

Harvesting the Vibration Energy of BiFeO₃ Nanosheets for Hydrogen Evolution

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Abstract: Vibration is one of the most prevalent energy sources in natural environment. Here, in this study, mechanical vibration is used for hydrogen generation and decomposition of dye molecules, with the help of BiFeO₃ (BFO) square nanosheets. A high hydrogen production rate of ~124.1 μmol/g is achieved under mechanical vibration (100 W) for 1 h at the resonant frequency of the BFO nanosheets. The decomposition ratio of Rhodamine B dye is up to ~94.1% after mechanically vibrating the BFO catalyst for 50 min. The vibration induced catalysis of the BFO square nanosheets may be attributed to the piezo-catalytic properties of BFO and the high specific surface area of the nanosheets. The uncompensated piezoelectric charges on the surfaces of BFO nanosheets induced by mechanical vibration result in a built-in electric field across the nanosheets. Unlike a photocatalyst for water splitting, which requires a proper band edge position for hydrogen evolution, such a requirement is not needed in piezo-catalytic water splitting, where the band tilting under the induced piezoelectric field will make the conduction band of BFO more negative than the H₂/H₂O redox potential (0 V) for hydrogen generation. The observed piezo-catalytic properties of BFO nanosheets pave the way towards a non-toxic, highly efficient and sustainable technology for hydrogen generation or dye decomposition through harvesting waste vibration energy from the environment.

Due to the limited fossil-fuels and their serious environmental impact, hydrogen energy has been recognized as an alternative form of clean energy in the future.^[1] At present, direct water electrolysis is one of the promising methods for hydrogen production.^[2] However, electrolysis has the disadvantage of large consumption of electricity.^[2] Since the first report on photocatalytic splitting of water on titanium dioxide (TiO₂) electrodes,^[2a] photocatalysis, which can generate electrical charges under light illumination, has demonstrated wide-range applications in the generation of

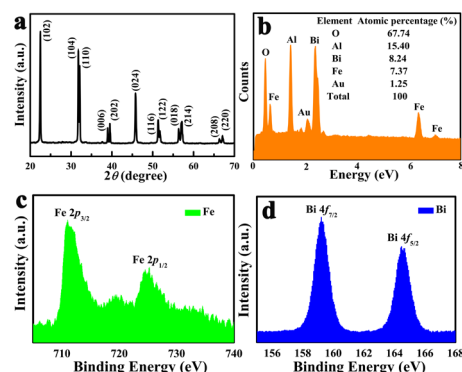
hydrogen fuels and waste water treatment.^[1a,1b,2c] TiO₂ quickly becomes one of the most popular materials in solar energy harvesting due to its easy synthesis and low cost.^[1a,1b,2a] However, TiO₂ possesses a large bandgap around 3.2 eV and can only absorb ultraviolet light, leading to low efficiency in the utilization of visible solar spectrum.^[3]

One approach to increase the solar energy harvesting efficiency is to develop new photocatalytic materials with a bandgap in the visible range.^[4] Bismuth ferrite (BiFeO₃) is an interesting ferroelectric material for hydrogen generation through photocatalytic water splitting due to its narrow band-gap (~2.2 eV) and good chemical stability.^[5] The narrow band gap of BiFeO₃ allows a large absorption of visible light up to 750 nm, which makes itself an attractive photocatalyst under visible light.^[6] For instance, Gao *et al.* used BiFeO₃ nanoparticles to decompose methyl orange dye under visible light irradiation.^[6] Cho *et al.* applied BiFeO₃ nanopowders for the visible light photocatalytic decomposition of Rhodamine B (RhB) dye in water.^[7] However, photocatalytic hydrogen generation cannot be achieved by using pure BiFeO₃ since its conduction band edge is around 0.33 eV, which is more positive than the H₂/H₂O redox couple potential.^[8] The coating of BiFeO₃ nanoparticles with a thin layer of SrTiO₃ may enable the H₂ evolution under visible light.^[8a]

It is noted that BiFeO₃ is also ferroelectric and piezoelectric with a large spontaneous polarization in excess of 100 μC·cm⁻² and a piezoelectric coefficient (*d*₃₃) of ~100 pm/V.^[9] It can convert mechanical energy into electric one through the piezoelectric effect.^[10] Similar to photocatalysis, where the photo-induced electric charges (electron-hole pairs in photocatalysis) participate in the catalytic redox reactions, in principle, piezoelectric charges (positive and negative ones) induced by mechanical vibrations can also be used to drive catalytic redox reactions, which can be named as piezo-catalysis.^[11,12] Although photocatalytic hydrogen evolution is not possible for BiFeO₃ due to its more positive conduction band edge than the redox potential for hydrogen evolution reaction (HER), we demonstrate in this work that, large enough piezoelectric field may induce a tilting of the conduction band that makes the HER energetically favorable in BiFeO₃ nanoparticles.

Generally, the catalytic performance of a catalyst depends strongly on its surface area and available catalytically active sites.^[13] Small size and large surface area of nanoparticles are beneficial to the quick charge transfer between the catalyst and the redox couples to achieve high catalytic activity.^[13] Our previous work showed that NaNbO₃ nanosheets possess higher pyro-catalytic activity than NaNbO₃ nanoparticles.^[14] Therefore, in this study, BiFeO₃ nanosheets were synthesized to achieve high catalytic activity.

Herein, under mechanical vibration, strong piezo-catalytic hydrogen evolution and dye decomposition are observed with the help of hydrothermally synthesized BiFeO₃ nanosheets. Under a mechanical vibration excitation (100 W) for 1 h, a hydrogen production rate of about 124.1 μmol/g is achieved. The decomposition ratio of RhB dye can be up to ~94.1% after vibrating BiFeO₃ catalyst for 50 min.



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