution. The degradation rate of RhB solution can be calculated by the following formula:

Degradation (%) = (1—C/C$_0$)*100%

C$_0$ indicates the absorbance of the initial solution, and C indicates the absorbance of the solution after reaction.

Piezocatalytic active material detection: The same amount of catalyst was dispersed in the aqueous solution of RhB (10 mL, 5 mg L^{-1}) and stirred in the dark for 60 min. Then the corresponding capture agent is added to the reaction mixture. Next, the reaction mixture is treated with ultrasonic as described previously. Take 5 mL of the suspension, centrifuge and take the supernatant, and use the ultraviolet-visible spectrophotometer to measure the absorbance of the RhB solution.

The terephthalic acid scavenger (TA) and sodium hydroxide (NaOH) are mixed to prepare a colorless aqueous solution. Disperse 8 mg of CWN-750 sample into 20 mL of the above solution. Under the same vibration conditions, 3 mL samples were taken every 5 min and centrifuged to obtain the supernatant. When the free radicals react with the TA solution, the TA solution is converted to 2-hydroxyterephthalic acid (HTA), which is measured on a French fluorescence spectrometer (FL3-111) with an excitation wavelength of 310 nm. The wavelength of fluorescence produced by ·OH is 425 nm.

Use potassium iodide (KI) and potassium hydrogen phthalate (C$_8$H$_5$KO$_4$) to determine the content of H$_2$O$_2$. Mix the catalyst with deionized water, and the operation method is consistent with the requirements of piezocatalytic H$_2$ production measurements. After sonicating for 1 hour, take 5 mL of the suspension and centrifuge to take 1 mL of the supernatant.

Usually, 1 mL of 0.1 mol L^{-1} $C_8H_5KO_4$ aqueous solution and 1 mL of 0.4 mol L^{-1} potassium iodide (KI) aqueous solution are added to the resulting solution and let stand for 30 min to react completely ($H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$). Since I_3^- has a strong absorption peak at 350 nm, the content of hydrogen peroxide was measured with the UV–Vis spectrometer.

Piezocatalytic H_2O_2 production measurements: 6 mg of powder sample CWN-750 in 15 mL of deionized water is dispersed. After the sample was uniformly dispersed in water, the reaction vessel is closed. The reaction vessel was evacuated, and Ar was introduced for repeated evacuation to remove residual air. Then the contents are transferred to the ultrasonic cleaner for ultrasonic treatment with 120 W power and 40 kHz frequency, and change the ultrasonic time for 15 min, 30 min, 45 min and 60 min. The temperature of piezocatalytic medium was kept at around 25 ℃ by changing the water every half an hour. After the end of the ultrasonication, 2 mL of the suspension is taken, centrifuged and then the supernatant is collected. Subsequently ultraviolet-visible spectrophotometer is used to measure the absorbance of the H_2O_2.

Electrochemical measurements: The electrochemical tests were performed on an electrochemical workstation (CHI760E, CH Instrument) with a conventional three-electrode battery. The Pt plate was used as the counter electrode, and the Ag/AgCl electrode was used as the reference electrode. The working electrode was prepared on the rotating ring-disk electrode (RRDE). The electrode material was prepared by dispersing 4mg of catalyst and 1 ml of mixed solution, the mixed solution was made by mixing 25 μL of Nafion solution, 250 μL of ethanol and 750 μL of water. Then the mixture was sonicated at room temperature for 60 minutes (i.e, a paste-like suspension was formed) to obtain a slurry. Then, 10 μL of slurry was applied to the rotating ring disk electrode. The working electrode was further dried at 40 °C for 10 minutes to improve adhesion. The exposed area of the working electrode is 0.196 cm^2. The electrochemical impedance spectroscopy (EIS) measurements were performed in 0.1 M aqueous Na_2SO_4 solution by applying an AC voltage with -1.4 V amplitude in a frequency range from 100000 Hz to 1 Hz. The polarization curve is performed in the same above mentioned three-electrode system, while the bias sweep range is from -1.6 to -0.6 V vs Ag/AgCl the electrolyte was 0.1 M aqueous Na_2SO_4 solution. All potentials are calibrated on a reversible hydrogen electrode (RHE). The equation used is as follows:[3]

