

Supplementary Material

Enhancement NiTiO₃ piezocatalytic hydrogen evolution by doping large radius elements

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1. Experimental section

1.1. Materials and reagents

All salts and other chemicals were of the highest purity available from commercial sources without further purification. DI water (18.25 MΩ·cm) applied in all the experiments was attained from a Molecular Lab Water Purifier.

1.2. Synthesis of NiTiO₃

Dissolve 0.03mol urea in 60ml ethylene glycol and keep stirring for 30minutes, slowly add 0.01mol tetra butyl titanate and stir continuously until the solution is clear, then 0.01mol nickel acetate was added and stirred for two hours to form a light green colloidal solution. The obtained colloidal solution was added to a 100ml Teflon-lined reactor, and the solvent-thermal reaction was carried out at 160°C for 6 hours. The light blue precursor was obtained by washing with ethanol and deionized water several times after centrifugation. After drying in oven at 70°C for 24 hours, the precursor was calcined at 600°C for 5 hours to obtain nickel titanate yellow powder.

1.3. Synthesis of M-NiTiO₃

The synthesis of M-NiTiO₃ is similar to original NiTiO₃, dissolve 0.03mol urea in

60ml ethylene glycol and keep stirring for 30minnutes, slowly add 0.01mol tetra butyl titanate and stir continuously until the solution is clear, then 0.0095mol nickel acetate and 0.0005mol other metal acetate was added and stirred for two hours to form a light green colloidal solution. The obtained colloidal solution was added to a 100ml Teflon-lined reactor, and the solvent-thermal reaction was carried out at 160°C for 6 hours. The light blue precursor was obtained by washing with ethanol and deionized water several times after centrifugation. After drying in oven at 70°C for 24 hours, the precursor was calcined at 600°C for 5 hours to obtain nickel titanate yellow powder.

1.4. Characterization

The morphology of samples was characterized by a field emission scanning electron microscope (SEM, Apreo S, Thermo Fisher Scientific). High-resolution transmission electron microscope (HRTEM, Tecnai F30, FEI, Netherland) with a high-resolution coupled to an X-ray energy dispersive spectrometer (EDS) detector were used to measure the lattice spacing. The crystal structure of samples was analyzed by X-ray diffraction (XRD, X'pert pro, Philips, Netherland) (10–80°). Raman spectroscopy was used to identify their properties. The elemental composition and chemical state were characterized by X-ray photoelectron spectrometer (XPS, Axis Supra, Shimadzu, Japan). UV–vis diffuse scattering (UV–vis, SPECORD 50plus, Analytikjena, Germany) was used to detect the optical properties of materials. A gas chromatograph (GC9790 plus, Fuli Instrument) with a thermal conductivity detector was used to detect the amount of H₂ produced by piezocatalysis

1.5. Electrochemical measurements

Mott-Schottky curve, electrochemical impedance spectra (EIS) and piezo current of samples were detected on CHI660D electrochemical workstation (CH Instruments Co.). The three-electrode system consists of a rotate the ring working electrode (RRDE, RRDE-3A, ALS Co. Ltd), a GCE counter electrode and an Ag/ AgCl reference electrode. Mott-Schottky curve, electrochemical impedance spectra (EIS) and piezo current all used 0.5M sodium sulfate solution(pH=5.5) as the electrolyte. The detailed prepare process for working electrode is as follows: 5 mg sample powder was fully dispersed in 1 mL DI water to form a homogeneous suspension. Then, 30 μ L ink was

pipetted on rotate the ring electrode surface. After the ink was naturally air-dried, 10 μL of Nafion (DuPont) solution was covered on the surface of the sample and then air-dried.

1.6. Piezocatalytic activity

The piezocatalytic activity of samples was evaluated by H_2 generation. Mechanical vibrations were provided by the KQ5200DA ultrasonic cleaner (40 kHz, 200W, KS Ultrasonic Instrument Co., LTD). The temperature during the reaction is controlled by circulating water in dark during the whole process. The piezocatalytic H_2 production were evaluated offline by gas chromatograph. In a typical experiment, 10 mg catalyst was dispersed in 30 mL glucose solution (0.1 mol/L). The aqueous suspension sealed in a 150 mL beaker was evacuated and purged by Ar for about 30 min to completely remove air. Then the piezocatalytic H_2 production was performed under vibration power in dark, 1 mL gas in the beaker was intermittently extracted and injected into a gas chromatograph (GC9790 plus) with a thermal conductivity detector. A calibration curve of moles of H_2 and peak area was used to calculate the amount of produced H_2 .

