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Supporting information

Tin chloride metal salt modified carbon nitride for efficient hydrogen and hydrogen peroxide production from pure water via piezocatalysis

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Experimental Section

Materials

Hydrogen peroxide (H_2O_2, 35%), hydrochloric acid (HCl, 37%), melamine ($C_3H_6N_6$, >98%, TCI), potassium iodide (KI, >99.5%, Merck Darmstadt), ammonium heptamolybdate tetrahydrate ($H_{32}Mo_7N_6O_{28}$, >99%), 1,4-Benzoquinone ($C_6H_4O_2$, >98%, Acros Organics), isopropanol (C_3H_8O), potassium chloride (KCl, > 99%, Fisher), tin chloride ($SnCl_2$，98%). All chemicals are used in experiments without further purification.

Samples preparation

Preparation of M: 2 g of melamine powder was placed in a covered crucible and heated in a furnace at 500 °C for 4 h under ambient atmosphere at a heating rate of 5 °C min^{-1}. The furnace was then cooled down naturally, and the yellow product obtained was collected and milled into fine powder to get CN.

Preparation of M-0.5Sn: 2 g of melamine and 4.35 g of $SnCl_2$ were mixed thoroughly in a mortar and then transferred into a covered crucible. The mixture was heated in a furnace at 500 °C for 4 h under ambient atmosphere at a heating rate of 5 °C min^{-1}. The furnace was then cooled down naturally, and the yellow product obtained was collected and washed with 1M HCl three times before it was dried at 90 °C overnight. M-Sn and M-0.25Sn were prepared through the same processes, except that the amount of $SnCl_2$ in the mixture changed to 8.70 g and 2.18 g for M-Sn and M-0.25Sn, respectively.

Preparation of M-0.5Sn-N_2: 2 g of melamine and 4.35 g of $SnCl_2$ were mixed thoroughly in a mortar and then transferred into a covered crucible. The mixture was heated in a furnace at 500 °C for 4 h under a nitrogen atmosphere at a heating rate of 5 °C min^{-1}. The furnace was then cooled down naturally, and the yellow product obtained was collected and washed with 1M HCl three times before it was dried at 90 °C overnight.

Preparation of CN-0.5Sn: 2 g of M and 4.35 g of $SnCl_2$ were mixed thoroughly in a mortar and then transferred into a covered crucible. The mixture was heated in a furnace at 500 °C for 4 h under ambient atmosphere at a heating rate of 5 °C min^{-1}. The furnace was then cooled down naturally, and the yellow product obtained was collected and washed with 1M HCl three times before it was dried at 90 °C overnight.

Preparation of M-0.5KSn: 2 g of melamine, 4.35 g of $SnCl_2$, and 0.65 g of KCl were mixed thoroughly in a mortar and then transferred into a covered crucible. The mixture was heated in a furnace at 500 °C for 4 h under ambient atmosphere at a heating rate of 5 °C min^{-1}. The furnace was then cooled down naturally, and the yellow product obtained was collected and washed with 1M HCl three times before it was dried at 90 °C overnight.

Materials Characterization

The crystallization of the samples was examined by an X-ray Diffractometer (XRD, Shimadzu 700) with Cu-K_α radiation (λ = 0.154 nm) in the range of 2 - 80°. The bonding states of the samples were tested by using an ATR Fourier-transform infrared spectroscope (FTIR, Spectrum Two, Perkin Elmer GmbH) in the range of 4000-450 cm^{-1} at ambient temperature and atmospheric pressure. The samples were used as such, without any previous pretreatment. A scanning electron microscope instrument (SEM, Zeiss Neon 40) was used to characterize the surface morphologies and microstructures of the samples. Energy dispersive X-ray incorporated with an ultra dry detector from Thermo Fisher Scientific was used to check the elemental distribution of the optimal samples. The samples were applied on top of a carbon pad and coated with ~5 nm Au for better conductivity via a sputter coater (SCD 500 model from BAL-TEC) before SEM testing. The high-resolution images of the samples were taken by transmission electron microscopy (TEM, JEOL ARM200CF) at an acceleration voltage of 200 kV. The samples were well dispersed in ethanol via ultrasonication before being dropped onto a copper grid for TEM testing. The composition of the non-metal elements was tested by a MICRO cube CHNOS elemental analyzer (Elementar Analysensysteme GmbH) in the CHNS mode and a 2mgChem80s Method. The compositions of the metal elements were tested by direct current plasma-atomic emission spectroscopy (DCP-AES, ARL Fisons SS-7), which involved dissolving the solid samples (~0.25 g) in aqua regia for digestion.

