Liquid-phase Exfoliated Two-dimensional Bi Nanosheet as a Durable Electro catalyst for Hydrogen Evolution Reaction

Chenguang Duan  
Xiangtan University School of Physics and Optoelectronics

Huating Liu  
Xiangtan University School of Physics and Optoelectronics

Zongyu Huang  
Xiangtan University School of Physics and Optoelectronics  https://orcid.org/0000-0002-3836-1528

Hui Qiao  
Xiangtan University School of Physics and Optoelectronics

Yang Zhou  
Xiangtan University School of Physics and Optoelectronics

Gengcheng Liao  
Xiangtan University School of Physics and Optoelectronics

Yundan Liu  
Xiangtan University School of Physics and Optoelectronics

Xiang Qi (✉ xqi@xtu.edu.cn)  
Faculty of Materials and Optoelectronic Physics, Xiangtan University, Hunan 411105, P. R. China  https://orcid.org/0000-0002-0939-8874

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Abstract
Electrocatalytic hydrogen evolution is an exercisable way to achieve large-scale application of hydrogen energy. It is of great significance to develop an effect, stable and cost-effective electrocatalyst. Here, we applied the two-dimensional (2D) bismuth (Bi) to the electrocatalytic hydrogen evolution, and proposed the strategies to enhance the catalytic performance of the catalyst. The exfoliated Bi nanosheets via sonication assisted liquid-phase exfoliation display higher electrocatalytic activity (overpotential of -958 mV vs RHE at 10 mA cm$^{-2}$) compared to the bulk counterpart. Theoretical calculations about Gibbs free energy from the hydrogen adsorption for 1 layer, 2 layers and 5 layers Bi also manifest the decrease of thickness is favorable for hydrogen evolution reaction (HER). To further evaluate the electrocatalytic performance of Bi nanosheets, the typical parameters measured in different H$^+$ concentration (C[H$^+$]) are carried out. The improved catalytic activity obtained in 0.5 M H$_2$SO$_4$ is attributed to enhancing the hydrogen adsorption and accelerating the charge transport on the surface of catalyst. Moreover, the durability of Bi nanosheets electrode has been tested, where the current is not evident fluctuation during the 40000 s electrolysis measurement indicating its excellent stability. The present work expands the application of Bi in the catalysis and provides the simple strategies to improve its hydrogen evolution performance.

1. Introduction
Hydrogen with high energy density and no carbon contaminant is considered as one of the most important energy carriers for humanity in the future[1−3]. Electrocatalytic hydrogen evolution, being a promising method for the large-scale production of hydrogen[4, 5], has been extensively studied in recent decades[6]. However, developing the effective, stable and cost-effective catalysts to meet the needs of hydrogen economy is still a huge challenge[7, 8]. Some significant advances have shown that 2D layered materials have great potential in the field of catalysis due to their unique structures and properties[9−13]. Black phosphorus (BP), a newly emerging 2D pnictogens[14, 15], has been widely used in catalysis due to high carrier mobility (1000 cm$^2$ V$^{-1}$ s$^{-1}$)[16], a large number of exposed active sites[17] and non-noble element[18, 19]. It has been reported that the application of BP to photocatalytic hydrogen production achieves a quantum efficiency of 42.55 % under the light of 430 nm and an energy conversion efficiency of 5.4 % at 353 K[20]. However, the inherently poor stability of BP under ambient conditions hinders its further development[21]. Recently, 2D Bi, with the similar structure and properties to BP has attracted a lot of attention due to its good environmental stability[22−25]. In addition, the advantages of low cost, low toxicity and environmental friendliness[26] make bismuth-based catalyst show great potential in the field of catalysis.