2. Figures

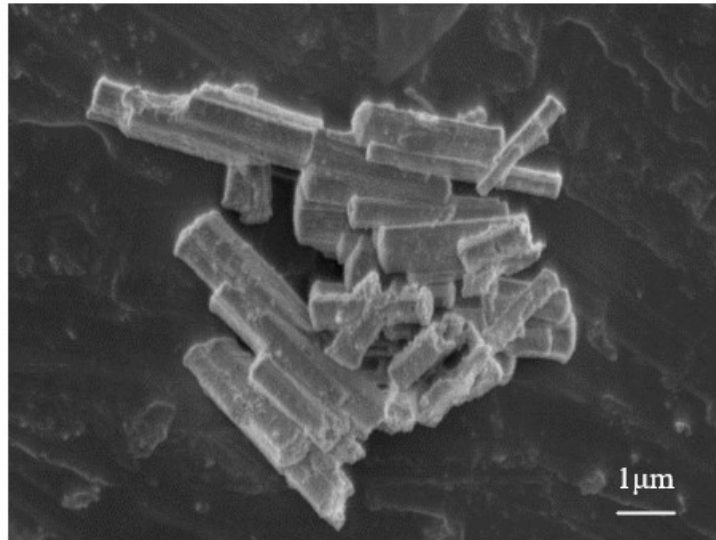


Fig. S1 SEM image of NiTiO₃.

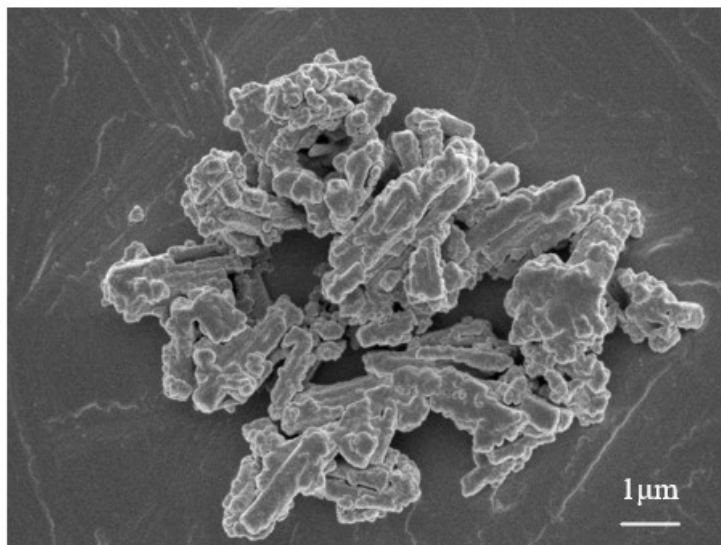


Fig. S2 SEM image of Cd-NiTiO₃.

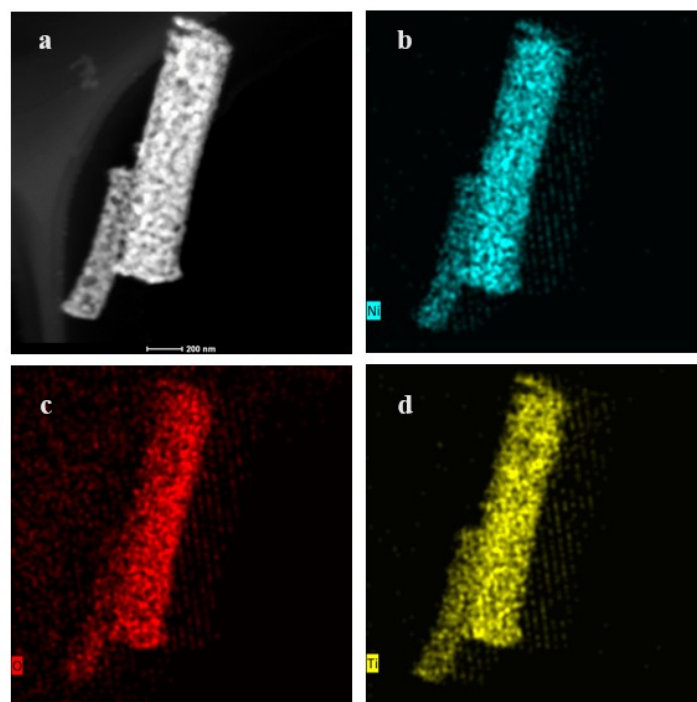


Fig. S3 High angle annular dark Field (HAADF), and the corresponding mapping images of NiTiO₃.