Piezo-current response testing

The electrochemical analysis utilized the MPG-2 electrochemical workstation in a three-electrode configuration. The working electrode was prepared as follows: 10 mg of the catalyst was dispersed in a mixture of ethanol (0.45 mL), water (0.5 mL), and Nafion solution (50 µL). An appropriate amount of the resulting suspension was drop-cast onto carbon paper to achieve a mass loading of 0.5 mg cm^{-2}. The catalyst-coated carbon paper was used as the working electrode. An Ag/AgCl electrode and a Pt wire served as the reference and counter electrodes, respectively. The electrolyte was 1 M KOH. The piezo-current response was evaluated by chronoamperometry. A constant potential of 0 V (vs. RHE) was applied, and the resulting current was recorded. Each ultrasound cycle consisted of 10 seconds on followed by 30 seconds off.

Piezoelectric effect testing

All measurements were performed by a commercial Asylum Research MFP-3D system at room temperature under ambient conditions. For SSPFM measurements, commercial silicon tips with conductive Ti/Ir coating (ASYELEC.01-R2, Asylum Research) were used. In the PFM measurements, a conductive ITO substrate was used and properly grounded to minimize potential measurement artifacts. The inverse optical lever sensitivity has been calibrated, and the Q factor of each sweeping curve at the resonance frequency has been subtracted to obtain the effective piezoresponse coefficients.

Piezocatalytic performance testing

Piezocatalytic production of hydrogen: In a run of the piezocatalytic hydrogen production process, the catalyst powder (10 mg) was first dispersed in 25 mL of pure water in a flask and then ultrasonicated for 5 min for good dispersion. After that, the dispersion was bubbled with Ar for 20 min and then sealed with a rubber stopper and parafilm. The fully sealed flask with the suspension was then inserted into an ultrasonic bath and exposed to ultrasonic vibration for a certain time (from 0.5 to 2 h). During the ultrasonication, the temperature of the ultrasound bath was controlled to be 17 °C using a cooling system. The experiments were all done in the dark. The gas produced was periodically withdrawn with a syringe and examined by gas chromatography (GC). To characterize the catalyst after the piezocatalytic reaction, the suspension was washed with water and centrifuged after 2 h of ultrasonication. The obtained solid was then dried in an oven at 90 ℃ overnight for XRD, FTIR, and XPS measurements.

Piezocatalytic production of hydrogen peroxide: In a run of the piezocatalytic hydrogen peroxide production process, catalyst powder (10 mg) was first dispersed in 25 mL of pure water in a flask and then ultrasonicated for 5 min for good dispersion. After that, the dispersion was sealed with parafilm. The fully sealed flask with the suspension was then inserted into an ultrasonic bath and exposed to ultrasonic vibration for a certain time (from 0.5 to 2 h). During the ultrasonication, the temperature of the ultrasound bath was controlled to be 17 °C using a cooling system. The experiments were all done in the dark. Samples were collected at different reaction times, centrifuged to separate the catalyst and subjected to H_2O_2 quantification.

Control experiments in Fig. S8: The control experiment under N_2 was done by bubbling the dispersion with N_2 for 20 min before the flask was fully sealed with parafilm. For other control experiments, benzoquinone (BQ, 3 mg) or isopropanol (IPA, 100 µL) was added to the dispersion before ultrasonication. The rest of the processes were as described above.

H_2O_2 quantification was conducted with 500 µL supernatant collected at different reaction times. After centrifugation to separate the catalyst, the aliquot was mixed with 2 mL 0.1 M KI solution and 50 µL 0.01 M $H_{32}Mo_7N_6O_{28}$ solution. The concentration of H_2O_2 was determined by analyzing the absorbance of the mixed solution at 352 nm after diluting it five times on an ultraviolet-visible spectrometer (UV-Vis, PerkinElmer Lambda).

