University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2019

Fabrication of hierarchically one-dimensional $\text{ZnxCd}_{1-x}\text{S}/\text{NiTiO}_3$ nanostructures and their enhanced photocatalytic water splitting activity

Ling Wang

Xi'an Jiaotong University

Guorui Yang

Xi'an Jiaotong University

Silan Wang

Xi'an Jiaotong University

Jianan Wang

Xi'an Jiaotong University

Muhammad Salman Nasir

University of Agriculture, Xi'an Jiaotong University

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Fabrication of hierarchically one-dimensional ZnxCd1-xS/NiTiO_3 nanostructures and their enhanced photocatalytic water splitting activity

Abstract

Hierarchically one-dimensional nanomaterials represent a kind of promising catalyst for photocatalytic of hydrogen generation, where the photoinduced charge carriers can effectively separate and be engaged in the target reaction. Herein, we report the synthesis of hierarchically one-dimensional ZnxCd1-xS/NiTiO_3 nanofibers and the investigations of their photocatalytic performance. These well-designed nanofibers demonstrate a typically one-dimensional heterostructure with an excellent continuity, and the element mapping, X-ray diffraction, and X-ray photoelectron spectroscopy collectively confirm the ZnxCd1-xS nanoparticles being decorated on the surface of NiTiO_3 nanofibers successfully. The ZnxCd1-xS/NiTiO_3 nanofibers exhibit enhanced efficiency in photocatalytic hydrogen production under visible light, compared with the ZnxCd1-xS/TiO_2 nanofibers. The electrochemical impedance spectra measurements reveal that ZnxCd1-xS/NiTiO_3 nanofibers facilitated the transport and separation of the photoexcited charge carriers. The superior photocatalytic performance is synthetically attributed to the visible-light-responsive NiTiO_3 substrate, pure phase, large region of interface and relatively small grain size.

Keywords

their, enhanced, photocatalytic, hierarchically, water, one-dimensional, splitting, activity, fabrication, znxcd1-xs/nitio_3 , nanostructures

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Wang, L., Yang, G., Wang, S., Wang, J., Nasir, M. Salman., Wang, C., Peng, S., Yan, W. & Ramakrishna, S. (2019). Fabrication of hierarchically one-dimensional ZnxCd1-xS/NiTiO_3 nanostructures and their enhanced photocatalytic water splitting activity. *International Journal of Hydrogen Energy*, 44 (59), 30974-30985.

Authors

Ling Wang, Guorui Yang, Silan Wang, Jianan Wang, Muhammad Salman Nasir, Caiyun Wang, Shengjie Peng, Wei Yan, and Seeram Ramakrishna

1 **Fabrication of Hierarchically One-dimensional $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{NiTiO}_3$**

2 **Nanostructures and Their Enhanced Photocatalytic Water Splitting**

3 **Activity**

4 Ling Wang¹, Guorui Yang^{1,2,*}, Silan Wang¹, Jianan Wang^{1,2}, Muhammad Salman Nasir^{1,3}, Caiyun Wang⁴, Shengjie
5 Peng⁵, Wei Yan^{1,*}, Seeram Ramakrishna⁵

6 ¹ Department of Environmental Science & Engineering, State Key Laboratory of Multiphase Flow
7 in Power Engineering, Xi'an Jiaotong University, Xi'an 710049 China

8 ² Department of Applied Chemistry, School of Science, MOE Key Laboratory for Nonequilibrium Synthesis and
9 Modulation of Condensed Matter, State Key Laboratory for Electrical Insulation and Power Equipment, Xi'an
10 Jiaotong University, Xi'an 710049, China

11 ³ Department of Structures and Environmental Engineering, University of Agriculture, Faisalabad, 38040 Pakistan

12 ⁴ ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of
13 Wollongong, New South Wales 2522, Australia

14 ⁵ Department of Mechanical Engineering, National University of Singapore, 117574 Singapore

15 *Corresponding author: Wei Yan, yanwei@xjtu.edu.cn; Guorui Yang, yangguorui@xjtu.edu.cn

