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Article

In situ synthesis of a nickel boron oxide/graphdiyne hybrid for enhanced photo/electrocatalytic H₂ evolution

Xue-Peng Yin[†], Shu-Wen Luo[†], Shang-Feng Tang, Xiu-Li Lu^{*}, Tong-Bu Lu[#]

MOE International Joint Laboratory of Materials Microstructure, Institute for New Energy Materials and Low Carbon Technologies, School of Material Science & Engineering, Tianjin University of Technology, Tianjin 300384, China

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ABSTRACT

Developing highly active catalysts for photo/electrocatalytic water splitting is an attractive strategy to produce H₂ as a renewable energy source. In this study, a new nickel boron oxide/graphdiyne (NiB₂/GDY) hybrid catalyst was prepared by a facile synthetic approach. Benefitting from the strong electron donating ability of graphdiyne, NiB₂/GDY showed an optimized electronic structure containing lower valence nickel atoms and demonstrated improved catalytic performance. As expected, NiB₂/GDY displayed a high photocatalytic H₂ evolution rate of 4.54 mmol g⁻¹ h⁻¹, 2.9 and 4.5 times higher than those of NiB₂/graphene and NiB₂, respectively. NiB₂/GDY also displayed outstanding electrocatalytic H₂ evolution activity in 1.0 M KOH solution, with a current density of 400 mA/cm² at an overpotential of 478.0 mV, which is lower than that of commercial Pt/C (505.3 mV@400 mA/cm²). This work demonstrates that GDY is an ideal support for the development of highly active catalysts for photo/electrocatalytic H₂ evolution.

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1. Introduction

Energy shortages and environmental issues have triggered considerable interest in alternative energy storage and conversion systems [1]. Hydrogen is regarded as a potential substitute for traditional fossil fuels, due to its high energy density and green combustion products [2,3]. Photo/electrocatalytic water splitting is a promising way of converting solar and electric energy into chemical fuels [4–7]. During the past few decades, significant efforts have been made to develop highly efficient catalysts for the H₂ evolution reaction (HER). Until now, the best HER catalysts have been based on the noble metals, such as platinum [8]. However, the scarcity and high cost of noble

metals hamper their large-scale application. Thus, it is extremely attractive to exploit earth-abundant and cost-efficient catalysts for the HER [9]. Considerable efforts have been devoted to developing new, more efficient non-noble-metal-based catalysts, such as transition-metal dichalcogenides [10–12], phosphides [13–16], carbides [17], and borates [18–20]. However, catalysts using non-noble metals alone often suffer from low active surface areas and inefficient diffusion of charge carriers, resulting in unsatisfactory catalytic performances. To improve their catalytic activities, a large number of non-noble-metal-based nanocomposites have been fabricated by integrating them on supports with high electron transfer rates and high surface areas, such as graphene [19,21,22] and

^{*} Corresponding author. Tel/Fax: +86-22-60215704; E-mail: luxiuli@email.tjut.edu.cn

[#] Corresponding author. E-mail: lutongbu@tjut.edu.cn

[†] These authors contributed equally to this work.

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carbon nanotubes [23,24]. Thus, designing non-noble-metal nanocomposite materials as photo/electrocatalysts with high numbers of surface-active sites and superior stabilities is highly desirable.

Graphdiyne (GDY), a new carbon allotrope, has shown great potential for photo/electrocatalytic water splitting due to its unique chemical and electronic structure [25]. Compared to graphene and other traditional carbon materials, GDY is composed of an sp^2 - and sp -hybridized carbon network, which affords GDY favorable semiconductor property, superior electrical conductivity, and robust stability. GDY also possesses uniformly dispersed pores and a large specific surface area, providing an enormous number of sites for anchoring metal ions and constructing stable non-noble-metal-based nanocomposites. Therefore, GDY has been proven to be an ideal support for in situ growth of stable nanocatalysts for water splitting. To date, TiO_2/GDY [26], CdS/GDY [27], and $\text{g-C}_3\text{N}_4/\text{GDY}$ [28] hybrids have been fabricated and applied to photocatalytic water splitting, with GDY displaying improved separation and migration of photoinduced charge carriers, leading to enhanced photocatalytic activities. In addition, MoS_2/GDY [29], WS_2/GDY [30], CoNC/GDY [31], FeCH/GDY [32], $\text{Ni-Co-P}/\text{GDY}$ [33], and CoLDH/GDY [34] hybrids have also been constructed to enhance their electrocatalytic water splitting performances. However, GDY has never been used to construct a nanocomposite that could be applied as a catalyst in both photocatalytic and electrocatalytic water splitting reactions for H_2 evolution.