2D Bi have the buckled honeycomb structure similar to BP, which can provide large number of active sites for catalytic reactions[27, 28]. Kim et al. grew the Bi nanosheets on the Cu substrate using the pulse electrodeposition method, finding the prepared nanosheets with large number of edge and corner sites had better catalytic performance than the Bi film[29]. Furthermore, the Bi as a natural semi-metallic
material has high intrinsic electron mobility \((5.7 \times 10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\)[30–32], which is believed to facilitate the catalytic reaction[33, 34]. Aktürk et al. used the first-principles phonon and finite temperature molecular dynamics calculation to demonstrate that 2D Bi has the excellent durability even at high temperatures[35]. The attractive qualities of 2D Bi presented above make it show great potential in the field of electrocatalysis. Most recently, Li et al. demonstrated 2D Bi nanosheets with effective p-orbital electron delocalization and sufficiently exposed active sites prepared by situ electrochemical reduction could significantly promote electrocatalytic NRR (\(\text{N}_2\) reduction reaction)[36]. Simultaneously, Su et al. reported that the ultrathin Bi nanosheet has an enhanced activity of \(\text{CO}_2\) electrocatalytic reduction due to its much higher electron state density around Fermi level than the bulk counterpart[37]. At the same time, the high catalytic activity of 2D Bi is also expected to be effective in electrocatalytic water splitting. Pillai et al. reported the adsorption energy of the hydrogen atom and oxygen atom on the surface of Bi were \(-1.418\) eV and \(-3.963\) eV, respectively. The small adsorption energy of the atomic hydrogen indicates that hydrogen evolution reaction is more likely to occur on the surface of 2D Bi[38, 39]. Therefore, exploring the application of bismuth in electrocatalytic hydrogen evolution has great significance due to the promising features of 2D Bi nanosheets.

In this work, the 2D Bi nanosheets were prepared by the simple sonication assisted liquid-phase exfoliation method. Benefitting from the exfoliation, 2D Bi has more active sites and shorter charge diffusion distance as compared to bulk counterpart[40, 41], which is the remarkable feature of efficient catalysis. The calculated Gibbs free energy was used to evaluate the hydrogen adsorption on the surface of 2D Bi with different layers. Further study about the electrochemical activity of Bi nanosheets in different \(\text{C}[\text{H}_2\text{SO}_4]\) solutions indicates high \(\text{C}[\text{H}^+]\) is more beneficial to the electrocatalytic hydrogen evolution. After the stability test for 40000 s, the Bi nanosheets still presents good electrochemical activity. This work explores the application of the 2D Bi in electrocatalytic hydrogen evolution and proposes acceptable ways to optimize its catalytic activity.

2. Experimental Section

2.1 Chemicals and Materials

Bulk bismuth (99.999%, Aladdin), Ethanol absolute (99.5%, Aladdin) and isopropyl alcohol (99.9%, Aladdin) was purchased from Aladdin Co., Ltd. (Fengxian District, Shanghai, China). All aqueous solutions were prepared with ultrapure DI water (resistivity of 18.2 M\(\Omega\) \cdot \text{cm}). The other reagents used in this experiment were of analytical grade and without further purification.

2.2 Synthesis of Materials

Bismuth nanosheets were prepared by the sonication assisted liquid-phase exfoliation method. The granular Bi (400 mg) were ground in an agate mortar for 20 min to make the particles small. Adding the Bi powders into the wide-mouth glass bottle with 90 mL isopropyl alcohol, which was tip sonicated in ice bath using probe sonication (BILON-1800Y, with the power of 30% of 1800 W) for 12 h. Subsequently, the
dispersions were centrifuged at 1000 rpm for 20 min to remove the large aggregates. The collected supernatant was further centrifuged at 7000 rpm for 30 min, and the required Bi nanosheets were acquired. Finally, the Bi nanosheets was obtained after washing and centrifugation for two times using ethanol and deionized water.

### 2.3 Preparation of Working Electrodes

The Bi nanosheets (2 mg) and 20 µL of Nafion solution (5 wt%) were mixed in 2 mL deionized water to prepare the homogeneous dispersion by the sonication (about 10 min). Drop 25 µL of the mixed solution (1 mg/mL) on the glassy carbon electrode with the area of 0.0706 cm$^2$ in batches and then the electrocatalytic performance of working electrode with 25 µg Bi nanosheets would be tested after drying in a vacuum environment for 5 hours.