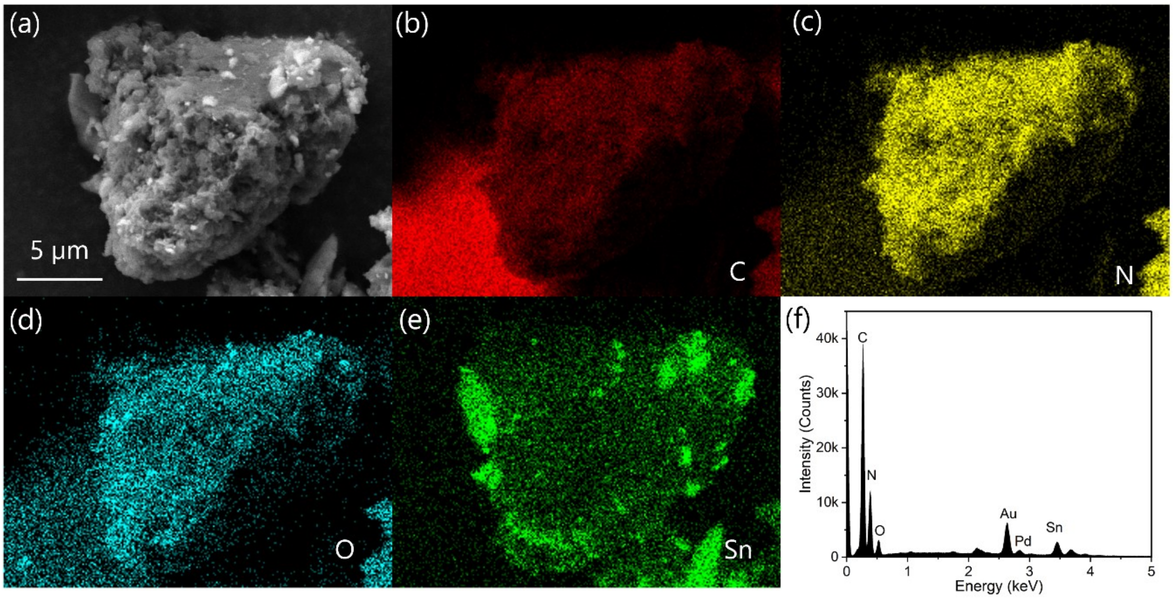

Fig. S1 SEM-EDS elemental mapping of M-0.5Sn. (a) SEM image in grey, (b) carbon, (c) nitrogen, (d) oxygen, (e) tin and (f) EDS spectra of the sample.