In this study, we prepared for the first time a strongly coupled nickel boron oxide/graphdiyne (NiB_i/GDY) hybrid through a facile room-temperature chemical route, for use as a highly active HER catalyst for photo/electrocatalytic H_2 evolution. NiB_i/GDY displayed improved H_2 evolution under visible light irradiation in aqueous solutions when using Eosin Y (EY) as a photosensitizer and triethanolamine (TEOA) as a sacrificial reagent, realizing 2.9 and 4.5 times higher H_2 evolution rates than those of $\text{NiB}_i/\text{graphene}$ and NiB_i , respectively. Furthermore, NiB_i/GDY showed high HER electrocatalytic activity, achieving a current density of $400 \text{ mA}/\text{cm}^2$ at an overpotential of 478.0 mV, lower than that of commercial Pt/C ($505.3 \text{ mV}/400 \text{ mA}/\text{cm}^2$). The improved catalytic performance can be attributed to the formation of strongly coupled NiB_i/GDY , in which the strongly electron donating GDY optimized the electronic structure of NiB_i with lower valence Ni sites. These results demonstrate that GDY could be a promising support for in situ synthesis of nanocomposites as highly active photo/electrocatalysts.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of graphdiyne

GDY was synthesized via an acetylenic cross-coupling reaction, as previously reported [25,35].

For the synthesis of GDY powder, 33 mg of hexaethynylbenzene (HEB) was dissolved in pyridine and slowly

added to a three-necked flask containing copper foils immersed in pyridine. The mixture was protected from light and then heated for 72 h at 110°C under an Ar atmosphere. After completion of the reaction, the GDY was washed with hot DMF, acetone, HCl, NaOH, and water in turn, and then dried at 50°C under vacuum for 12 h.

For the synthesis of GDY nanowalls, HEB (10 mg) was dissolved in acetone and added slowly to a three-necked flask containing five treated Cu foams immersed in a mixture of acetone, pyridine, and tetramethylethylenediamine (TMEDA) with a volume ratio of 100:5:1. The mixed solution was heated in the dark and under an Ar atmosphere for 12 h at 50°C . After the reaction, the GDY nanowalls grown on the Cu foams were washed sequentially with heated DMF and acetone, and dried at 50°C under vacuum for 12 h.

2.1.2. Synthesis of NiB_i/GDY

For NiB_i/GDY used in photocatalytic HER, GDY powder (8 mg) was dispersed into 4 mL of ultrapure water. Then, an aqueous solution of $\text{Ni}(\text{NO}_3)_2$ (40 mM, 508 μL) was added to the GDY solution with continuous stirring. After 3 min, 100 μL of a sodium borohydride (NaBH_4) solution (3 mg/mL) was added for a further 2 min. The obtained NiB_i/GDY was then washed and dried overnight under vacuum.

For NiB_i/GDY used in electrocatalytic HER, a piece of GDY nanowall was immersed in a solution of $\text{Ni}(\text{NO}_3)_2$ (40 mM, 20 mL) for 40 min. Then, an NaBH_4 solution (0.5 M, 4 mL) was added and allowed to react for another 2 h. After the reaction, the NiB_i/GDY was washed with pure water to get rid of extra Ni^{2+} and NiB_i . The NiB_i/GDY sample was obtained after drying in air.

2.1.3. Synthesis of $\text{NiB}_i/\text{graphene}$

Graphene (8 mg) was homodispersed in 4 mL of ultrapure water. Subsequently, an aqueous solution of $\text{Ni}(\text{NO}_3)_2$ (40 mM, 508 μL) was added to the graphene solution under continuous stirring. After reacting for 3 min, 100 μL of NaBH_4 solution (3 mg/mL) was added for another 2 min. The $\text{NiB}_i/\text{graphene}$ was obtained after washing and drying under vacuum overnight.

