

Supporting Information

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Piezopotential-Driven Redox Reactions at the Surface of Piezoelectric Materials**

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Supplementary Information

Experimental Details

Piezoelectric cantilever: The piezoelectric cantilever used a $68[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-32[\text{PbTiO}_3]$ (PMN-PT) single crystal slab as the piezoelectric component. The PMN-PT wafer was received from TRS Technologies, Inc. and has a thickness of 0.25 mm. Both sides [the (00±1) surfaces] of the PMN-PT wafer were covered with electrodes consisting of 30 nm chromium and 200nm gold. The as-received PMN-PT wafer was diced into slabs with a size of 24 mm × 4mm. The slabs were then poled along the <001> direction by applying an electric field of 20,000 V/cm for 30 minutes at room temperature. The processed PMN-PT slabs demonstrated a piezoelectric coefficient of 2200-2700 pC/N. The PMN-PT slab was affixed by ECCOBOND® 45 epoxy to a brass beam (60 mm × 5 mm × 0.25 mm), which was encapsulated by a ~250 μm layer of epoxy to isolate the brass beam from the aqueous environment. ~0.5 mm-wide bottom surface of the PMN-PT was suspended over the side of the cantilever so that both oppositely charged piezoelectric surface can access the aqueous environment. Electrical leads were fastened to both electrodes by silver paste and subsequently berried in epoxy for piezoelectric potential measurement. The base-end of the brass cantilever was restrained to an immobile acrylic block and the free-end was connected to a lever arm attached to an actuator.

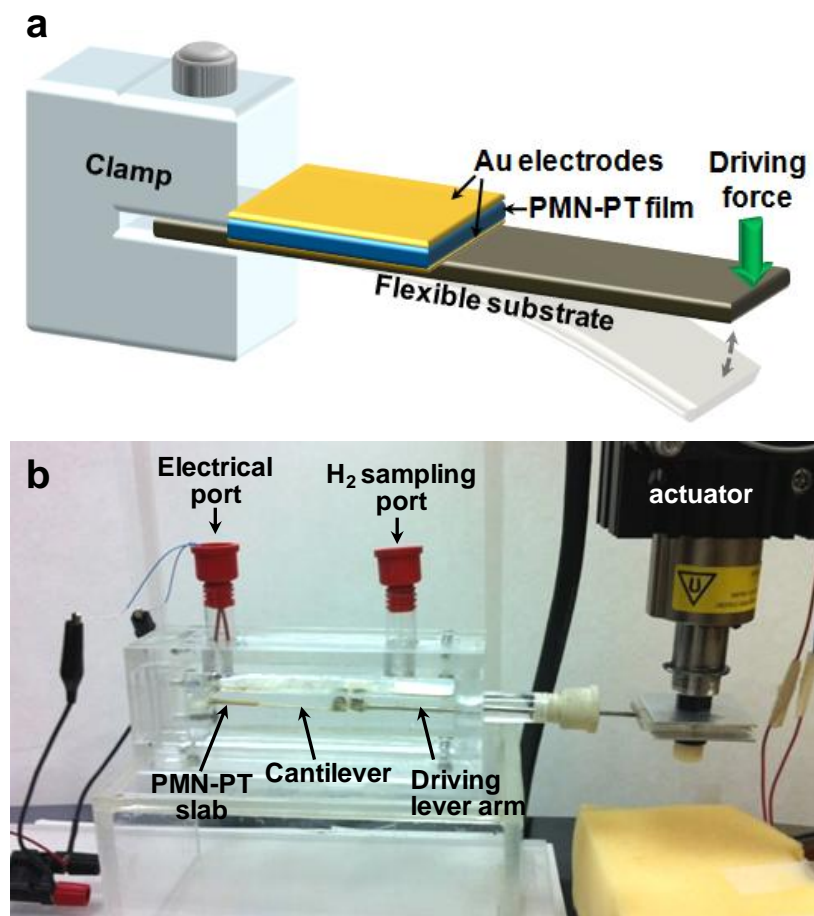


Figure S1. Experimental setup. **a**, The piezoelectric cantilever setup for studying the piezocatalytic effect. It consists of a flexible substrate for strain induction, a piezoelectric element for generation of piezoelectric potential, and a clamp for securing the cantilever's base. **b**, Photo of the experimental setup and reaction apparatus used for studying piezocatalyzed hydrogen evolution from water.