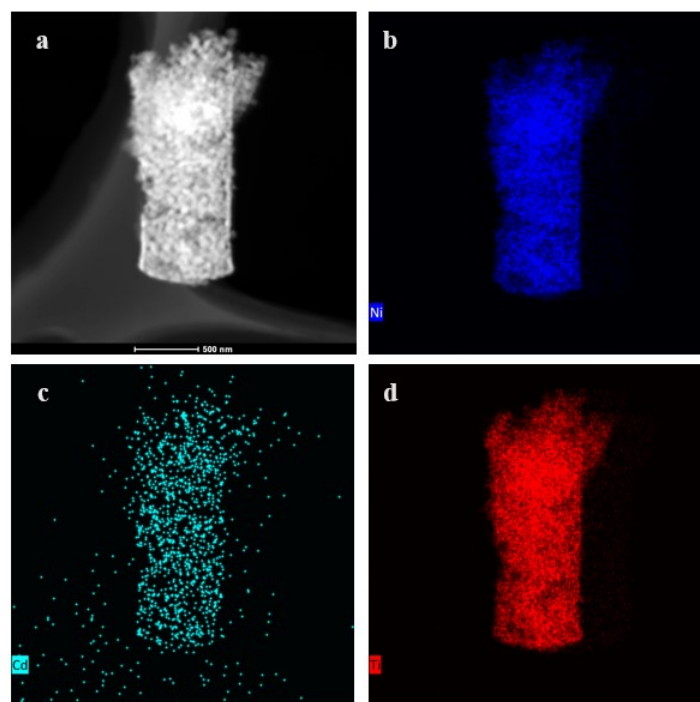


Fig. S4 High angle toroidal dark Field (HAADF), and the corresponding mapping images of Cd-NiTiO₃.

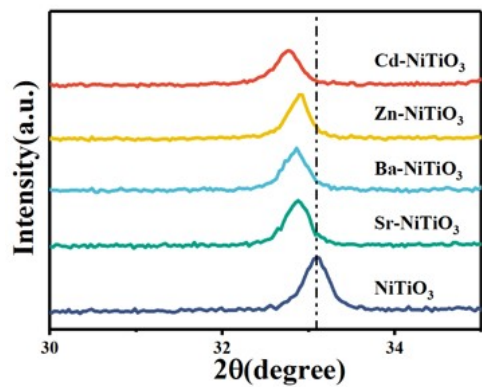


Fig. S5 XRD image of NiTiO₃ and doped NiTiO₃.

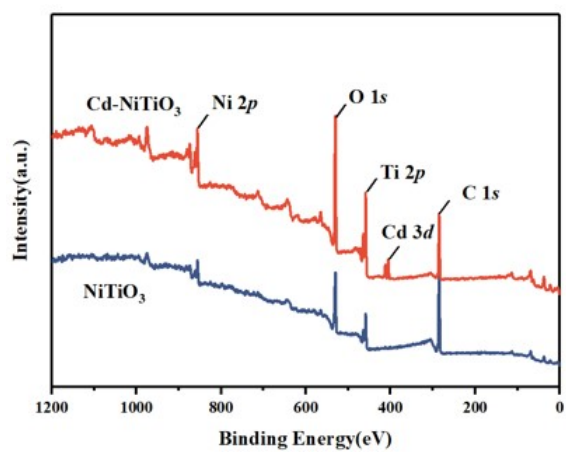


Fig. S6 Survey spectrum of NiTiO₃ and Cd-NiTiO₃.

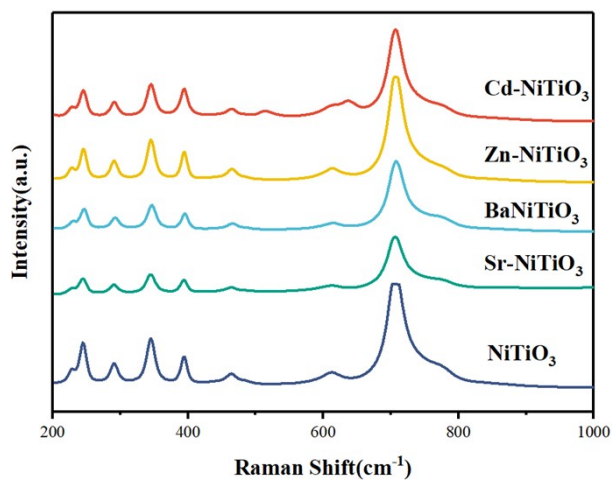


Fig. S7 Raman spectrum of NiTiO₃ and doped NiTiO₃.