2.1.4. Synthesis of NiB_i

NaBH_4 solution (0.5 M, 4 mL) was added to an aqueous solution of $\text{Ni}(\text{NO}_3)_2$ (40 mM, 20 mL) under continuous stirring. After reacting for 2 h at room temperature, a black sample was acquired by centrifugation and washed three times each with pure water and ethanol. The NiB_i sample was finally obtained after drying under vacuum overnight.

2.2. Characterization

The surface morphologies of the as-prepared samples were determined by scanning electron microscopy (SEM, Verios 460L Ultrahigh Resolution Scanning Electron Microscope) and energy dispersive X-ray spectrometry (EDS). Transmission electron microscopy (TEM) was performed using a Tecnai G2 Spirit TWIN at an acceleration voltage of 120 kV. The compositions and surface electronic states of the as-prepared samples

were measured using X-ray photoelectron spectroscopy (XPS, ESCA LAB250Xi). Raman spectra were analyzed using a high-resolution laser confocal fiber Raman spectrometer (HORIBA EVOLVION, HORIBA Jobinyvon, France) with an excitation wavelength of 532 nm. A fluorescence spectrophotometer (F-7000, Hitachi, Tokyo, Japan) was employed to obtain the photoluminescence (PL) spectra. Fluorescence decay spectra were measured on a MiroTime 200 time-resolved confocal fluorescence instrument.

2.3. Photocatalytic H_2 evolution measurements

In a typical experiment, 2 mg of the as-prepared catalyst was dispersed in 5 mL of a 10% (v/v) aqueous solution of TEOA, then 3 mg of EY was added. Before irradiation, the solution was purged with Ar for 30 min to remove air, followed by irradiation with a 300 W Xe lamp equipped with a UV-cutoff filter ($\lambda > 400$ nm). The reactant solution was maintained at 25 °C by a flow of cooling water. The evolved H_2 was detected using a gas chromatograph (GC-2014+ATF, 230C, Shimadzu, Japan) equipped with a thermal conductivity detector (TCD).

2.4. Electrochemical measurements

Electrochemical measurements were performed on a standardized three-electrode system (CHI 760E, CH Instruments) with a working electrode, a saturated Ag/AgCl reference electrode, and a carbon rod counter electrode. The as-prepared samples were directly used as the working electrode. Linear sweep voltammetry (LSV) measurements were performed in 1.0 M KOH electrolyte at a scan rate of 5.0 mV/s. All potentials were referenced to the reversible hydrogen electrode (RHE) from the Ag/AgCl reference electrode as follows: $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.198 + 0.059 \times \text{pH}$. For comparison, 9.0 mg of Pt/C was dispersed in 2.5 mL water/ethanol (v/v = 4:1) containing 100 μL of a 5 wt% Nafion solution. The mixture was sonicated for 1 h, then 140 μL of the catalyst ink was loaded onto the Cu foam. The NiBi and $\text{NiBi}/\text{graphene}$ inks were prepared by dispersing 4 mg of the respective catalyst into 970 μL of ethanol/water (v/v = 1:1) containing 30 μL of a 5 wt% Nafion solution and sonicating them for 1 h. Then, 67 μL of the NiBi -containing ink or 250 μL of the $\text{NiBi}/\text{graphene}$ -containing ink was loading onto the Cu foam. All tests were performed without further iR compensation.

3. Results and discussion

The NiBi/GDY hybrid was prepared by a simple chemical synthesis strategy performed at room temperature. For comparison, pure NiBi and NiBi grown on graphene ($\text{NiBi}/\text{graphene}$) were also prepared following a similar method to prepare NiBi/GDY . To prepare NiBi/GDY , GDY was immersed in a solution containing Ni^{2+} ions, which could interact with the butadiyne linkages ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$) and anchor on to GDY, as illustrated in Scheme 1. After further reaction with NaBH_4 , the NiBi nanosheets were grown in situ on the GDY, leading to the formation of the NiBi/GDY hybrid. The surface morphology and

Scheme 1. The *in situ* growth of NiBi on GDY at room temperature.