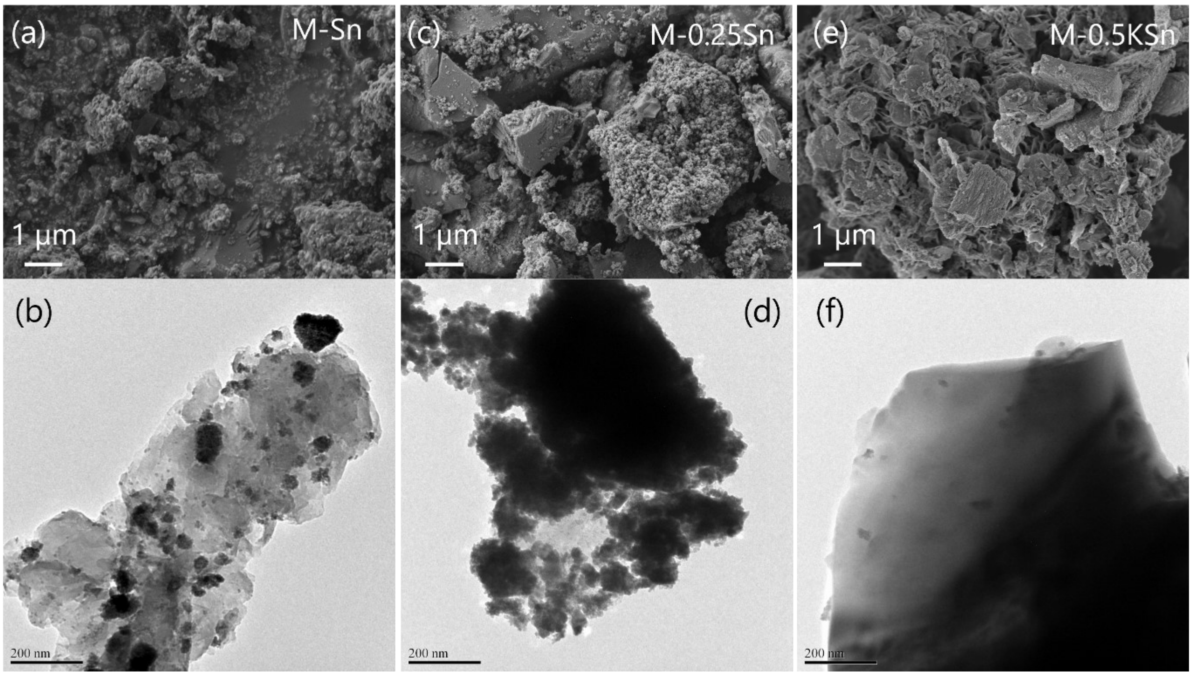

Fig. S2 Morphologies of (a-b) M-1.0Sn, (c-d) M-0.25Sn and (e-f) M-0.5KSn.

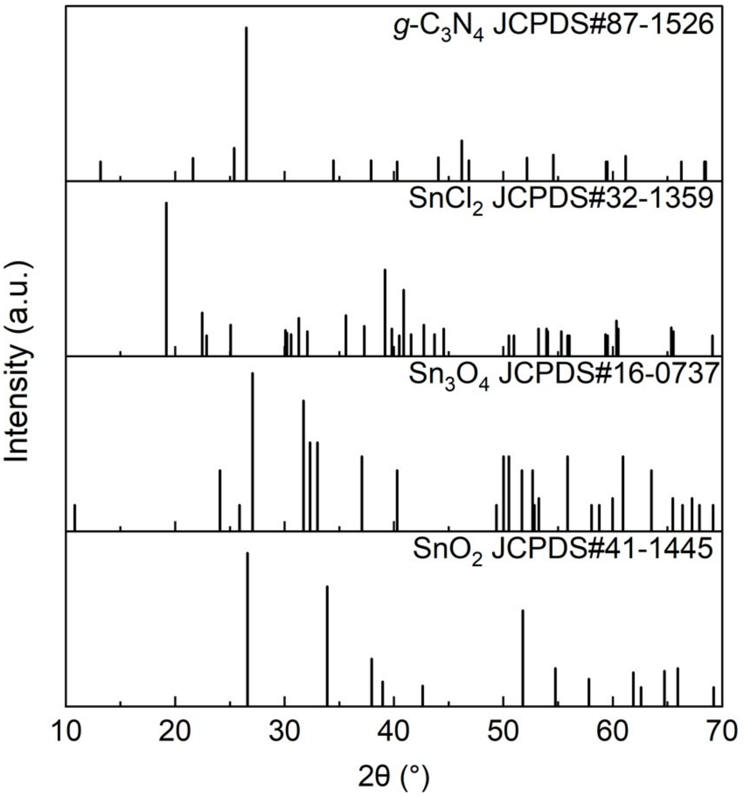

Fig. S3 XRD patterns of *g*-C_3N_4 (JCPDS#87-1526), $SnCl_2$ (JCPDS#32-1359), Sn_3O_4 (JCPDS#16-0737), and SnO_2 (JCPDS#41-1445).