16 **Abstract:** Hierarchically one-dimensional nanomaterials represent a kind of promising catalyst for
17 photocatalytic of hydrogen generation, where the photoinduced charge carriers can effectively
18 separate and be engaged in the target reaction. Herein, we report the synthesis of hierarchically one-
19 dimensional $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{NiTiO}_3$ nanofibers and the investigations of their photocatalytic performance.
20 These well-designed nanofibers demonstrate a typically one-dimensional heterostructure with an
21 excellent continuity, and the element mapping, X-ray diffraction, and X-ray photoelectron
22 spectroscopy collectively confirm the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles being decorated on the surface of

1 NiTiO₃ nanofibers successfully. The Zn_xCd_{1-x}S/NiTiO₃ nanofibers exhibit enhanced efficiency in
2 photocatalytic hydrogen production under visible light, compared with the Zn_xCd_{1-x}S/TiO₂ nanofibers.
3 The electrochemical impedance spectra measurements reveal that Zn_xCd_{1-x}S/NiTiO₃ nanofibers
4 facilitated the transport and separation of the photoexcited charge carriers. The superior
5 photocatalytic performance is synthetically attributed to the visible-light-responsive NiTiO₃ substrate,
6 pure phase, large region of interface and relatively small grain size.

7 **Keywords:** Electrospinning; NiTiO₃; nanofiber; hydrogen; water splitting

8 **1. Introduction**

9 Developing new renewable energy has been become an important task in recent years because of
10 the severe energy crisis due to the depletion of fossil fuels and climate change resulted from increase
11 in CO₂ atmospheric concentration[1]. Thus, development of reliable, sustainable, clean energy
12 without CO₂ emission to substitute the current used fossil fuels is of critical. The largest renewable
13 energy resource is provided by the sun. The direct conversion of solar energy to chemical energy can
14 be performed through two different routes, namely, CO₂ reduction into hydrocarbons[2] and
15 Hydrogen (H₂) generation[3]. H₂ is currently considered as an ideal potential clean energy carrier
16 because of its high-energy-density and carbon-free and also easily transportable[4, 5]. The
17 development of novel efficient hydrogen production technologies seems to be topical in hydrogen
18 energy engineering[6]. Solar-driven photocatalytic water splitting for hydrogen production represents
19 an environmentally friendly and economically viable approach to store solar energy, which is also a
20 promising strategy to address global excessive reliance on the fossil fuels[5, 7, 8]. Since the pioneer
21 work of photoelectrochemical water splitting on TiO₂ photoelectrode reported by Fujishima and
22 Honda in 1972 which demonstrated photoassisted electrochemical water splitting into H₂ and

1 oxygen[9], various photocatalysts have been applied for solar light driven catalytic H₂ production[10].
2 To date, a large number of semiconductors have been reported as an ideal photocatalysts for
3 photocatalytic water splitting, such as CuWO₄, TiO₂, KNbO₃, Bi₂O₃, Ta₃N₅, etc[4, 11-14]. Among
4 the different photocatalysts, TiO₂ has been one of the most researched materials for photocatalytic H₂
5 generation due to its high chemical stability and suitable reduction potential[14-16]. Unfortunately,
6 the photocatalytic efficiency of TiO₂ is mainly restricted because of its wide band gap (3.0~3.2 eV)
7 that makes TiO₂ only response to ultraviolet (UV) light (just takes up 5% of the total solar spectrum),
8 and rapid recombination of the photogenerated charge carriers[17].

9 Transition metal titanates, as a multifunctional materials family, were extensively researched in the
10 last few decades[18, 19]. Nickel Titanate (NiTiO₃), as an important member of this family, has been
11 comprehensively explored as the anode of Li-ion batteries[20, 21], inorganic sensitized solar cells[22],
12 electrodes[23], gas sensors[24], photocatalysts[25], etc. Of particular note, NiTiO₃ possesses high
13 photo-response within the visible-light spectra due to its narrow band gap of 2.18 eV and appropriate
14 band structure[26]. Additionally, the NiTiO₃ material pertains to prominent advantages of low cost,
15 environmental friendliness, abundance on earth, and good chemical stability, which is comparable to
16 the TiO₂. Therefore, NiTiO₃, especially the NiTiO₃ based heterojunctions, have been extensively
17 employed as significant photocatalysts for photocatalytic water splitting and photodegradation of
18 organic pollutants[27-29].