Reaction apparatus and experiment setup: The reaction apparatus is shown in Figure S1. The container containing the cantilever was composed of acrylic with joints secured with WeldOn #16 Clear, Medium Bodied Solvent Cement. The ports for mechanical actuation, atmospheric sampling and electrical characterization of the piezoelectric cantilever were composed of 12 mm diameter test tubes. Straining of the piezoelectric cantilever was achieved remotely via two epoxy encapsulated magnetic cubes placed at the tips of the cantilever beam and the driving lever arm. The driving lever arm extends outside the acrylic container through a rubber stopper.

The other end of the lever arm is connected to a computer controlled actuator. The actuator can achieve actuation $<10\ \mu\text{m}$ position precision covering a range of frequencies and straining patterns that are sufficient for the straining experiments. The insulated electrical leads connected to the piezoelectric electrodes were directed through a stopper in the electrical characterization port. Before each experiment, the 105.5 ml volume acrylic container was filled with 70 ml of solution (DI or electrolyte), leaving an air volume of 35.5 ml. Syringe needles were inserted into both the electrical port and the atmospheric port, and prepurified grade 99.998% nitrogen gas was purged through the system for 10 minutes to remove atmospheric hydrogen gas. At the beginning of each experiment, the electrical leads were connected to a digital oscilloscope to measure and record the piezoelectric voltage. The straining amplitude was adjusted accordingly to reach the desired piezoelectric response. After voltage measurement and adjustment, the leads were disconnected from the oscilloscope to prevent charge leakage through the electronics during hydrogen evolution experiments. Upon completion of the designed experimental run, hydrogen concentration in the air volume of the container was measured.

Hydrogen measurement: The hydrogen concentration was measured by an AMETEK Analyzer ta3000F hydrogen gas analyzer, which is able to detect hydrogen from 10 ppb – 3000 ppb with a precision of ± 1 ppb or $\pm 10\%$ of reading, whichever is greater. The analyzer was flushed with a control nitrogen stream in order to ensure proper functioning. A reaction apparatus possessing a piezoelectric cantilever and a DI or electrolyte solution was nitrogen purged for 10 minutes to determine the background baseline. To acquire an atmospheric sample, a syringe needle was punctured through the stopper of the sampling port. The 1 cc syringe was then filled with atmosphere extracted from the container. This atmospheric sample was injected into the sample inlet of the hydrogen gas analyzer for concentration quantification. Each atmospheric sampled was measured twice.

