Harvesting the Vibration Energy of $BiFeO_3$ Nanosheets for Hydrogen Evolution

Huilin You[a],[b],[d], Zheng Wu[b],[d],*, Luohong Zhang[b], Yiran Ying[a], Yan Liu[a], Linfeng Fei[a], Xinxin Chen[a], Yanmin Jia[c],[d],*, Yaojin Wang[e], Feifei Wang[f], Sheng Ju[g], Jinli Qiao[h], Chi-Hang Lam[a], and Haitao Huang[a],*

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 $BiFeO_3$ (BFO) square nanosheets. A high hydrogen production rate of ~124.1 μmol/g is achieved under mechanical vibration (100 W) for 1h 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 H_2/H_2O 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.

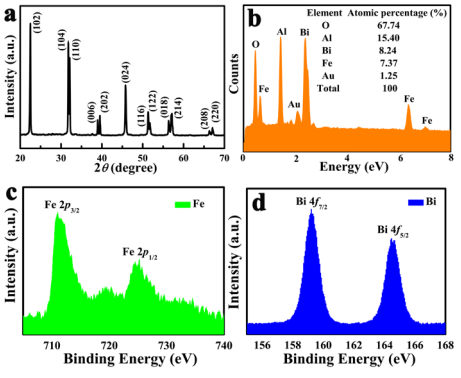
Due to the limited fossil-fuels and their serious environmental impact, hydrogen energy has been recognized as an alternative form of clean energy in the future.[1] At present, direct water electrolysis is one of the promising methods for hydrogen production.[2] However, electrolysis has the disadvantage of large consumption of electricity.[2] Since the first report on photocatalytic splitting of water on titanium dioxide (TiO_2) 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] TiO_2 quickly becomes one of the most popular materials in solar energy harvesting due to its easy synthesis and low cost.[1a,1b,2a] However, TiO_2 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 ($BiFeO_3$) is an interesting ferroelectric material for hydrogen generation through photocatalytic water splitting due to its narrow band-gap (~2.2eV) and good chemical stability.[5] The narrow band gap of $BiFeO_3$ 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 $BiFeO_3$ nanoparticles to decompose methyl orange dye under visible light irradiation.[6] Cho *et al*. applied $BiFeO_3$ 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 $BiFeO_3$ since its conduction band edge is around 0.33 eV, which is more positive than the H_2/H_2O redox couple potential.[8] The coating of $BiFeO_3$ nanoparticles with a thin layer of $SrTiO_3$ may enable the H_2 evolution under visible light.[8a]

It is noted that $BiFeO_3$ is also ferroelectric and piezoelectric with a large spontaneous polarization in excess of 100 $\mu C \cdot cm^{-2}$ 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 photocatlytic hydrogen evolution is not possible for $BiFeO_3$ 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 $BiFeO_3$ 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 $NaNbO_3$ nanosheets possess higher pyro-catalytic activity than $NaNbO_3$ nanoparticles.[14] Therefore, in this study, $BiFeO_3$ 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 $BiFeO_3$ nanosheets. Under a mechanical vibration excitation (100 W) for 1h, 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 $BiFeO_3$ catalyst for 50 min.



[a] Huilin You, Yiran Ying, Yan Liu, Linfeng Fei, Xinxin Chen, Chi-Hang Lam and Haitao Huang*
Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong SAR, China;
[b] Huilin You, Luohong Zhang and Zheng Wu*
College of Environmental and Chemical Engineering, Xi'an Polytechnic University, Xi'an 710048, China;
[c] Yanmin Jia*
School of Science, Xi'an University of Posts and Communications, Xi'an 710121, China;
[d] Huilin You, Zheng Wu* and Yanmin Jia*
College of Geography and Environmental Science and Department of Physics, Zhejiang Normal University, Jinhua, 321004, China;
[e] Yaojin Wang
School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China;
[f] Feifei Wang
Department of Physics, Shanghai Normal University, Shanghai, 200235, China;
[g] Sheng Ju
College of Physics, Optoelectronics and Energy and Jiangsu Key Laboratory of Thin Films, Soochow University, Suzhou, 215006, China;
[h] Jinli Qiao
College of Environmental Science and Engineering, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, 201620, China.
*E-Mail: wuzheng@zjnu.edu.cn (Z. Wu), ymjia@zjnu.edu.cn (Y. Jia) and aphhuang@polyu.edu.hk (H. Huang).

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