$$R_{(RHE)} = R_{(Ag/AgCl)} + 0.197 + 0.059PH$$

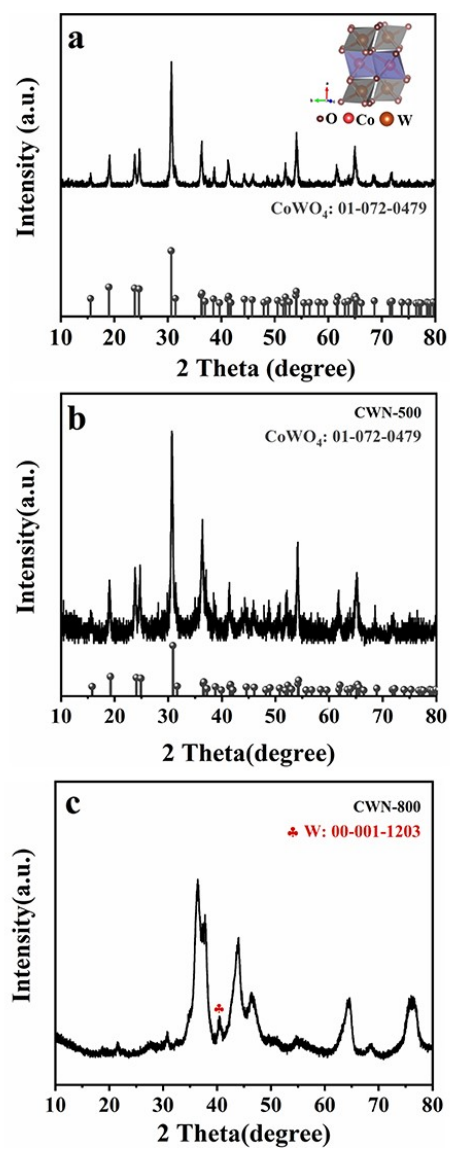# II. Supplementary illustrations and explanations