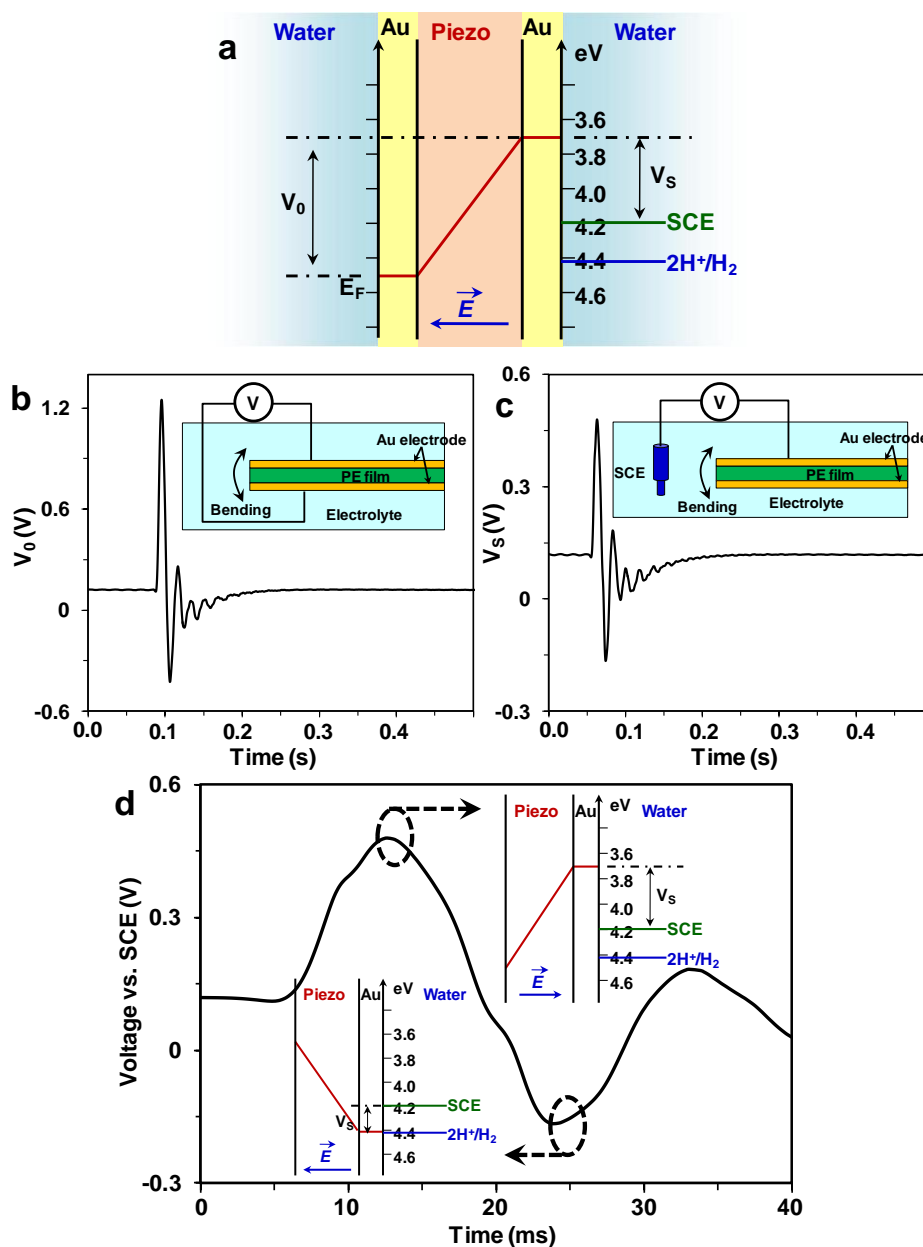


Fig. S2. Electrical potential characterization of the piezoelectric material with respect to a saturated calomel electrode (SCE). **a**, diagram of the potential profile across the piezoelectric element under minor strain as elucidated by reference to the SCE. V_0 represents the piezoelectric potential observed between the two electrodes; while V_S represents the potential difference between one electrode and the standard SCE. **b**, The piezoelectrical potential measured across the piezoelectric material that was under a sudden impact-load of strain pulse and then released for damped oscillation. The maximum potential difference was ~ 1.2 V. **c**, The potential profile

measured on a single electrode of the piezoelectric material versus SCE. The applied strain was the same as that used in **b**. The maximum potential was $\sim 0.5\text{V}$, demonstrating the potential difference between the counter electrode and SCE as that illustrated in **a**. **d**, The potential measured on one side of the piezoelectric material versus SCE during an oscillatory period of strain. The positive and negative values of the potential suggest that the relative electrochemical potential of the electrode can be driven higher and lower than the standard SCE level by the direct piezoelectric effect. The potential appearing on the electrode surface is thermodynamically capable of driving proton reduction reactions in its immediate vicinity.