### 2.4 Characterization of Electrocatalyst

The structural of Bi nanosheets can be characterized by X-ray diffraction and Raman spectra. Here, we obtain the information of X-ray diffraction by Ultima IV with Cu/Ka radiation and Raman spectra by HORIBA JY Raman microscope with excitation laser wavelength of 532 nm at ambient temperature. Besides, scanning electron microscopy (VEGA3 SBH, Tescan) is used to characterize the morphology and structure of Bi nanosheets.

### 2.5 Electrochemical Measurements of Bi nanosheets

The electrochemical performance of as-prepared materials is tested by the electrochemical workstation (CHI660E, CH Instruments, Inc., Shanghai) equipped with a standard three-electrode (Working electrode, Reference electrode, Counter electrode). The glassy carbon electrode modified with Bi, Pt foil and saturated calomel electrode are used as the working electrode, counter electrode and reference electrode, respectively.

### 3. Results And Discussion

The typical process of sonication assisted liquid-phase exfoliation for preparing Bi nanosheets has been illustrated in the Fig. 1. The advantage of large-scale production of Bi nanosheets can meet the potential demand of industry. Figure 2a is the SEM image of Bi before exfoliation. It is clear that the surface of pristine bulk Bi is compact and flat. In contrast, the exfoliated materials, as shown in Fig. 2b, exhibit irregularly shaped straight, smooth edges, as well as the apparent lateral diameters are not uniform, indicating that the 2D Bi nanosheets are successfully exfoliated from the bulk counterparts by the liquid-phase exfoliation. In order to further study the crystal structure, the Raman spectra of bulk Bi and exfoliated Bi nanosheets are carried out in the Fig. 2c. It is known that $E_g$ and $A_{1g}$ peak are corresponding to an in-plane vibrational mode at low wavenumbers ($v$) and out-of-plane vibrational mode at high $v$, respectively, which are consistent with previous reports[42]. This proves that the structure of Bi nanosheets is not destroyed in the process of liquid-phase exfoliation. Compared with the Raman peaks of the bulk Bi, the peak intensities of exfoliated Bi reduced, indicating the reduced number of layers[43]. In
addition, the slight blue shift toward a higher wavenumber is attributed to the decrease of lateral dimensions and the reduction of thickness of Bi[44]. Figure 2d shows the XRD patterns of Bi nanosheets, where the diffraction peaks located at 22.5°, 23.8°, 27.1°, 38.0°, 39.6°, 44.6°, 45.9°, 46.0°, 46.7°, 48.7°, 56.0°, 59.3° corresponds well to (003), (101), (012), (104), (110), (105), (006), (113), (021), (202), (024), (107) planes of Bi crystal planes (JCPDF Card No.85-1329). Sharp diffraction peaks of exfoliated Bi nanosheets indicate that the sample possesses excellent crystalline nature.

The electrocatalytic performance of Bi for HER was evaluated in 0.5 M H$_2$SO$_4$ solution by the electrochemical workstation. Figure 3a displays the schematic illustration of three-electrode electrochemical cell. The polarization curves of the current density plotted against potential in Fig. 3b presents the electrocatalytic activity of the Bi nanosheets and the bulk Bi. The exfoliated Bi nanosheets require a lower potential of -0.96 V (versus RHE, reversible hydrogen electrode) to reach the current density of 10 mA/cm$^2$ than the bulk Bi (-1.06 V vs. RHE). The enhanced electrochemical activity of Bi nanosheets is attributed to the sufficient exposed active sites and shortened charge diffusion distance after the exfoliation[45]. \textbf{(Fig. S1} shows the LSV curves of GC$_{\text{bare}}$ and Bi nanosheets measured in 0.5 M H$_2$SO$_4$ at a scan rate of 10 mV/s. \textbf{Fig. S2} shows Tafel plots of GC$_{\text{bare}}$ and Bi nanosheets in 0.5 M H$_2$SO$_4$.\textbf{) Moreover, the excellent catalytic performance of Bi nanosheets is reconfirmed by the Tafel plots, which can be received from the fitted LSV curve by the equation $\eta = a + b \log |j|$ (where $\eta$ is the overpotential, $j$ is the current density and b is the Tafel slope). Compared with the Tafel slope (163 mV/dec) of the bulk Bi in the Fig. 3c, the Tafel slope (122 mV/dec) of Bi nanosheets measured in 0.5 M H$_2$SO$_4$ is smaller, indicating a dramatically improved electrocatalytic H$_2$ generation performance. The reaction kinetics of hydrogen evolution reaction at the electrode interface is further investigated by the electrochemical impedance spectroscopy (EIS). Charge transfer resistance ($R_C$) of Bi nanosheets has a significant decrease in comparison with the bulk Bi according to the Nyquist plots in \textbf{Fig. S3}. Bi nanosheets as the working electrode possess a much smaller resistance, which is believed that the nanostructure is beneficial for electronic transport and reduction of parasitic Ohmic losses. Furthermore, the first-principles calculation is used to explore the dependence of electrocatalytic activities on the thickness of Bi. The Gibbs free energy ($\Delta G$) of Bi with 1, 2 and 5 layers toward HER has been presented in the Fig. 3d (the details about the theoretical calculations are presented in \textbf{Fig. S4}). It is observed that the $\Delta G$ decreases as the reduction of layer number, which suggests the reducing the thickness of Bi is beneficial to hydrogen evolution reaction.