Fig. S1 XRD pattern of (a) CoWO$_4$. (The inset is the model of CoWO$_4$); (b) CWN-500 and (c) CWN-800.
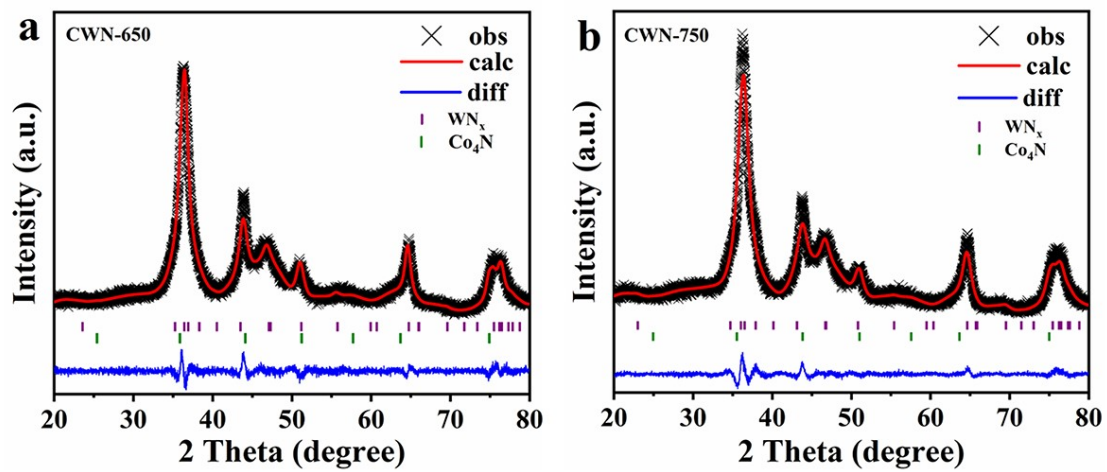
Fig. S2 The rietveld-fitted XRD pattern of (a) CWN-650 nanoparticles and (b) CWN-750 nanoparticles.
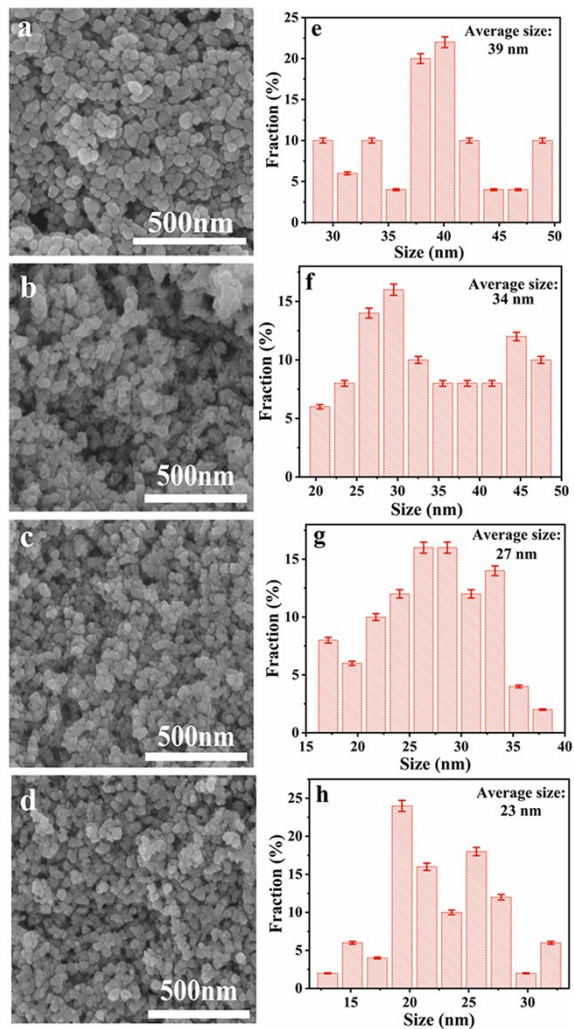
Fig. S3 SEM images of (a) CoWO₄, (b) CWN-550, (c) CWN-650 and (d) CWN-750; The diameters statistic histogram of (e)

CoWO₄, (f) CWN-550, (g) CWN-650 and (h) CWN-750.