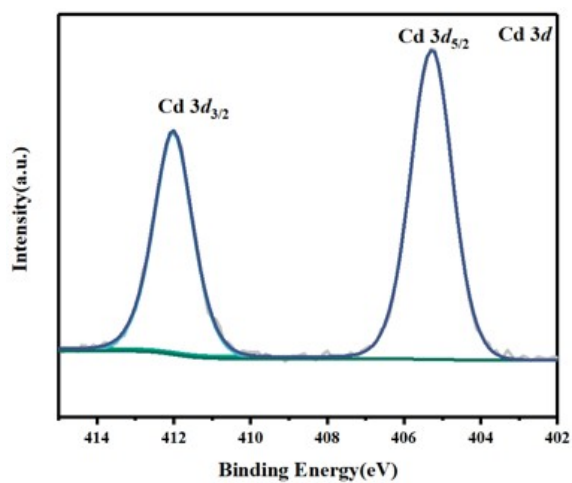


Fig. S8 High resolution Cd 3d spectrum of Cd-NiTiO₃.

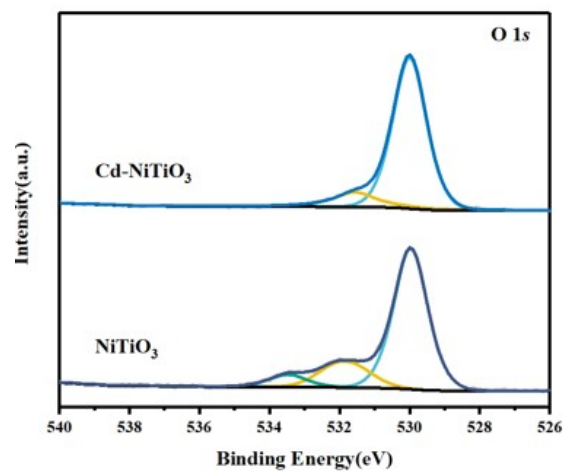


Fig. S9 High resolution O 1s spectrum of NiTiO₃ and Cd-NiTiO₃.

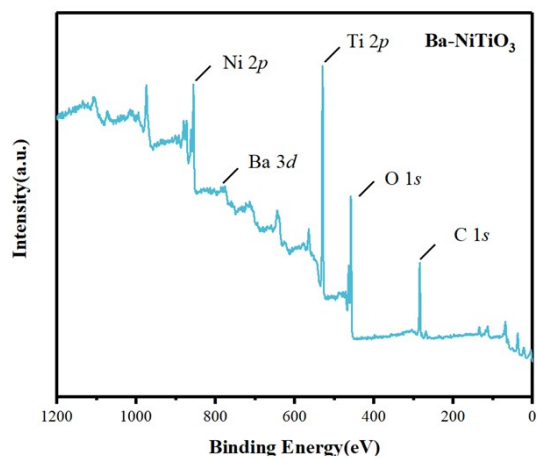


Fig. S10 Survey spectrum of Ba-NiTiO₃.

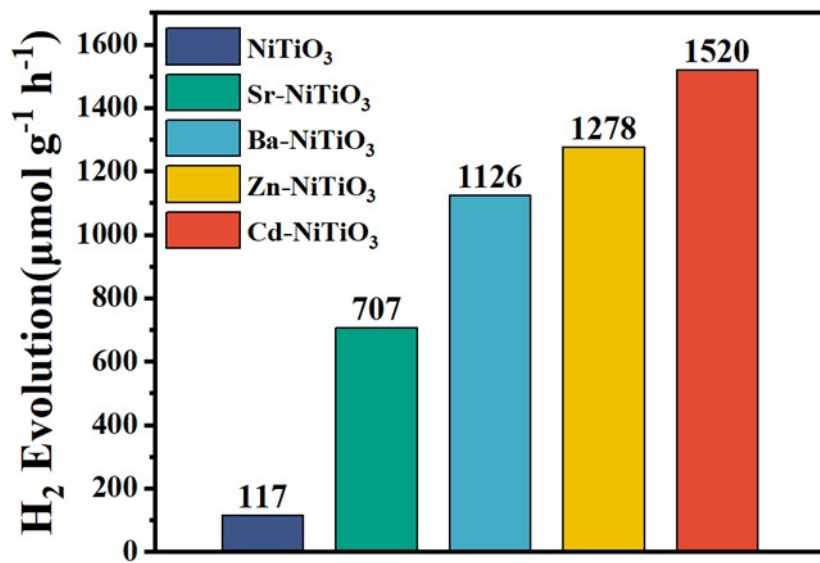


Fig. S11 H₂ production rate with serials NiTiO₃ catalyst.

