

is found that the H adsorption is energetically favorable on the (100) surface of BiFeO₃ (Figure S9). Furthermore, to provide direct evidence of the electro-catalytic activity of BiFeO₃ towards hydrogen production, we measured the HER performance of BiFeO₃ nanosheets (Figure S10). Hydrogen evolution can be clearly observed at a potential above ~400 mV (Figure S10).

The piezo-catalytic effect was also verified for dye decomposition. Figure S11a shows the piezo-catalytic decomposition of Rhodamine B (RhB) dye under mechanical vibration of BiFeO₃ nanosheets. The piezo-catalytic decomposition ratio of RhB dye reaches 94.1% after mechanical vibration for 50 min (Figure S11b) and the RhB dye solution becomes almost completely transparent (inset of Figure S11b). No obvious dye decomposition occurs without the addition of BiFeO₃ nanosheets (Figure S11b). Low-frequency piezo-catalytic decomposition of RhB dye was also conducted by mechanical stirring of the solution containing BiFeO₃ nanosheets (Figure S12a). Under this low-frequency mechanical stirring, the decomposition ratio of RhB is around 76.4% after 10 h (Figure S12b). The low-frequency piezo-catalytic properties enable the harvesting of waste mechanical energy from environment for water treatment in the future.

Apart from the piezo-catalytic properties of BiFeO₃ demonstrated in this work, BiFeO₃ is also a proven photocatalyst.^[17,19,20,21a] Therefore, a higher hydrogen production rate may be achieved via the combination of piezo-catalysis with photocatalysis, where the simultaneous harvesting of sunlight and natural vibration energy can be realized. There are plenty of rooms for the engineering of the synergistic effect of piezo-catalysis and photocatalysis for enhanced catalytic performance of ferroelectric materials in the future.

For practical applications, it is interesting to note that oceans provide a rich variety of noise sources with a wide range of frequencies.^[23] The low-frequency band (10 to 500 Hz) is dominated by commercial shipping and seismic exploration. The medium-frequency band (500 Hz to 500 kHz) is primarily due to sea-surface agitation, various sonars and small vessels. The high-frequency band (>25 kHz) is mainly due to thermal noise. According to equation 2 and 3, the resonant frequency of a piezoelectric material can be tuned by geometry and the selection of material. There are many different kinds of piezoelectric materials, such as, quartz, tourmaline, barium titanate (BaTiO₃), lead zirconate titanate (PZT) and its solid solution with lead magnesium niobate (PMN), polyvinylidene fluoride (PVDF), sodium/potassium niobate (NaNbO₃, KNbO₃), and zinc oxide (ZnO), etc., which add the degree of freedom in materials selection for piezo-catalysis. The availability of the wide frequency spectrum of natural vibration sources makes the harvesting of waste mechanical vibration energy for clean energy generation or environmental pollution treatment very promising. Two possible applications of piezo-catalysis we can envisage at this stage are (1) the utilization of ocean wave vibration for hydrogen evolution and water treatment, and (2) the self-cleaning of the surface of modern buildings, both of which can work together with photocatalysis to obtain some synergistic effects.

In summary, a strong piezo-catalytic hydrogen production via hydrothermally synthesized BiFeO₃ square nanosheets is realized at a rate of 124.1 $\mu\text{mol/g}$ under a 100 W vibration excitation at the resonant frequency for 1 h. The piezo-catalytic decomposition ratio of RhB dye can be up to ~94.1% after vibrating BiFeO₃ nanosheets for 50 min. The piezo-catalytic property of the BiFeO₃ square nanosheets is attributed to the tilting of the conduction band under the strong piezoelectric field induced by mechanical vibration, which make the conduction band more negative than the H₂/H₂O redox potential, enabling the hydrogen evolution. Our work demonstrated that the potential of BiFeO₃ for piezo-catalytic hydrogen production via harvesting waste vibration energy from the environment.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Hydrogen • Energy conversion • BiFeO₃

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