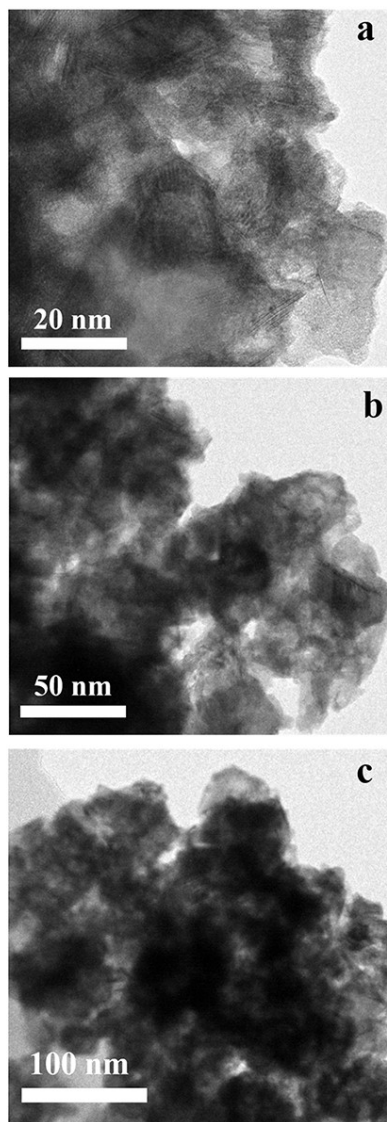**Fig. S4** (a-c) Typical TEM images of CWN-550 at different magnifications.
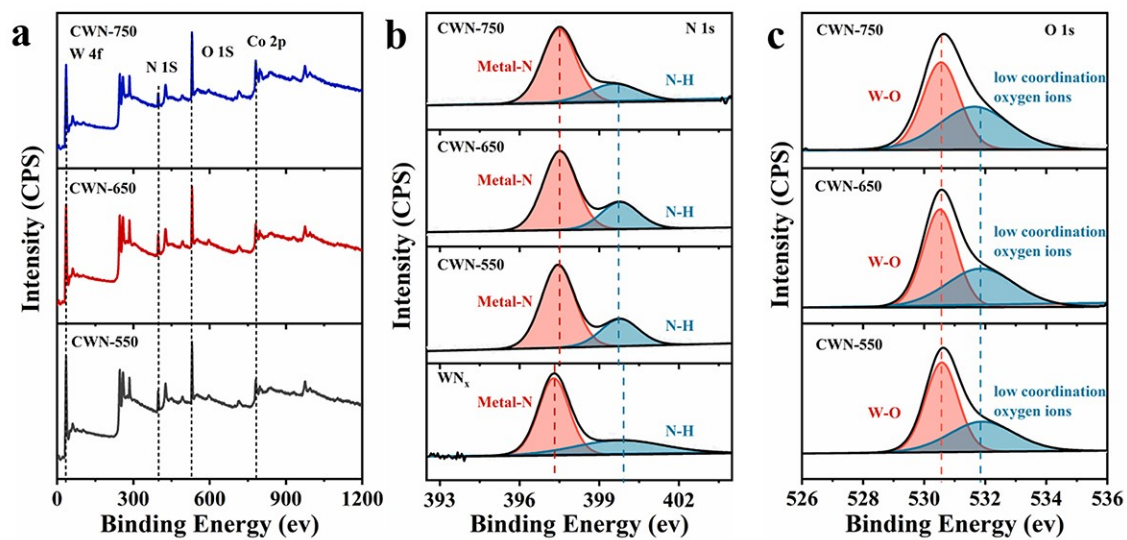
Fig. S5 (a) XPS survey spectra, high resolution (b) N 1s and (c) O 1s XPS spectra of different CWN-based samples.