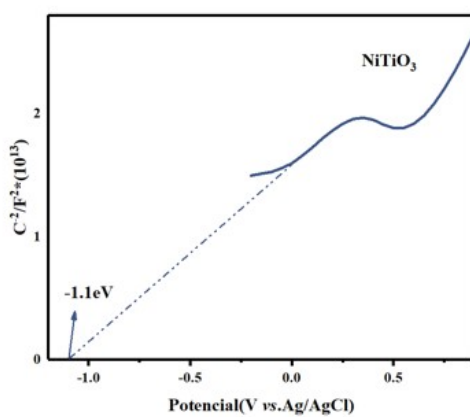


Fig. S12 Mott-schottky curve of NiTiO₃.

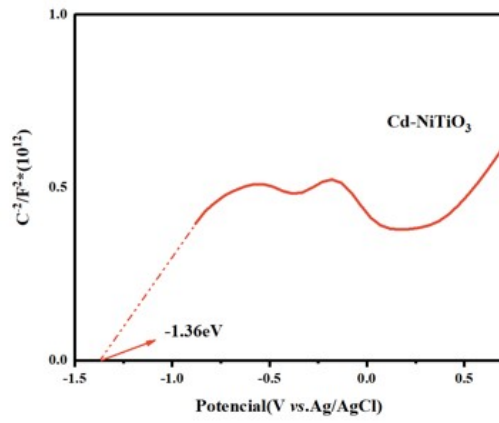


Fig. S13 Mott-schottky curve of Cd-NiTiO₃.

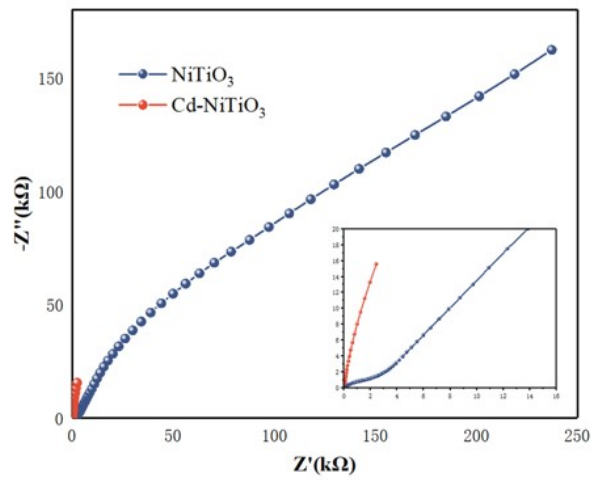


Fig. S14 Impedance spectrum of NiTiO₃ and Cd-NiTiO₃.

