

mechanical vibration, the thin BiFeO<sub>3</sub> nanosheet will easily bend. Due to the piezoelectric effect, lots of positive and negative charges will be generated on the catalyst's surface. The negative electric charges ( $q^-$ ) generated on the BiFeO<sub>3</sub> nanosheets' surfaces will effectively attract the dissociated hydrogen ions in the water to produce H<sub>2</sub>. Meanwhile, the positive charges ( $q^+$ ) accumulated on the other side of the BiFeO<sub>3</sub> nanosheets will be consumed by the sacrificial agents (SO<sub>3</sub><sup>2-</sup>).<sup>[17]</sup> It should be mentioned that the bandgap of our synthesized BiFeO<sub>3</sub> is about 2.27 eV and the flat band potential is 0.32 V vs. RHE, as shown in Figure S3. As shown in Figure 4c, the holes generated on the top of valence band (VB) are often energetically favorable for the oxidation of various organic pollutants.<sup>[6,7]</sup> However, the electrons generated on the bottom of conduction band (CB) is not energetically favorable for hydrogen evolution reaction (HER). Photo-catalytic hydrogen production experiment was conducted to verify that photocatalytic hydrogen generation cannot be achieved by using the synthesized BiFeO<sub>3</sub> nanosheets (Figure S4). We show here that the piezoelectric induced internal electric field can tilt the CB and enable the catalytic HER. Under the mechanical deformation of piezoelectric BiFeO<sub>3</sub> nanosheets, the open-circuit voltage ( $V_p$ ) created across the two surfaces of a nanosheet can be calculated as:<sup>[12]</sup>

$$V_p = \frac{w_3 \cdot T_3 \cdot d_{33}}{\epsilon_0 \cdot \epsilon_r} \quad (1)$$

where  $T_3$  is the applied stress in the normal direction of the nanosheet,  $d_{33}$  is the piezoelectric moduli,  $\epsilon_0$  is the vacuum permittivity,  $\epsilon_r$  is the relative permittivity in the normal direction and  $w_3$  is the thickness of the piezoelectric nanosheet. The applied stress  $T_3$ ,  $d_{33}$ ,  $\epsilon_r$  of the BiFeO<sub>3</sub> nanosheets in the current study are estimated to be about  $1.01 \times 10^5$  kPa, 100 pm/V, and 26, respectively.<sup>[9a,9b,18,19]</sup> The thickness of the piezoelectric nanosheet is characterized to be 20 nm according to Atomic force microscopy (AFM) image in Figure S5. The calculated open-circuit voltage across the BiFeO<sub>3</sub> nanosheet is about 0.88 V. Based on a rough estimation, the tilting of CB results in the band edge to be lifted up at the negatively charged side, slightly more negative than the H<sub>2</sub>/H<sub>2</sub>O redox potential (0 V) for HER. Thus, the piezo-catalytic hydrogen generation of water can be realized on pure BiFeO<sub>3</sub> material. Equation (1) further implies that the piezo-catalysis can be easily tuned by variation of nanoparticle geometry and materials properties.

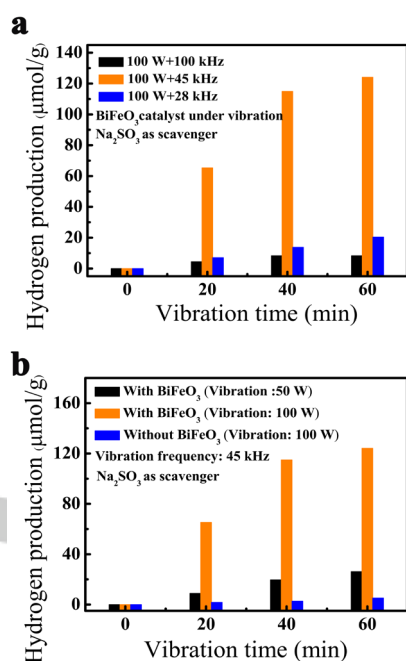


Figure 5 The piezo-catalytic hydrogen production from water splitting under vibration by BiFeO<sub>3</sub> nanosheets (a) at different vibration frequencies; (b) with different mechanical power.