Note: The peak at 530.5 eV in the O 1s spectra can be related to the W-O bond, and the peak at 531.6 eV can be attributed to the presence of low-coordination oxygen ions on the surface (Fig. S5c).[4, 5]
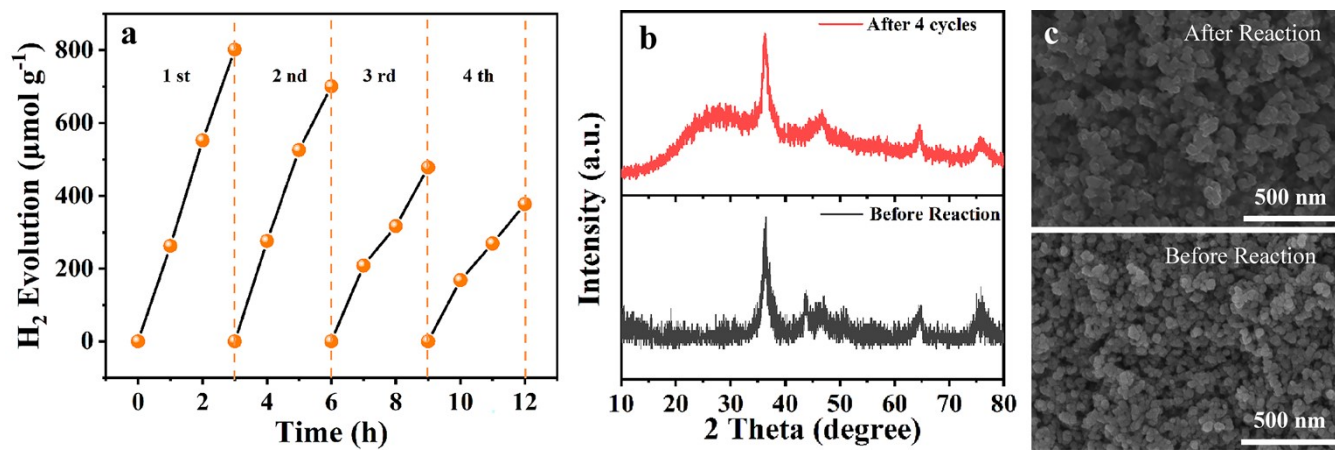
Fig. S6 (a) The cyclic test of piezocatalytic H_2 production over the CWN-750. (b) The XRD pattern of the CWN-750 sample before and after stability test. (c) The SEM image of the CWN-750 sample before and after stability test.
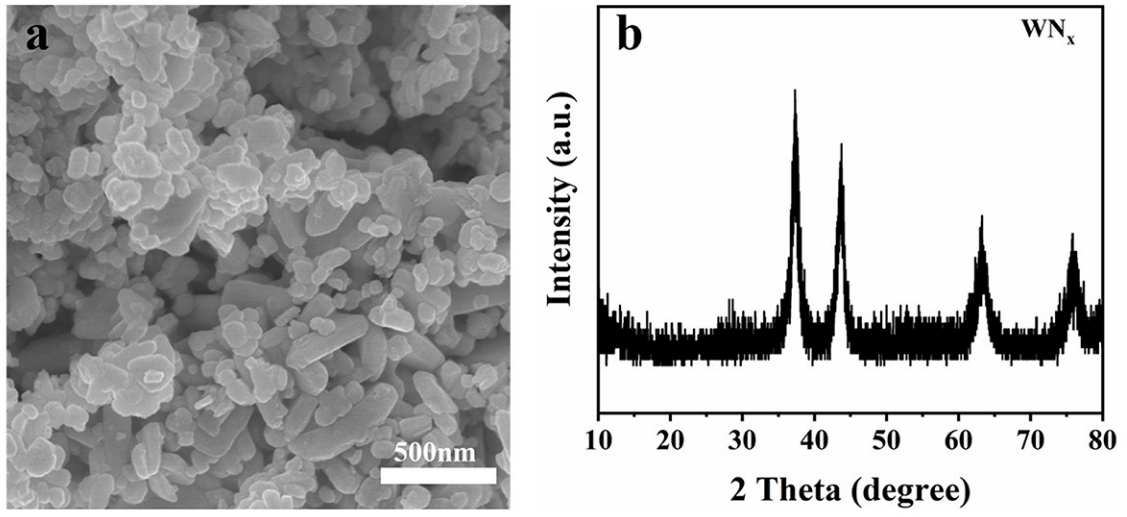