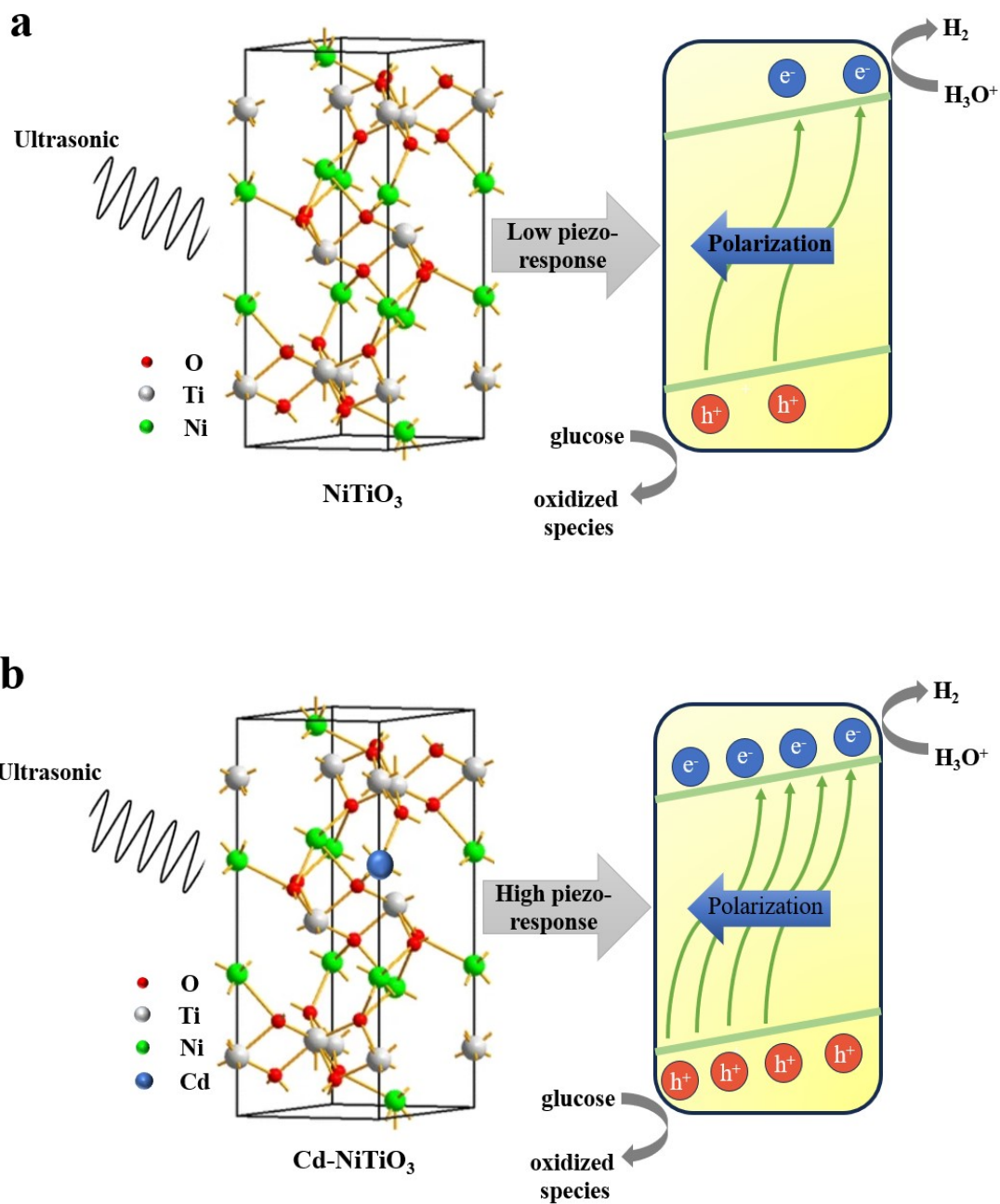


Fig. S15 The mechanism of NiTiO_3 (a) and Cd-NiTiO_3 (b) piezocatalytic water splitting to produce H_2 .

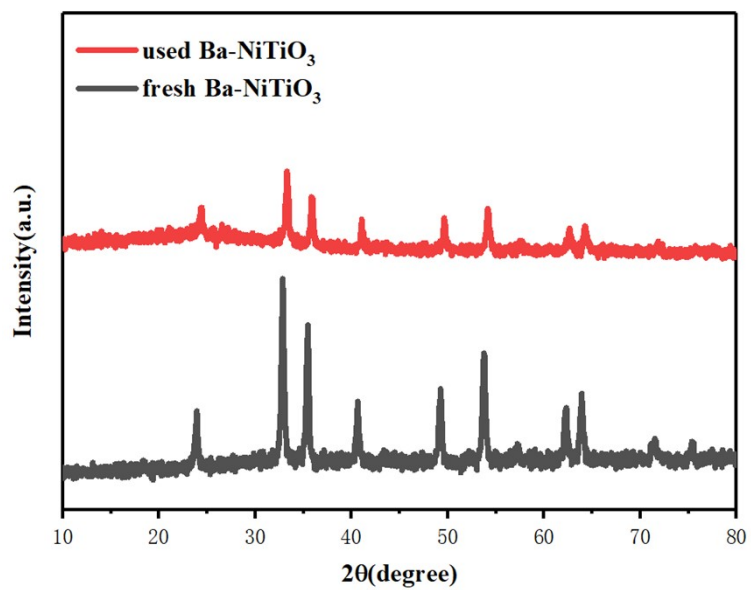


Fig. S16 XRD of Ba-NiTiO₃ before and after reaction.

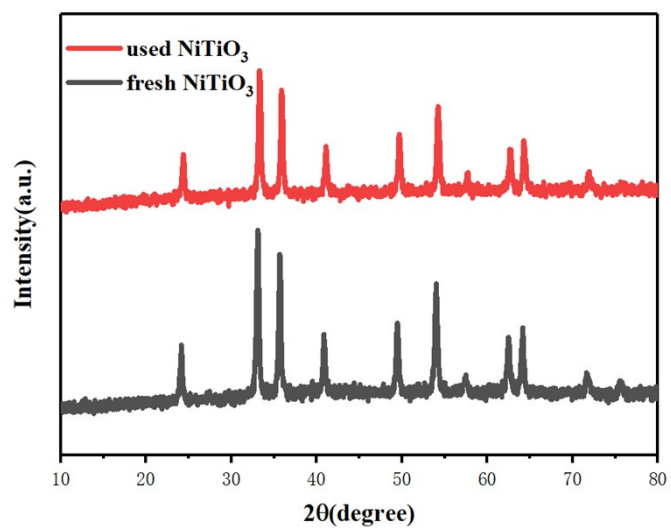


Fig. S17 XRD of NiTiO₃ before and after reaction.