composition of the as-prepared NiBi/GDY were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS). The SEM image of GDY (Fig. 1a) shows a nanosheet array morphology with an irregular nanowall structure. After NiBi nanosheets were evenly grown on the surface of GDY, the surface morphology became wrinkled (Fig. 1b), indicating the successful growth of NiBi on GDY. The TEM images further confirm the successful construction of the NiBi/GDY hybrid (Figs. e 1c, 1d, and Fig. S1). TEM images were also obtained for $\text{NiBi}/\text{graphene}$ and pure NiBi (Fig. S2 and Fig. 1e, respectively). $\text{NiBi}/\text{graphene}$ showed NiBi nanosheets homogeneously organized on the surface of the graphene. Unlike NiBi/GDY and $\text{NiBi}/\text{graphene}$, pure NiBi exhibited a hierarchical structure comprised of aggregated nanosheets (Fig. 1e). In addition, the insets of Figs. 1d, 1e, and S2 show the selected area electron diffraction (SAED) patterns of NiBi/GDY , NiBi , and $\text{NiBi}/\text{graphene}$, respectively, verifying the amorphous structures of the as-prepared samples. Furthermore, the HR-TEM image (Fig. S1b) and X-ray powder diffraction (XRD) patterns (Fig. S1c) of NiBi/GDY show no distinct lattice fringes or crystal diffraction peaks, respectively, confirming its amorphous structure [36]. EDS mapping images (Fig. 1f) also reveal uniform distributions of C (green), Ni (red), B (blue), and O (pink) in NiBi/GDY . The above results show that the NiBi/GDY hybrid was successfully

Fig. 1. SEM images of GDY (a) and NiBi/GDY (b); TEM images of NiBi/GDY (c,d) and NiBi (e); The insets of d and e are the corresponding SAED images of NiBi/GDY and NiBi , respectively; (f) EDS mapping images of NiBi/GDY .

synthesized via in situ growth of NiB_i on GDY.

The chemical compositions and electronic structures of samples were evaluated by XRD, Raman spectroscopy, and XPS. As exhibited in Fig. 2a, the XRD pattern of NiB_i/GDY demonstrates no distinct diffraction patterns attributable to crystalline nickel compounds, corresponding to the results of the SAED measurements. Fig. 2b shows the Raman spectrum of GDY, which contains four distinct peaks at 1394.4, 1544.4, 1923.8, and 2183.3 cm⁻¹ in accordance with reported data [25]. Specifically, the peaks at 1394.4 and 1544.4 cm⁻¹ are attributed to the D band (the breathing vibration of *sp*² carbons) and G band (the first-order scattering of the *E*_{2g} mode of the in-phase stretching vibration of *sp*² carbons) of aromatic rings, respectively. Meanwhile, the peaks at 1923.8 and 2183.3 cm⁻¹ belong to the typical vibrations of conjugated diyne links (–C≡C–C≡C–) in GDY. As for NiB_i/GDY, the G band peak exhibited an obvious hypsochromic shift to 1580.7 cm⁻¹ due to electronic interactions and the electron-donating nature of GDY [28]. In addition, the peaks assigned to –C≡C–C≡C– became weaker compared to those of GDY, which could be attributed to the formation of chemical interactions between NiB_i and GDY [37]. As shown in Fig. S3, the survey XPS pattern shows the presence of C, O, B, and Ni in NiB_i/GDY, which is consistent with the results of the EDS analysis. The high-resolution C 1s spectrum of NiB_i/GDY is shown in Fig. S4a. The C 1s peak can be deconvoluted into four subpeaks at 284.42, 285.09, 286.40, and 288.57 eV, which can be assigned to C–C (*sp*²), C–C (*sp*), C–O, and C=O species, respectively [38]. The high-resolution Ni 2p spectra of NiB_i and NiB_i/GDY were also compared. As shown in