19 Wang *et al.* prepared CdS/NiTiO₃/CoS nanocomposite by a simple one-pot route, which showed
20 absorption in both visible and near infrared (NIR) regions benefiting from the component of NiTiO₃.
21 The H₂ evolved over the CdS/NiTiO₃/CoS nanocomposite under whole visible to NIR irradiation is
22 22 times higher than that produced over pure CdS. The superior photocatalytic performance over the
23 CdS/NiTiO₃/CoS nanocomposite can be ascribed to its wide spectrum response and the formation of

a CdS/NiTiO₃/CoS heterojunction[30]. Graphene/NiTiO₃ and TiO₂/NiTiO₃ nanocomposites also exhibited significantly high photocatalytic water splitting[29, 31]. Various other NiTiO₃ derived photocatalysts, such as Bi₂MoO₆/NiTiO₃, Ag₃VO₄/NiTiO₃, g-C₃N₄/NiTiO₃, reduced graphene /NiTiO₃, and Fe₂O₃/NiTiO₃, have been reported for degradation of organic pollutant[26, 27, 32-34].

Generally, the guest materials decorating on NiTiO₃ tend to possess more negative conduction band (CB) potential than that of NiTiO₃, which assists the electrons flowing into the NiTiO₃. As the previous report indicated, the CB offset between guest materials and NiTiO₃ may be not large enough to generate strong driving force for effective injection of electrons to the CB of NiTiO₃, but the CB potential of the guest materials is usually constant[35, 36]. Fortunately, the solid solutions provide the opportunity for allowing the band gap modulation by means of simply adjusting the ratios between different metal elements[37]. For example, the band gap of solid solution Cd_{1-x}Zn_xS varies from 2.4 to 3.6 at different x values, which also exhibits significantly higher photocatalytic activity than the parent substance of CdS and ZnS. To the best of our knowledge, there are however few reports on the fabrication of Cd_{1-x}Zn_xS/NiTiO₃ nanocomposites toward photocatalytic H₂ evolution from water splitting[38, 39].

Motivated by the abovementioned concerns, hierarchical Cd_{1-x}Zn_xS/NiTiO₃ nanofibers were prepared by a facile two-step approach. Cd_{1-x}Zn_xS nanoparticles were uniformly distributed on the NiTiO₃ nanofibers to construct hierarchical nanostructures. The matched band alignments and hierarchical heterostructures can significantly strengthen the transfer and spatial separation of photogenerated electron/hole (e⁻/h⁺) pairs. The one-dimensional (1D) Cd_{1-x}Zn_xS/NiTiO₃ heterostructures displayed higher photocatalytic efficiency of photocatalytic H₂ production than pristine Cd_{1-x}Zn_xS nanoparticles and NiTiO₃ nanofibers. Moreover, the formation mechanism of Cd_{1-x}Zn_xS/NiTiO₃ heterojunctional nanofibers was proposed based on the results of time-dependent

1 experiments.

2 **2. Experimental section**

3 **2.1 Chemicals and materials**

4 All of the reagents are of analytical purity grade and used without further purification. Poly (vinyl
5 pyrrolidone) (PVP Mw $\approx 1.3 \times 10^6$) was obtained from BASF chemical company in Germany. Nickel
6 acetate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$), Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$),
7 cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), thioacetamide (TAA), acetic acid (CH_3COOH) and methyl
8 alcohol (CH_3OH) were purchased from Sinopharm Chemical Reagent Co., Ltd.

9 **2.2 Preparation of hierarchical $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{NiTiO}_3$ nanofibers**

10 *2.2.1 Preparation of NiTiO_3 nanofibers*

11 0.05 mmol of $\text{Ti}(\text{OC}_4\text{H}_9)_4$, 0.05 mmol of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 1.5 g PVP were dissolved in
12 the mixed solution containing methyl alcohol and acetic acid under vigorous stirring to obtain clear
13 solution after 6 h. Before electrospinning, 5 mL of the precursor solution was transferred into a plastic
14 syringe with a stainless needle. A voltage of 12 kV was used for the spinneret. The collector employed
15 a sheet of aluminum foil, which was placed 12 cm away from the steel needle. Finally, the as-spun
16 fibers were calcined at 500 °C, 600 °C, and 700 °C, respectively, with a ramp rate of 5 °C in the air to
17 fabricate the NiTiO_3 nanofibers, which were denoted as NT-5, NT-6 and NT-7. The TiO_2 nanofibers
18 were fabricated via the same conditions without adding $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ followed by calcinating
19 at 600 °C, labelled as T.