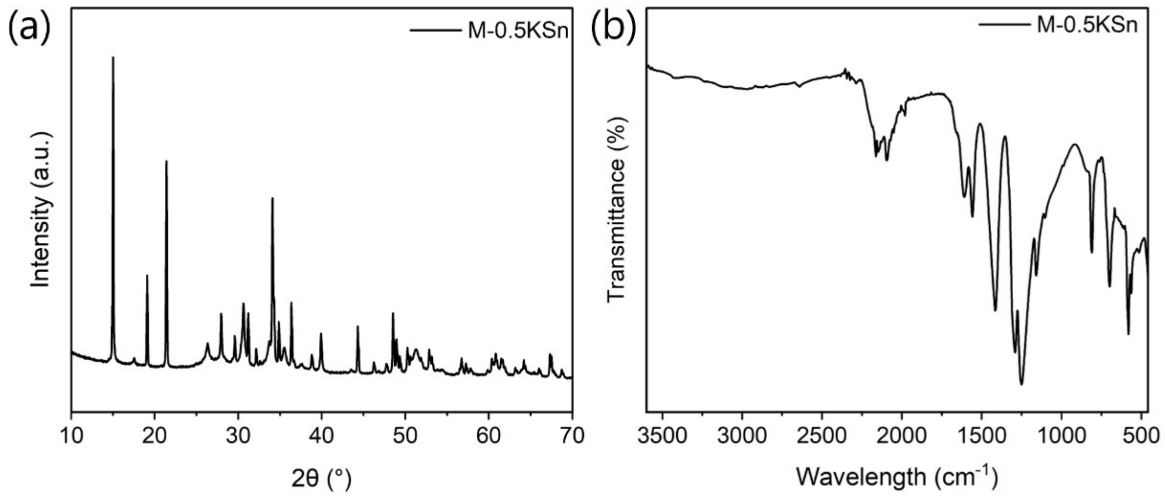

Fig. S4 (a) XRD pattern and (b) FTIR spectrum of M-0.5KSn.

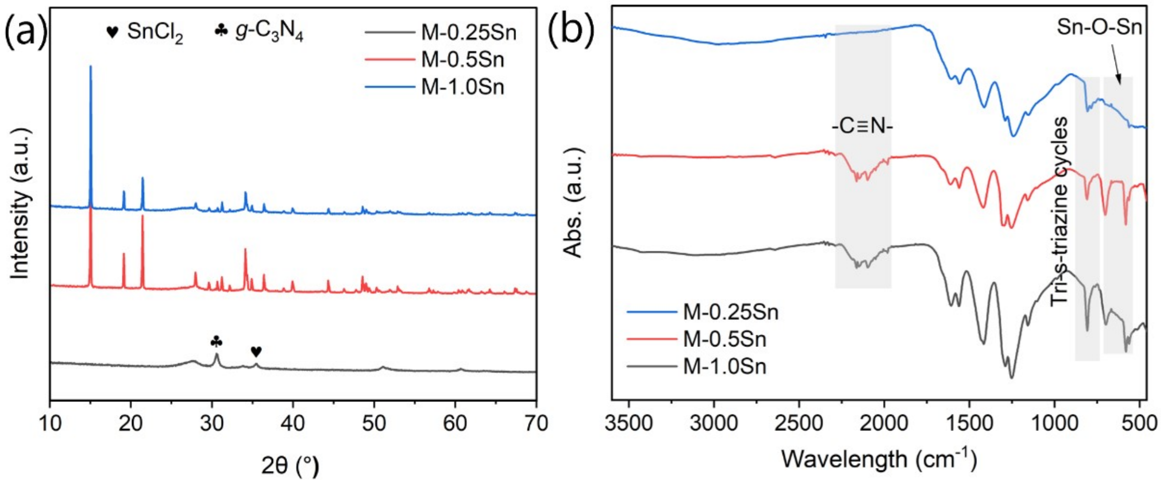

Fig. S5 (a) XRD patterns and (b) FTIR spectra of M-1.0Sn, M-0.5Sn, and M-0.25Sn.