Figs. S4b and S4c, NiB_i showed two distinct Ni 2p_{3/2} sub-peaks located at 855.9 and 875.5 eV, which could correspond to Ni²⁺ and Ni³⁺, respectively (as a result of the partial oxidation of the surface). On the other hand, NiB_i/GDY exhibited one main Ni 2p_{3/2} peak located at 855.74 eV, which is slightly lower than that seen in NiB_i, indicating a lower valence of Ni than Ni²⁺. This lower valence state demonstrates the strong interaction between NiB_i and GDY, which could optimize the electronic structure and enhance the catalytic performance, as reported in the literature [39–41]. Furthermore, the binding energies of the peaks attributed to Ni 2p_{3/2} and Ni 2p_{1/2} in NiB_i and NiB_i/graphene are higher than those seen for NiB_i/GDY (Figs. 2c and S5), indicating the presence of Ni ions with lower valence states in NiB_i/GDY than those seen in NiB_i and NiB_i/graphene. This demonstrates that the strong coupling effect between NiB_i and GDY in the NiB_i/GDY hybrid has efficiently tuned the electronic structure of NiB_i. In addition, the B 1s spectrum of NiB_i/GDY shows a peak at 192.1 eV (Fig. 2d). This can be attributed to B³⁺ from boron oxide species, proving the successful formation of NiB_i/GDY.

The photocatalytic H₂ evolution performances of NiB_i/GDY, NiB_i/graphene, NiB_i, and GDY were measured in aqueous solutions using TEOA as a sacrificial reagent and EY as a photosensitizer under visible light irradiation (λ > 400 nm). As shown in Fig. 3a, the time courses of the photocatalytic H₂ evolution reactions demonstrate that NiB_i/GDY showed the best H₂ evolution activity. The amount of H₂ evolved by NiB_i/GDY increased sharply with the time, reaching 31.78 mmol/g after 7 h. This was 2.9 and 4.5 times higher than the performances of Ni-

Fig. 2. (a) XRD patterns of GDY and NiB_i/GDY, (b) Raman spectra of GDY and NiB_i/GDY, (c) Ni 2p, and (d) B 1s XPS patterns of NiB_i and NiB_i/GDY.

Fig. 3. (a) Time dependence of photocatalytic H₂ generation using NiB_i/GDY, NiB_i/graphene, NiB_i, and GDY catalysts (Reaction conditions: 2 mg catalyst, 3 mg Eosin Y, 5 mL aqueous solution containing 10 vol% TEOA, Xe-lamp (300 W, $\lambda > 400$ nm)). (b) Photocatalytic activity recycling test for NiB_i/GDY. (c) Steady-state photoluminescence spectra of NiB_i/GDY, NiB_i/graphene, and NiB_i. (d) Time-resolved fluorescence decay spectra of NiB_i/GDY, NiB_i/graphene, and NiB_i.

Bi/graphene (10.82 mmol/g) and NiB_i (7.02 mmol/g), respectively. The high H₂ evolution activity of NiB_i/GDY can be attributed to its two-dimensional π -conjugated structure, superior electrical conductivity, and the large specific surface area of GDY. The stability of NiB_i/GDY when used for H₂ evolution was also measured by re-dispersing the catalyst in fresh EY/TEOA reaction solutions every 7 h. As shown in Fig. S6a and Fig. 3b, NiB_i/GDY maintained its photocatalytic performance 11 h, showing no loss in H₂ yield after 5 cycles of 7 h, displaying its excellent stability. Meanwhile, a TEM image of NiB_i/GDY after the photocatalytic reaction was also taken (Fig. S6b), confirming the stability of the hybrid during the photocatalytic reaction. In contrast, when using the same ratio of NiB_i to GDY in NiB_i/GDY, the mixture showed poor H₂ reduction activity (Fig. S7). This comparison highlights the importance of the strong coupling effect between GDY and NiB_i in NiB_i/GDY, which optimizes the electronic structure of NiB_i and enhances the photocatalytic HER performance.

The apparent quantum efficiency (AQE) of NiB_i/GDY is shown in Fig. S8. To better comprehend the photocatalytic process, the photoluminescence (PL) and time-resolved fluorescence (TRF) spectra measured. As shown in Fig. 3c, the PL spectrum of an aqueous solution of EY without any catalyst (blank) showed the strongest emission due to severe recombination of photoinduced charge carriers and low H₂ evolution activity. Meanwhile, obvious PL quenching was observed when NiB_i, NiB_i/graphene, or NiB_i/GDY were added to the EY solution, demonstrating that the presence of these materials signif-