Fig. S7 (a) SEM image and (b) XRD pattern of WN$_x$.
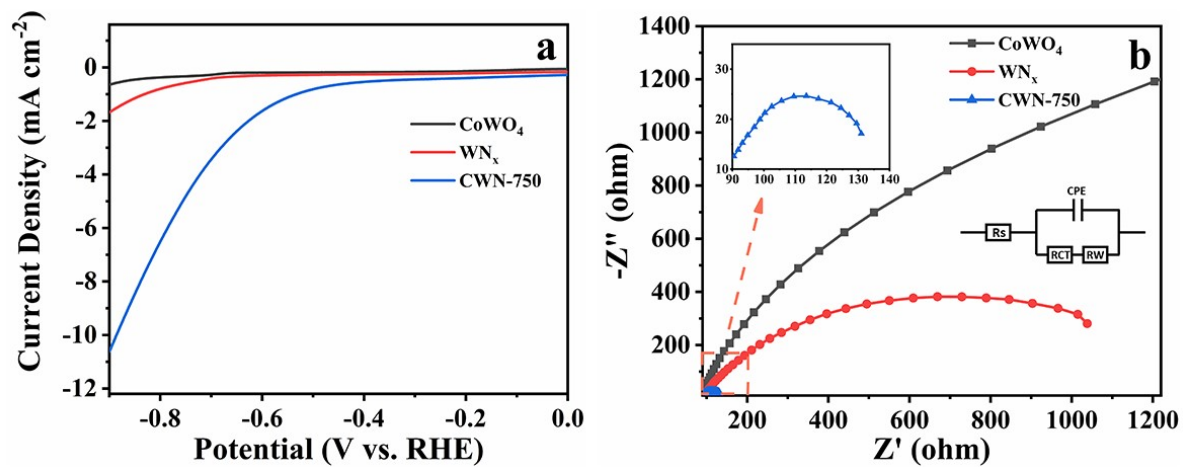
Fig. S8 (a) Polarization curves and (b) electrochemical impedance spectra of CoWO$_4$, WN$_x$ and CWN-750.
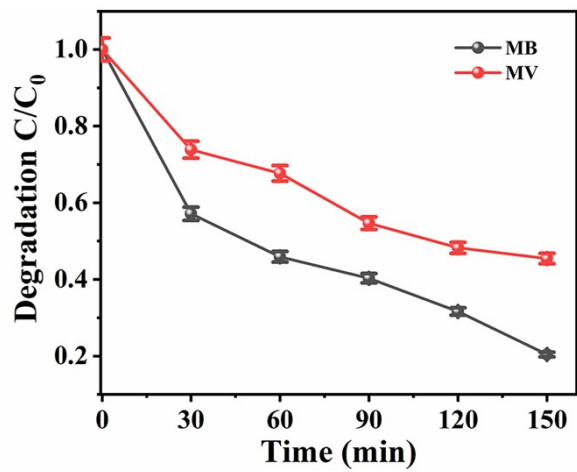
Fig. S9 Piezoelectric catalytic degradation of MB and MV dye by CWN-750.
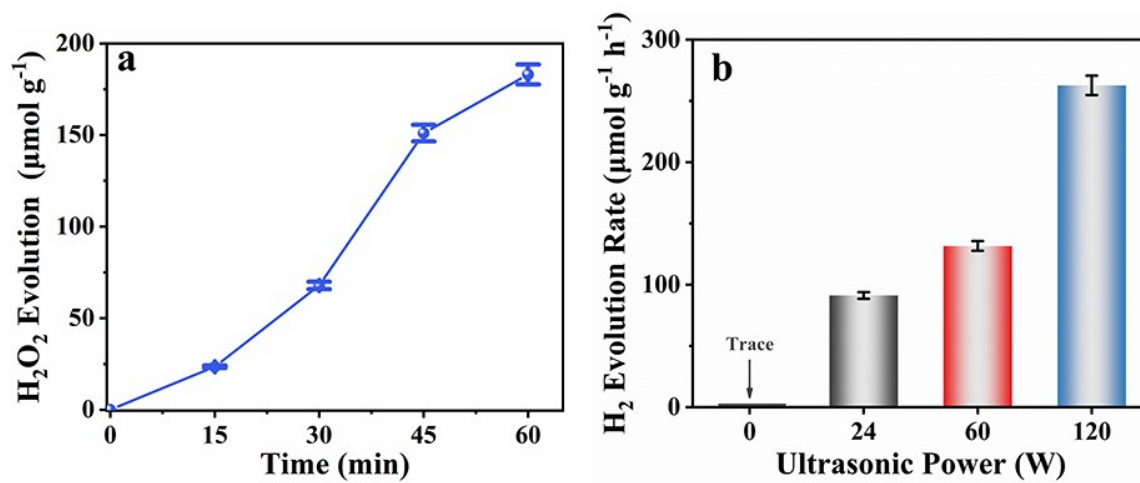
Fig. S10 (a) The ultrasonic hydrogen peroxide production of CWN-750 after ultrasonication for 15 min, 30 min, 45 min and