To further evaluate the HER performance of Bi nanosheets, the vital parameters measured in 0.05 M, 0.1 M, 0.3 M and 0.5 M H$_2$SO$_4$ solutions were carried out, respectively. Figure 4a depicts typical HER polarization curves of Bi nanosheets from -0.1 V to -1.4 V vs. RHE in different C[H$_2$SO$_4$] solutions. The Bi nanosheets exhibit a lower overpotential of -0.96 V vs. RHE at 10 mA/cm$^2$ in 0.5 M H$_2$SO$_4$ solution, indicating the exfoliated nanosheets have the higher hydrogen evolution activity. The effect of C[H$^+$] on overpotential at the current density of 10 mA/cm$^2$ has been shown in the Fig. 4d (blue line). Besides, the green line (Fig. 4d) depicts the current density increases rapidly with increasing of C[H$^+$] under the same
bias voltage (-1 V vs. RHE). In the Table S2, current density of 18.71 mA cm\(^{-2}\) obtained in the 0.5 M H\(_2\)SO\(_4\) solution is much higher than that (2.41 mA cm\(^{-2}\)) in the 0.05 M H\(_2\)SO\(_4\) solution, demonstrating high C[H\(^+\)] can significantly promote the electrocatalytic performance of Bi nanosheets. Tafel plots and EISs have also been performed to further gain insight into the inherent mechanism on enhanced hydrogen evolution of Bi nanosheets in high C[H\(^+\)] solution. In Fig. 4b, the lowest Tafel slope (122 mV dec\(^{-1}\)) is obtained in the 0.50 M H\(_2\)SO\(_4\) solution, suggesting that Bi nanosheets have a relatively good electrocatalytic hydrogen evolution performance. The red line in the Fig. 4d shows that concentration-dependent Tafel slope over the Bi nanosheets. The Tafel slope decreases from the 215 mV dec\(^{-1}\) to 122 mV dec\(^{-1}\) with increasing of C[H\(_2\)SO\(_4\)] from 0.05 M to 0.50 M, illuminating high C[H\(^+\)] can enhance the hydrogen evolution reaction. Besides, we used the EIS spectrums measurand in 0.05 M, 0.1 M, 0.3 M and 0.5 M H\(_2\)SO\(_4\) under initial potential of 1.0 V and low frequency of 0.01 Hz to further explain the reaction kinetics of HER on the Bi nanosheets in different C[H\(_2\)SO\(_4\)] solutions. The EIS spectrum of Bi nanosheets in the 0.5 M H\(_2\)SO\(_4\) (Fig. 4c) solution reveals a characteristic semicircle with a minimum diameter in high frequency region (inset of Fig. 4c) which implies a lowest charge transfer resistance (R\(_{CT}\)). Obviously, the high C[H\(^+\)] can enhance the hydrogen reaction on the Bi surface and accelerate the charge transport at the reaction interface.