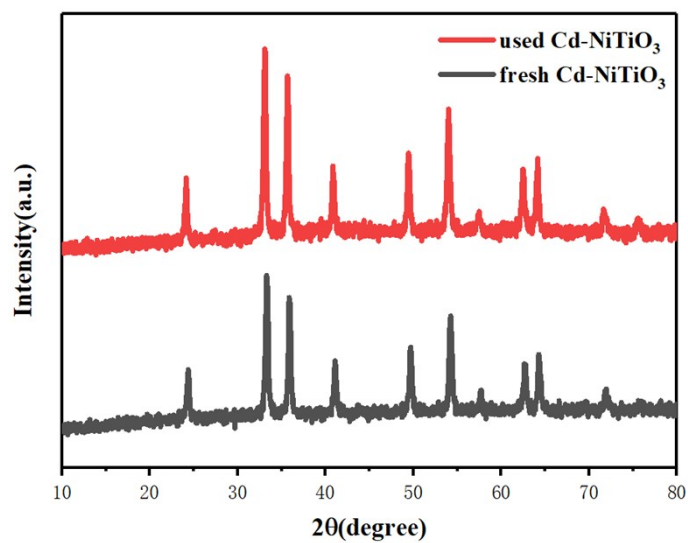


Fig. S18 XRD of Cd-NiTiO₃ before and after reaction.

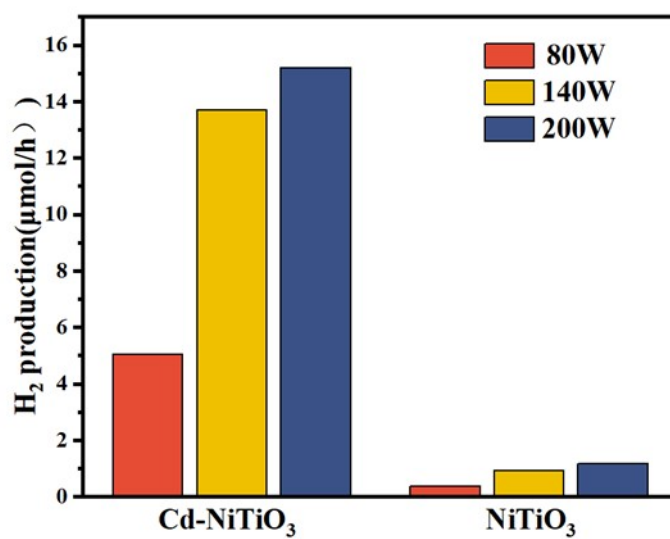


Fig. S19 Comparison of hydrogen production rates of Cd-NiTiO₃ and NiTiO₃ at different ultrasonic powers.