icantly promoted the separation of photoinduced charge carriers and that they could act as photocatalysts for H₂ evolution. To further understand the photophysical characteristics of the photoexcited carriers in these systems, the TRF spectra of the samples were measured. As shown in Fig. 3d, the average lifetimes obtained from the TRF spectra of blank, NiB_i, NiB_i/graphene, and NiB_i/GDY samples were 1.04, 0.76, 0.68, and 0.58 ns, respectively. These results demonstrate that NiB_i/GDY displayed an obvious improvement in the charge carrier separation efficiency in EY solutions when compared to NiB_i/graphene and NiB_i, corresponding to the results of the PL measurements. In short, NiB_i/GDY possesses a good ability to promote the separation of photoinduced electrons and holes generated in EY due to the strong coupling effect, resulting in extremely high catalytic activity and stability when used for photocatalytic H₂ evolution.

The electrocatalytic HER activities of NiB_i/GDY, NiB_i/graphene, NiB_i, and GDY were also investigated in 1.0 M KOH using a standard three-electrode electrochemical cell. Commercial Pt/C (20 wt%) was used as a reference to accurately evaluate the HER activity. Linear sweep voltammetry (LSV) curves of the different samples were measured at a scan rate of 5 mV/s, as shown in Fig. 4a. As expected, NiB_i/GDY showed enhanced HER activity when compared to GDY, NiB_i/graphene, and NiB_i. Notably, NiB_i/GDY achieved a high current density of 400 mA/cm² at an overpotential of 478.0 mV, whereas a higher overpotential of 505.3 mV was required to achieve such a current density for the commercial Pt/C catalyst.

Fig. 4. (a) LSV curves of electrochemical HER activities. (b) Electrochemical surface area (ECSA) measurements of NiBi/GDY, NiBi/graphene, and NiBi vs. scan rate. (c) Nyquist plots for NiBi, NiBi/graphene, and NiBi/GDY samples at -0.2 V vs. RHE. (d) Polarization curves of NiBi/GDY obtained initially and after 2000 cycles (inset: time dependence of the cathodic current density of NiBi/GDY over 40 h).

In addition, Fig. S9 shows that the Tafel slope of NiBi/GDY was $156.1 \text{ mV dec}^{-1}$, lower than that of NiBi ($298.0 \text{ mV dec}^{-1}$), demonstrating that the Volmer step was rate-determining and that rapid HER kinetics were realized in NiBi/GDY by accelerating the Volmer reaction [42]. The excellent HER performance of NiBi/GDY was possibly due to the strong coupling between NiBi and GDY, the latter of which significantly improves the conductivity of NiBi/GDY. The electrochemical surface areas of NiBi, NiBi/graphene, and NiBi/GDY were evaluated using their double-layer capacitances (C_{dl}), which were obtained from CV curves measured in the non-Faradic potential range from 0.644 – 0.744 V at rates varying from 20 – 60 mV/s in 1.0 M KOH (Figs. 4b and S10). The C_{dl} of NiBi/GDY was calculated to be 23.7 mF/cm^2 , much higher than those of NiBi (11.7 mF/cm^2) and NiBi/graphene (9.9 mF/cm^2), indicating a higher number of exposed active sites after the formation of the NiBi/GDY hybrid. To further understand the kinetic of the HER, Nyquist plots were measured (Fig. 4c), with these showing that the charge transfer resistance of NiBi/GDY was much lower than those of NiBi and NiBi/graphene. Moreover, both current density-time and long-term CV cycling curves (2000 cycles) confirmed the stability of NiBi/GDY during the HER (Fig. 4d). The Ni $2p$ XPS profiles were also compared to determine the stability of NiBi/GDY during the HER. As shown in Fig. S11, the oxidation states of the catalysts after the electrocatalytic H_2 evolution test were similar to those of the as-prepared samples, showing the good stability of NiBi/GDY. These results illustrate that NiBi/GDY possessed excellent activity and stability for the electrocatalytic HER.