20 *2.2.2 Preparation of hierarchical $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{NiTiO}_3$ nanofibers*

21 The $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles were grown on the surface of NiTiO_3 nanofibers via a simple
22 hydrothermal method. Typically, 0.7 mmol of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.3 mmol of
23 $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 1.0 mmol of TAA were added into 50 mL of deionized water under

1 magnetic stirring, then 1 mmol of NiTiO₃ nanofibers were added into the solution. The solution was
2 then transferred into 100 mL of Teflon-lined stainless steel, followed by a hydrothermal treatment at
3 200 °C for 24 h. The obtained samples were rinsed with deionized water and ethanol for three times,
4 respectively, and then dried under vacuum at 100 °C for 24 h. Finally, the samples of CZ/NT-5,
5 CZ/NT-6, and CZ/NT-7 were obtained (Cd_{1-x}Zn_xS were marked as CZ), respectively, based on
6 different NiTiO₃ substrates. By comparison, pure Cd_{1-x}Zn_xS nanoparticles were also synthesized by
7 using the above method without adding NiTiO₃ nanofibers, while the Cd_{1-x}Zn_xS/TiO₂ nanofibers that
8 were abbreviated to CZ/T prepared through replacing NiTiO₃ nanofibers with TiO₂ nanofibers.

9 **2.3 Characterization**

10 JEOL JSM 6700F scanning electron microscopy (SEM) with a field emission gun source attached
11 with energy dispersive spectroscopy detector was used for SEM and EDS characterization. JEOL
12 G2F30 field emission transmission electron microscopy (TEM) with an acceleration voltage of 300
13 kV was used for TEM observations. X'pert MPD Pro (PANalytical Co.) X-ray powder diffraction
14 (XRD) was employed to collect the XRD patterns, using Cu K α radiation (40 kV, 40 mA). The X-ray
15 Photoelectron Spectroscopy (XPS) was done with an Axis Ultra, Kratos (UK) XPS system at
16 monochromatic Al K α radiation. The binding energies were calibrated with respect to the signal for
17 adventitious carbon (binding energy = 284.8 eV). Ultraviolet-visible diffused reflectance spectra
18 (DRS) was obtained using HITACHI UV4100 spectrometer with BaSO₄ as the reflectance standard
19 operating from 240 to 800 nm wavelengths. The N₂ adsorption-desorption isotherms were recorded
20 via recruiting an ASAP 2020 instrument, from which the specific surface areas were calculated
21 according to the Brunauer-Emmett-Teller (BET) methods. The zeta potential was measured by
22 Malvern Zetasizer Nano ZS90. X-ray fluorescence spectrum (XRF) was collected from Bruker S4
23 PIONEER instrument.

2.4 Photocatalytic tests

The photocatalyst (25 mg) was dispersed via a magnetic stirrer in 50 mL of aqueous solution containing sodium sulfite (Na_2SO_3 , 0.35 M) and sodium sulfide (Na_2S , 0.25 M) as electron donors. In the wake of being flushed by N_2 gas for 30 min to remove the air inside, the photocatalytic liquid system was irradiated by visible light ($\lambda \geq 420$ nm) from a Xe lamp equipped with a cutoff filter ($\lambda > 420$ nm). The amount of H_2 evolution was measured on a gas chromatography (Agilent Technologies: 6890N) with TCD equipped with a 5 Å molecular sieve using N_2 as the carrier gas. Blank experiments confirmed that no hydrogen was produced in the absence of the photocatalysts or light irradiation.

2.5. Photoelectrochemical (PEC) measurement

The electrochemical measurements were performed on a Chenhua CHI660D electrochemical workstation in a three-electrode system. A platinum wire and an Ag/AgCl (saturated KCl) were used as the counter electrode and the reference electrode, respectively, employing a 0.1 M of NaS and 0.02 M of Na_2SO_3 aqueous electrolyte under an ambient temperature (25 °C). The slurry was prepared by adding 3 mg of the as-prepared photocatalyst into the mixture solution of 50 μL of perfluorosulfonic acid polymer, 0.5 mL of isopropanol and 2 mL of ultrapure water. The working electrodes were obtained via depositing the slurry onto a glassy carbon electrode tip with an effective area of 0.20 cm^2 and dried at room temperature overnight. The electrochemical impedance spectra (EIS) was conducted under the DC potential of 0.2 V under illumination.