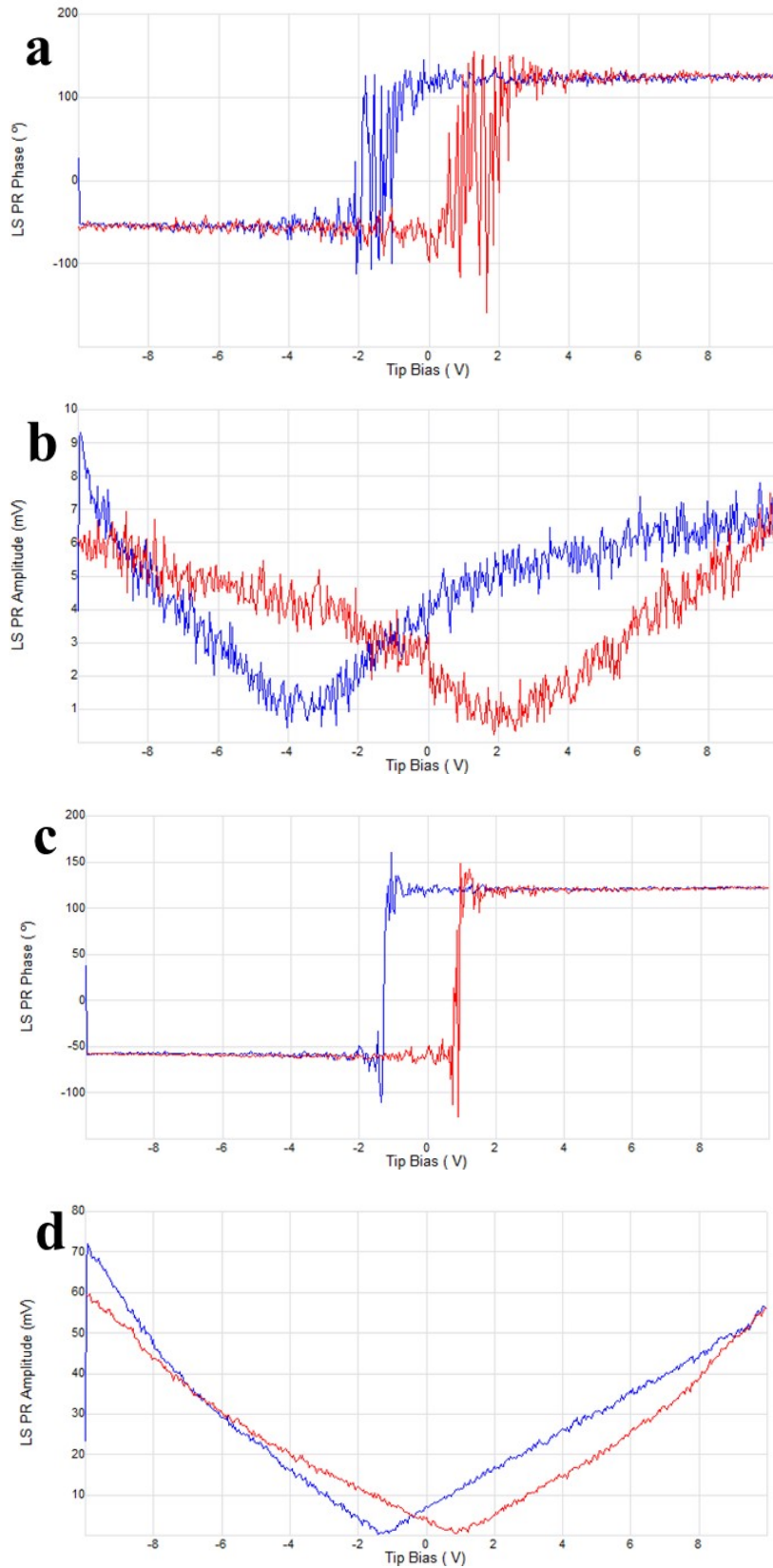


Fig. S20 The hysteresis loop and butterfly loop curves of (a-b) NiTiO₃ and (c-d) Cd-NiTiO₃.

Table S1 Comparison of some typical piezocatalysts and Cd-NiTiO₃.

Catalyst	H ₂ production (μmol g ⁻¹ h ⁻¹)	reference
Sr _{0.5} Ba _{0.5} Nb ₂ O ₆	109.4	1
BiFeO ₃	124.1	2
Ni@GaN	88.3	3
1%Pt@Sn _{0.97} Ag _{0.03} S ₂	399	4
V-NaNbO ₃	346.2	5
Bi ₂ MoO ₆ -BaTiO ₃	152.57	6
ZnS	1080	7
CdS@SnS ₂	452.6	8
Cd-NiTiO ₃	1520	This work

Table S2 Composition analysis from XPS

Catalyst	Doped element	at. %
Ba-NiTiO ₃	Ba	0.50
Sr-NiTiO ₃	Sr	0.72
Cd-NiTiO ₃	Cd	2.48
Zn-NiTiO ₃	Zn	2.85

References

1. J. Dai, N. Shao, S. Zhang, Z. Zhao, Y. Long, S. Zhao, S. Li, C. Zhao, Z. Zhang, W. Liu, *ACS Appl. Mater. Interfaces*. 2021, **13**, 7259-7267.
2. H. You, Z. Wu, L. Zhang, Y. Ying, Y. Liu, L. Fei, X. Chen, Y. Jia, Y. Wang, F. Wang, S. Ju, J. Qiao, C.H. Lam, H. Huang, *Angew. Chem. Int. Ed.* 2019, **58**, 11779-11784.
3. M. Zhang, S. Zhao, Z. Zhao, S. Li, F. Wang, *ACS Appl. Mater. Interfaces*. 2021, **13**, 10916-10924.
4. W. Tian, J. Han, L. Wan, N. Li, D. Chen, Q. Xu, H. Li, J. Lu, *Nano energy*, 2023, **107**, 108165.
5. Y. Li, L. Li, F. Liu, B. Wang, F. Gao, C. Liu, J. Fang, F. Huang, Z. Lin, M. Wang, *Nano Res.* 2022, **15**, 7986–7993.
6. K. Zhang, X. Sun, H. Wang, Y. Ma, H. Huang, T. Ma, *Nano energy*, 2024, **121**, 109206.
7. W. Feng, J. Yuan, L. Zhang, W. Hu, Z. Wu, X. Wang, X. Huang, P. Liu, S. Zhang, *Appl. Catal. B Environ.*, 2020, **227**, 119250.
8. R. Xiong, Y. Song, K. Li, Y. Xiao, B. Cheng, S. Lei, *J. Mater. Chem. A*, 2023, **11**, 18398–18408.