4. Conclusions

In summary, we have successfully prepared a new NiBi/GDY hybrid at room temperature via a facile chemical strategy, and investigated its HER catalytic performance for photo/electrocatalytic water splitting. Benefitting from the strong coupling effect between GDY and NiBi, the electron-donating GDY lowered the valence of nickel in NiBi/GDY, resulting in an optimized electronic structure and enhanced photocatalytic HER performance for the NiBi/GDY hybrid. This material showed a H_2 evolution rate of $4.54 \text{ mmol g}^{-1} \text{ h}^{-1}$, which was 2.9 and 4.5 times higher than those of NiBi/graphene and NiBi, respectively, and demonstrated a better electrocatalytic HER performance than commercial Pt/C at high current density. This work not only provides a facile method for the construction of a highly efficient GDY-based catalyst for the HER, but also brings new insights into the development of non-noble-metal catalysts.

Electronic supporting information

Supporting information is available in the online version of this article.

Conflict of Interest

The authors declare no conflict of interest.

Graphical Abstract

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In situ synthesis of a nickel boron oxide/graphdiyne hybrid for enhanced photo/electrocatalytic H₂ evolution

Xue-Peng Yin, Shu-Wen Luo, Shang-Feng Tang, Xiu-Li Lu*, Tong-Bu Lu*
Tianjin University of Technology

A new nickel boron oxide/graphdiyne (NiB_x/GDY) hybrid is synthesized by a facile room-temperature synthesis approach and shows outstanding photocatalytic and electrocatalytic H₂ evolution activities.

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原位合成氧化镍硼/石墨炔杂化材料用于提高光/电催化产氢性能

殷学鹏[†], 罗舒文[†], 唐上峰, 卢秀利^{*}, 鲁统部[#]

天津理工大学材料科学与工程学院新能源材料与低碳技术研究院, 材料微结构教育部国际合作联合实验室, 天津300384

摘要: 当今世界面临严峻的能源紧缺和环境污染问题, 发展高效无污染的清洁能源替代传统化石能源成为近几十年科研工作者的研究热点. 其中, 氢能由于具有高燃烧值和产物无污染等优点成为理想的替代能源. 光/电催化水分解产生氢气是最有效的制氢方法之一. 目前, 高活性的产氢催化剂仍以贵金属为主, 但贵金属价格高昂和稀缺性等限制了其大规模应用, 因此, 开发和设计廉价、高效的非贵金属产氢催化剂变得尤为重要. 为了提高非贵金属催化剂的催化活性, 基于非贵金属的复合材料的构建被广泛研究. 例如, 通过非贵金属和碳材料的复合, 能够提高比表面积和电子传输速率, 优化活性位点的电子结构, 从而提高催化活性.

石墨炔(GDY)作为一种新兴碳材料, 由 sp^2 -和 sp -杂化碳共同组成. 由于GDY具有高度 π 共轭结构, 大的比表面积和独特的双炔键, 可作为载体与非贵金属离子相互作用形成复合材料, 制备高效产氢催化剂. 基于此, 本文在室温下原位合成了强耦合相互作用的氧化镍硼/石墨炔(NiB_x /GDY)催化剂, 并将其应用于光/电催化产氢反应. 在光催化产氢反应中, 采用曙红为光敏剂, 三乙醇胺为牺牲剂, 可见光下 NiB_x /GDY的光催化产氢速率可达 $4.54 \text{ mmol g}^{-1} \text{ h}^{-1}$, 产氢速率分别是氧化镍硼/石墨烯(NiB_x /graphene)和 NiB_x 的2.9倍和4.5倍. 此外, NiB_x /GDY在 1.0 M KOH 溶液中也表现出良好电催化产氢性能, 电流密度为 400 mA/cm^2 时其过电位为 478.0 mV , 低于商业铂碳($505.3 \text{ mV}@400 \text{ mA/cm}^2$). NiB_x /GDY在光/电催化产氢实验中表现出的较好催化性能可归因于 NiB_x 和GDY之间强耦合相互作用对 NiB_x 电子结构的优化. 上述研究结果表明, 石墨炔可作为理想载体制备高效的光/电催化剂, 同时本文为设计高效稳定的非贵金属产氢催化剂提供了一定的借鉴意义.

关键词: 石墨炔; 杂化材料; 光/电催化剂; 水分解反应; 氢析出

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*通讯联系人. 电话/传真: (022)60215704; 电子信箱: luxuli@email.tjut.edu.cn

#通讯联系人. 电子信箱: lutongbu@tjut.edu.cn

[†]共同第一作者.

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