60 min; (b) Hydrogen evolution performances of CWN-750 under different ultrasonic power.

Table S1. Unit cell lattice parameters and molar ratio of Co_4N and WN_x in various CWN-based samples.

| Sample	Phase name	Lattice parameters							
		a (nm)	b (nm)	c (nm)	α (°)	β (°)	γ (°)	V (nm³)	molar ratio
CWN-550	WN_x	2.8965	2.8965	15.6314	90.00	90.00	120.00	113.57	0.13
	Co_4N	3.5952	3.5952	3.5952	90.00	90.00	90.00	46.47	0.87
CWN-650	WN_x	2.9036	2.9036	15.5852	90.00	90.00	120.00	113.79	0.15
	Co_4N	3.6074	3.6074	3.6074	90.00	90.00	90.00	46.94	0.85
CWN-750	WN_x	2.8856	2.8856	15.5336	90.00	90.00	120.00	112.01	0.23
	Co_4N	3.5834	3.5834	3.5834	90.00	90.00	90.00	90.00	0.77

Table S2. Indices of crystal face and interplanar distances (d) of Co_4N and WN_x in CWN-550 nanoparticles.

Co₄N				WNₓ			
H	K	L	d (nm)	H	K	L	d (nm)
1	0	0	0.360	0	0	4	0.392
1	1	0	0.254	0	0	6	0.262
1	1	1	0.210	1	0	0	0.251
2	0	0	0.180	1	0	1	0.250
2	1	0	0.161	1	0	2	0.239
2	1	1	0.147	1	0	3	0.227
2	2	0	0.127	1	0	4	0.211
2	2	1	0.120	1	0	5	0.196
3	0	0	0.120	0	0	8	0.196
				1	0	6	0.181
				10	0	7	0.167
				1	0	10	0.157
				1	0	8	0.155
				1	1	0	0.145
				1	0	9	0.143
				1	1	2	0.142
				1	1	4	0.136
				0	0	10	0.133
				1	0	12	0.131
				2	1	6	0.127
				2	0	0	0.125
				2	0	1	0.125
				2	0	2	0.124
				1	0	11	0.124
				2	0	3	0.122

Table S3. Comparison of piezocatalytic hydrogen production performance over previous reported piezocatalysts and CWN nanoparticles in this work.

Piezocatalysts	Catalytic Conditions	Sacrificial Agents	H_2 production	Ref.
$KNbO_3/MoS_2$ heterostructures	Ultrasonic vibration (110 W, 40 kHz)	Triethanolamine (15 vol%)	50.8 $\mu mol \cdot g^{-1} \cdot h^{-1}$	6
$BiFeO_3$ nanosheets	Ultrasonic: 100 W, 45 kHz	Na_2SO_3 (0.05M)	124.1 $\mu mol \cdot g^{-1} \cdot h^{-1}$	7
WSe_2 nanosheets	Ultrasonic vibration (110 W, 40 kHz)	Fe^{2+} (0.01 M)	11.3 $\mu mol \cdot g^{-1} \cdot h^{-1}$	8
WS_2 nanosheets	Ultrasonic vibration (110 W, 40 kHz)	Fe^{2+} (0.01 M)	14.8 $\mu mol \cdot g^{-1} \cdot h^{-1}$	8
MoS_2 nanosheets (acidification treatment)	Ultrasonic vibration (280 W, 40 kHz)	Fe^{2+}	70 $\mu mol \cdot g^{-1} \cdot h^{-1}$	9
Bi_2WO_6 nanosheets	ultrasonic: 40 kHz	TEOA (20% v/v)	191.3 $\mu mol \cdot g^{-1} \cdot h^{-1}$	10
CWN-750 nanoparticles	**Ultrasonic vibration (120 W, 40 kHz)**	**None**	**262.7 $\mu mol \cdot g^{-1} h^{-1}$**	**This work**

III. Supplementary References

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