The stability of Bi nanosheets as the catalyst for HER in the different C[H\(_2\)SO\(_4\)] solution is investigated by the long-term durability test. As shown in Fig. 5a, the current densities provided by Bi nanosheets under 1.3 V (vs. SCE) in 0.05 M, 0.1 M, 0.3 M and 0.5 M H\(_2\)SO\(_4\) solutions exhibit no significant loss over a period of 40000 seconds, demonstrating Bi nanosheets have excellent stability. In 0.5 M H\(_2\)SO\(_4\) solutions, there is the largest current density (about 75 mA) under the potential of 1.3 V vs. SCE, which is consistent with previous experimental results. Nevertheless, there is a large noise on the stable current density curves when the large current passes through the work electrode. The maximal amplitude of current density at equilibrium position for 0.5 M H\(_2\)SO\(_4\) is believed that the produced hydrogen caused interference to the catalyst surface. The polarization curves (Fig. 5b) that were performed for Bi nanosheets in 0.05 M H\(_2\)SO\(_4\) (Fig. 5c, d and e were measured in 0.1 M, 0.3 M and 0.5 M H\(_2\)SO\(_4\), respectively) before and after 40000 s HER experiments ranging from −0.5 to -1.6 vs. SCE display no noticeable change of electrode current, which further confirmed Bi nanosheets can be a potentially stable electrocatalyst for HER.

4. Conclusion

In this work, the 2D Bi nanosheets had been exfoliated successfully from the Bi powders by the sonication assisted liquid-phase exfoliation. The exfoliated Bi nanosheets have much higher electrocatalytic activity, which is attributed to the sufficient exposure of active sites and short charge diffusion distance. Theoretical calculation also shows that the reduction of thickness of Bi can improve its electrocatalytic performance due to the enhanced hydrogen adsorption on catalyst surface. Further research on catalytic activity of the Bi nanosheets in different C[H\(_2\)SO\(_4\)] solutions reveals that the high C[H\(^+\)] is more beneficial to the electrocatalytic hydrogen evolution. Long-term hydrogen evolution under
large bias voltage in different $\text{C[\text{H}_2\text{SO}_4]}$ solutions has been carried out, which demonstrates excellent durability and efficient electrocatalytic activity of Bi nanosheets. This work explores the application of the 2D Bi in electrocatalytic hydrogen evolution, and proposes the strategies to enhance the electrocatalytic performance of the catalyst.

**Declarations**

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Figures
Figure 1

Schematic illustration of preparation for Bi nanosheets via sonication assisted liquid-phase exfoliation.
Figure 2

(a) SEM image of the bulk Bi. (b) SEM image of the exfoliated Bi nanosheets. (c) The Raman spectra of Bi nanosheets and bulk Bi. (d) XRD patterns of Bi nanosheets.
Figure 3

(a) Schematic illustration of electrocatalytic performance measurement. (b) The LSV curves of bulk Bi and Bi nanosheets in 0.5 M H2SO4 at a scan rate of 10 mV s⁻¹. (c) Tafel plots of bulk Bi and Bi nanosheets in 0.5 M H2SO4. (d) The theoretical calculation about Gibbs free energy (ΔG) of Bi with 1, 2 and 5 layers toward HER.
Figure 4

(a) LSV curves of Bi nanosheets from -0.1 V to -1.4 V in 0.05 M, 0.1 M, 0.3 M and 0.5 M H2SO4. (b) Tafel plots of Bi nanosheets in 0.05 M, 0.1 M, 0.3 M and 0.5 M H2SO4. (c) The EISs of Bi nanosheets in 0.05 M, 0.1 M, 0.3 M and 0.5 M H2SO4 under initial potential of 1 V and low frequency of 0.01 Hz. Inset image is the zoom in EIS plots of high-frequency area. (d) The Tafel slope, current density at 1.0 V and potential at 10 mA/cm² as a function of C[H⁺].
Figure 5

(a) is the long-term durability test for Bi nanosheets under 1.3 V vs. SCE in 0.05 M, 0.1 M, 0.3 M and 0.5 M H2SO4 over a period of 40000 seconds. (b), (c), (d) and (e) are the LSV curves of Bi nanosheets before and after 40000 seconds HER experiments ranging from -0.5 to -1.6 V vs. SCE in 0.05 M, 0.1 M, 0.3 M and 0.5 M H2SO4, respectively.