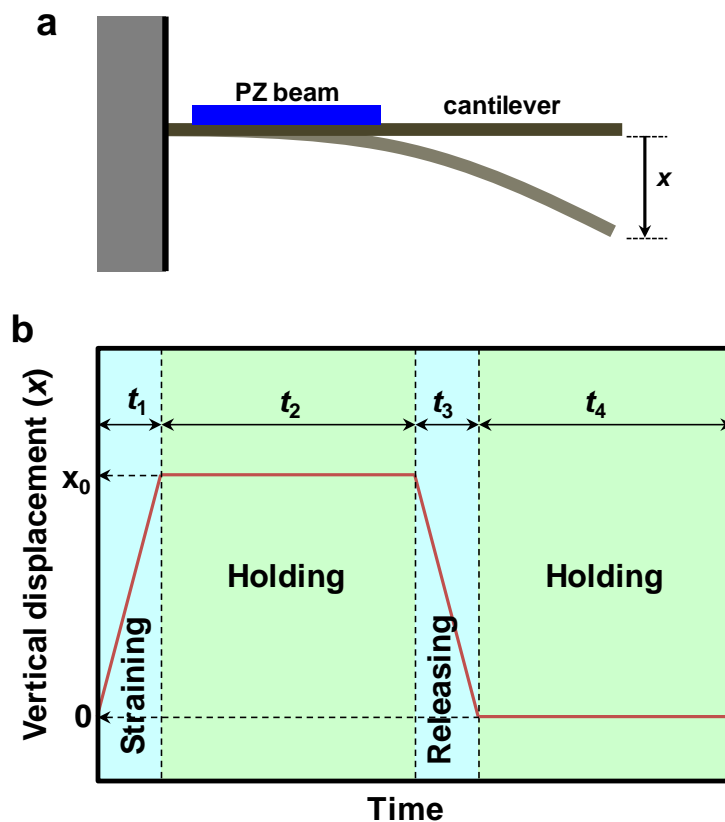


Fig. S3. Experimental design of the straining and holding control. **a**, A diagram demonstrating how strain was imposed on the piezoelectric cantilever via vertical displacement of the cantilever tip by a distance of x . **b**, One straining cycle depicted by the displacement of the piezoelectric cantilever tip (x) as a function of time. One cycle includes four segments: (1) straining: an enforced linear increase of x , reaching the maximum displacement of x_0 over time t_1 ; (2) holding: the piezoelectric cantilever held at the maximum displacement x_0 for time t_2 ; (3)

releasing: a linear return of the displacement back to 0 over a time t_3 ; (4) holding: the piezoelectric cantilever held at the displacement 0 for time t_4 . The displacement was program controlled and repeated for designed cycles. In all experiments, straining times t_1 and t_3 were set equal and their value held constant; while t_2 and t_4 were set equal but their value varied for investigating the holding time influence toward the piezocatalyzed hydrogen evolution.