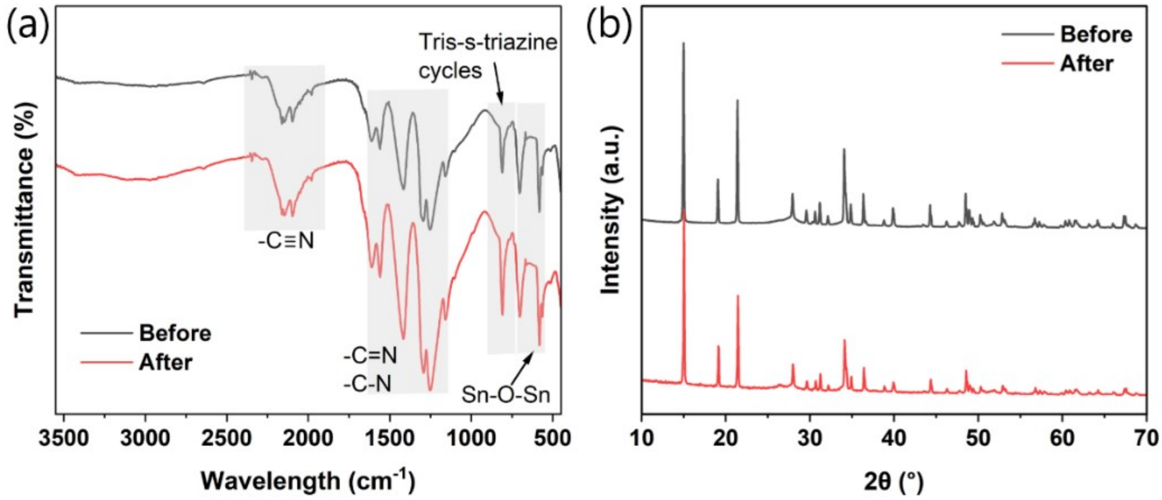

Fig. S6 (a) FTIR spectra and (b) XRD patterns of M-0.5Sn before and after catalytic reaction.

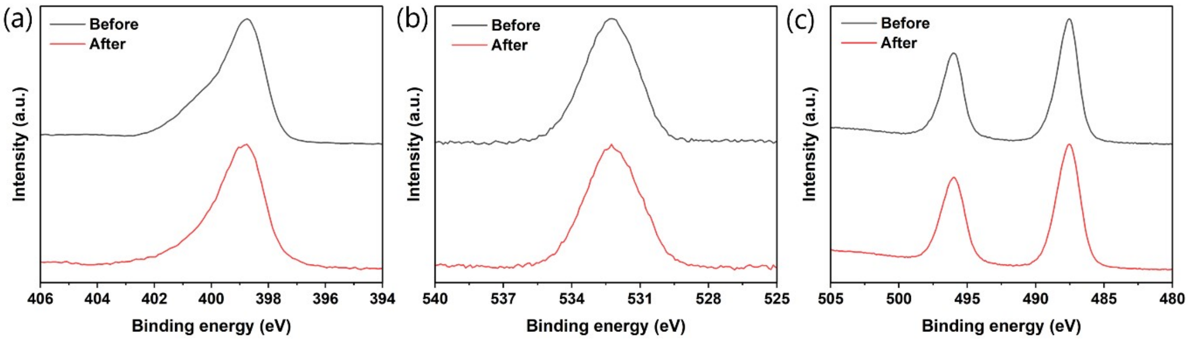

Fig. S7 High-resolution XPS spectra of a) N 1s, b) O 1s, and c) Sn 3d of M-0.5Sn before and after catalytic reaction. The XPS measurements for Fig. S6 were performed using an Omicron ESCA+ system from Omicron NanoTechnology GmbH with monochromatized Al Kα X-ray radiation (1486.3 eV) with a spot diameter of 0.6 mm and a hemispherical analyzer (base pressure < 10^{-9} mbar). Recording of the spectra occurred at a pass energy of 100 eV (survey), or 20 eV (narrow scans), at an angle of 60 ° to the sample surface. In the XPS preparation, the materials were applied onto carbon pads. For data processing, the software Casa XPS was applied with charge correction utilizing the C 1s signal.