Figure 5a shows the piezo-catalytic hydrogen generation result, where the total hydrogen production per gram of catalyst under the vibration power of 100 W for 1 hour is up to 20.4, 124.1, and 8.3 μmol at the frequency of 28, 45, and 100 kHz, respectively. The 1st-order resonance frequency ( $f^r$ ) of BiFeO<sub>3</sub> square nanosheet can be estimated by the following equation,<sup>[20]</sup>

$$f^r = \frac{\pi}{2} \left[ \frac{1}{L^2} + \frac{1}{W^2} \right] \sqrt{\frac{D}{\rho}} \quad (2)$$

where  $L$ ,  $W$ ,  $\rho$ , and  $D$  are the length, width, density, and bending rigidity of the nanosheet, respectively. The bending rigidity  $D$  is defined as,

$$D = \frac{E \cdot h^3}{12(1-\nu^2)} \quad (3)$$

where  $E$ ,  $\nu$  and  $h$  are the Young's modulus, Poisson ratio, and thickness of the material, respectively. For BiFeO<sub>3</sub> nanosheet used in this study, these values are about 51 GPa, 0.33, and 20 nm, respectively.<sup>[21]</sup> Taking the density as 8344 kg/m<sup>3</sup>, the resonance frequency of BiFeO<sub>3</sub> nanosheet is estimated to be around 46.5 kHz. This result confirms that the highest piezo-catalytic hydrogen generation can be obtained at the resonance frequency of a piezoelectric material (Figure 5a), where the mechanical vibration energy can be more efficiently transferred to the electrical one.

Figure 5b shows the influence of vibration power on hydrogen production. For 1 h mechanical vibration at a frequency of 45 kHz, the hydrogen production of BiFeO<sub>3</sub> nanosheet is about 26.1 μmol·g<sup>-1</sup> under the vibration power of 50 W, which is much lower than that under the vibration power of 100 W. The relationship between the piezoelectric charges ( $Q$ ) per unit area on the BiFeO<sub>3</sub> nanosheet surface, the piezoelectric coefficient ( $d$ ), and the external stress ( $T$ ) can be described as  $Q=d \cdot T$ . Higher vibration power can lead to higher stress  $T$ , which induces more piezoelectric charges on the catalyst's surface, resulting in higher hydrogen production rate. Without the catalyst, almost no hydrogen can be generated under the vibration power of 100 W (Figure 5b). It should be noted that although the charge carriers in BiFeO<sub>3</sub> are localized and tightly bound,<sup>[22]</sup> the piezo-generated electrons and holes will be recombined due to conduction across the small nanosheet thickness or vanished due to the quick relaxation of mechanical stress. To suppress the rapid recombination or vanish of the piezoelectrically induced positive and negative charges and increase the lifetime of the negative charges for hydrogen generation, Na<sub>2</sub>SO<sub>3</sub> sacrificial agent was used to effectively scavenge the positive charges, similar to what is usually done in photocatalytic hydrogen generation.<sup>[17]</sup>

The stability of the BiFeO<sub>3</sub> nanosheets after 60 min piezo-catalysis can be reflected from the XRD patterns (Figure S6) taken before and after the piezo-catalysis, which are quite similar to each other and no secondary phases can be detected. After piezo-catalysis for 60 mins, a number of cracked nanosheets (Figure S7) were generated due to the high power (100 W) of the ultrasonic machine used. Working at the resonant frequency is another reason that the BiFeO<sub>3</sub> nanosheets are easily cracked. This result agrees well with the experimental result (Figure 5) that the hydrogen production rate decreases with increasing reaction time. Decreasing the ultrasound power and tuning the frequency away from resonance will reduce the number of cracked nanosheets. To minimize the effect of temperature on piezo-catalysis, the water in the ultrasonic bath was changed every 20 min. As shown in Figure S8, water temperature change rate was 0.33 °C min<sup>-1</sup>. The temperature variation was controlled to be below 4 °C.

Density functional theory (DFT) calculations were carried out to study the protonation on the (100) surface of the BiFeO<sub>3</sub> nanosheets. It