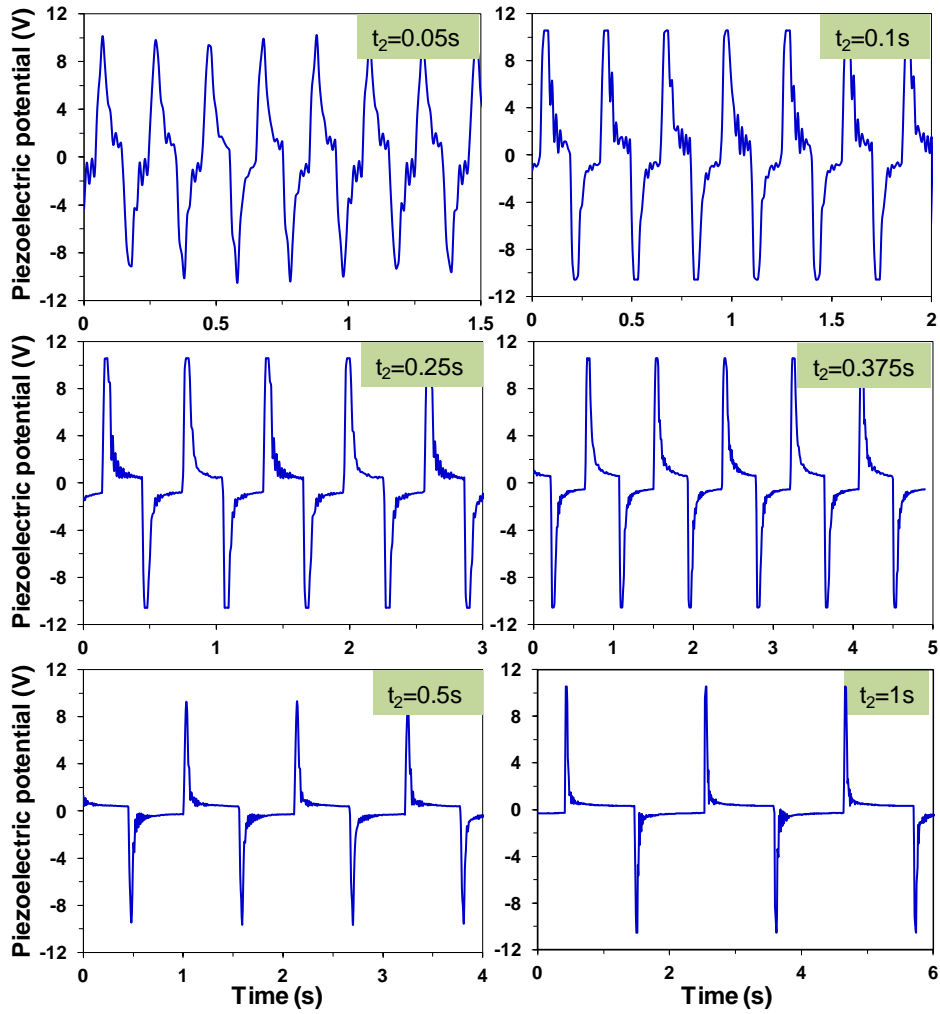


Fig. S4. The piezoelectric potential profiles measured under different straining patterns for studying the influence of holding time toward the piezocatalyzed hydrogen evolution. In all experiments, the straining and releasing times were set equal ($t_1 = t_3 = 50$ ms). The holding times ($t_2 = t_4$) were varied from 0.05 to 2.0 s as marked in the top-right corner of each figure (the 2.0 s curve is shown in Fig. 3A of the main text). Because of the constant straining time t_1 , the

piezoelectric material experienced the same strain rate, and thus nearly identical peak piezoelectric potentials were obtained. From these curves, the quantity of charges depleted from the piezoelectric material can be calculated as a function of the holding time.

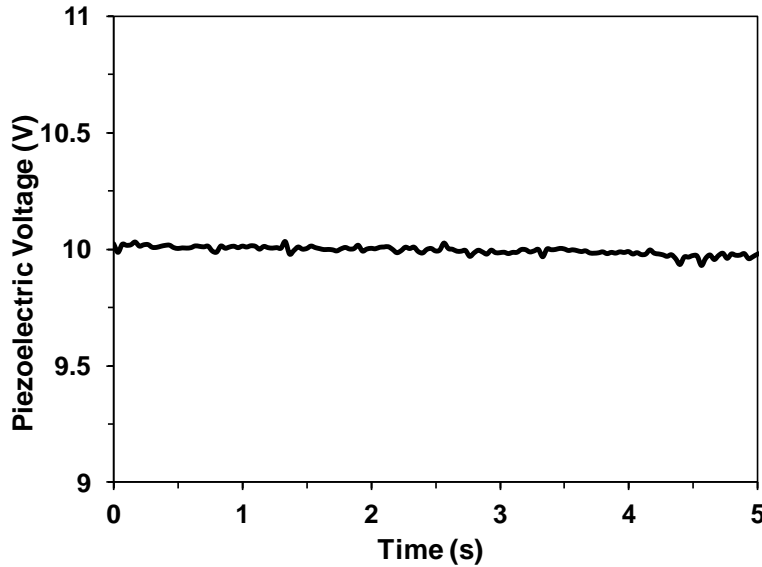


Fig. S5. Method for calculating the number of released charges from the piezoelectric potential profiles. Above curve is the piezoelectric potential profile when the piezoelectric beam was strained and held in air. This curve reveals the rate of piezoelectric charge leakage due to the measurement system. Starting from a piezoelectric potential of ~10 V (identical to the holding experiments), the magnitude of potential drain was within the noise level during a 5 second period. Therefore, when calculating the quantity of charge drained in an aqueous environment for a maximum 2 second period, the charge drained through the measurement equipment is negligible.

Hence, the piezoelectric potential drop was attributed completely to charge depletion mechanisms in the aqueous environment (i.e. capacitive or Faradic currents). Thus, total charge released from the piezoelectric surface over a single straining cycle was determined by:

$$\Delta Q = \frac{\Delta V \epsilon_m}{2d} .$$

ΔQ is the total charge removed from a single side of the piezoelectric material. ΔV is the piezoelectric potential difference between the peak value and the value right before the opposite

strain was applied. They were determined from the voltage curves shown in Fig. S4. ϵ_m and d are the electrical permittivity and thickness of the PMN-PT slab with values of 6.6406×10^{-8} F/m and 0.25 mm, respectively.