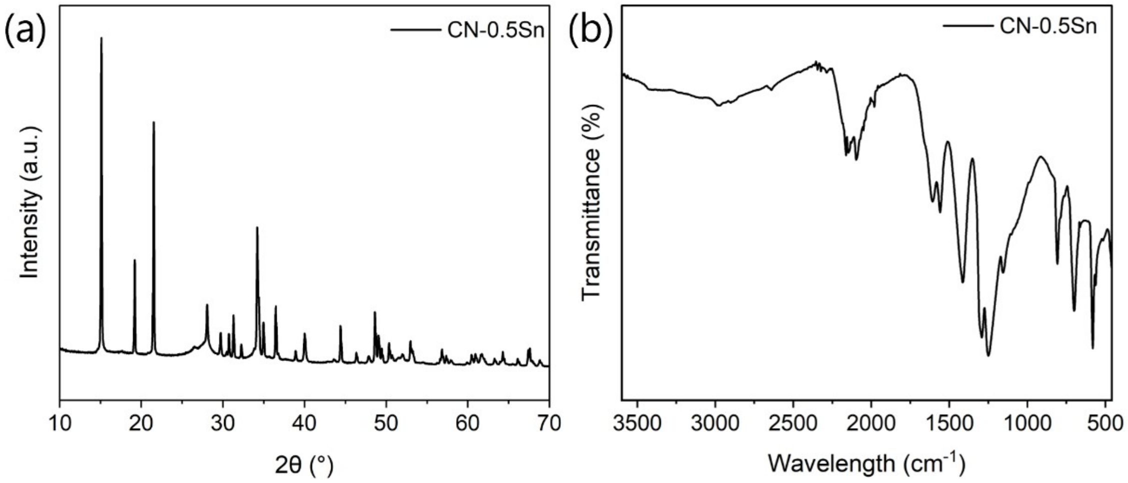

Fig. S8 (a) XRD pattern and (b) FTIR spectrum of CN-0.5Sn.

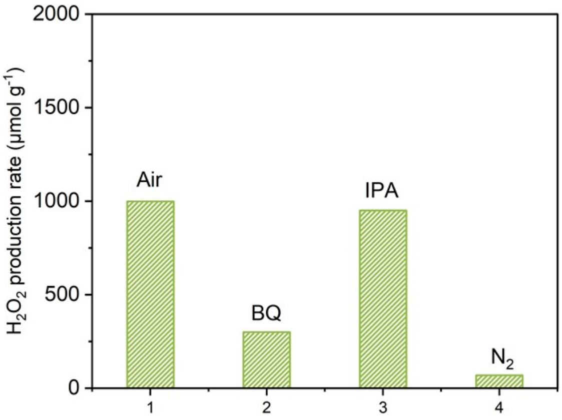

Fig. S9 H_2O_2 evolution rate of M-0.5Sn tested under different conditions for 1 h.

Table S1. Carbon (C) and nitrogen (N) compositions according to EDX in weight % and metals according to ICP in weight %.

Sample	**Composition wt.%**			**ICP (wt.%)**	
	C	**N**	**H**	**K**	**Sn**
M	33.995	59.89	2.03	-	-
M-0.5KSn	13.32	26.55	1.37	0.0335	37.2305
M-Sn	17.34	31.99	1.57	0.0024	32.8257
M-0.5Sn	20.58	37.67	1.67	0.0009	25.6337
M-0.25Sn	7.81	12.56	-	0.019	44.8034
M-0.5Sn-N_2	29.09	49.52	2.8	0.0441	0.7751

Table S2. Comparison of the piezocatalytic performances of catalysts in reported works and this study.

Catalysts	**Piezocatalytic condition**	**H_2 evolution rate (µmol g^{-1} h^{-1})**	**H_2O_2 production rate (µmol g^{-1} h^{-1})**	**Ref.**
M-0.5Sn	80 W, 40 kHz	3846.46	999.11	**This work**
CN-1BT	80 W, 40 kHz	4427.2	809	[1]
N-TiO_2@C NSs	200 W, 45 kHz	390	/	[2]
P-C_3N_4/PVDF-HFP	300 W, 40 kHz Ethanol as an additive	/	33.43	[3]
BIO/CN	120 W, 40 kHz	/	1299	[4]
Cv/Nv-C_3N_4	150 W, 53 kHz	/	680	[5]
UiO-66(Zr)-F4	110 W, 40 kHz	178	/	[6]

References

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