3. Results and discussion

As shown in **Figure S1** (Supporting Information), the pristine NiTiO_3 nanofibers, including NT-5, NT-6 and NT-7, exhibited a well-defined 1D nanostructures and integrally emerged as interconnected flyover-like networks, which inherited from the as-electrospun precursor nanofibers (**Figure S1 a and b**, Supporting Information). The sample NT-7 was coarser than the sample NT-5 and NT-6 because

of its larger crystal size (**Figure S1 c-h**, Supporting Information). It was worth noting that all of the pristine NiTiO_3 nanofibers possessed smooth surfaces without any secondary structures.

After the hydrothermal growth, the nanofibers still remained 1D nanofibrous morphology and the excellent continuity (**Figure 1**). However, it is easy to observe that the entire surface of samples NT-5 and NT-6 were uniformly decorated with $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles (as indicated by the XRF analysis in **table S1**, Supporting Information). In comparison, the secondary $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanostructures came with aggregation and distributed loosely on the surface of sample NT-7. This phenomenon was attributed to the larger crystal size and low surface area of sample NT-7, which lead to the lack of sites for $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ growth. The $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles which were prepared in the absence of substrate nanofibers exhibiting a serious aggregation tendency (**Figure S1 i and j**, Supporting Information).

Figure 1. SEM images with different magnifications of (a, d) sample CZ/NT-5, (b, e) CZ/NT-6 and (c, f) CZ/NT-7.

TEM and high-resolution TEM (HRTEM) images in **Figure 2a** and **b** revealed that the NiTiO_3 nanofibers were composed of packed nanosized particulates, and displayed a porous surface without any secondary structures. Figure 2c showed the typical TEM image of an individual NiTiO_3 nanofiber

1 densely covered by $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles. The HRTEM image collected from the interface region
2 in Figure 2d had a lattice distance of 0.27 nm in the backbone area, which was ascribed to the (104)
3 plane of the NiTiO_3 [40]. The fringe spacings of 0.34 nm were corresponded to the (002) faces of
4 hexagonal $\text{Cd}_x\text{Zn}_{1-x}\text{S}$. The ordered lattice fringes with an inter-planar space of 0.34 nm in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$
5 were between the (111) ZnS crystal plane (0.31 nm) and (002) CdS plane (0.36 nm), indicating the
6 formation of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solution. The elemental mapping from the high-angle annular dark-field
7 scanning transmission electron microscopy (HAADF-STEM) image (**Figure 2e**) clearly showed that
8 the signals for Ni, Ti and O were only detected in the core region (**Figure2 f-h**), while Cd, Zn and S
9 signals were exclusively found in the shell layer(**Figure2 i-k**), confirming that the $\text{Cd}_x\text{Zn}_{1-x}\text{S}/\text{NiTiO}_3$
10 hierarchical heterostructures were fabricated in this work.

11
12 **Figure 2.** (a, b) TEM and HRTEM images of the sample NT; (c, d) TEM and HRTEM images of the
13 sample CZ/NT-6; (e) HAADF-STEM image of a single fiber of sample CZ/NT-6 with corresponding

EDS maps of (f) Ni, (g) Ti, (h) O, (i) Cd, (j) Zn and (k) S.

XRD patterns collected from different samples (**Figure S2a**, Supporting Information) clearly revealed that the sample NT-6 and NT-7 were pure ilmenite NiTiO_3 . The XRD peaks found in these two samples at 24.1° , 33.1° , 35.7° , 40.9° , 49.5° , 54.0° , 57.5° , 62.4° and 64.1° could be well assigned to the (012), (104), (110), (113), (024), (116), (018), (124) and (300) planes for NiTiO_3 (JCPDS No. 33-0960)[41]. On the other hand, impurity reflections could be found in sample NT-5 centered at 25.4° , 27.4° and 37.3° , which were indexed to anatase TiO_2 (JCPDS No. 21-1272), rutile TiO_2 (JCPDS No. 21-1276) and NiO (JCPDS No. 44-1159), respectively. Conspicuously, the diffraction peaks became more intensive and sharper from sample NT-5 to NT-7. In other words, the crystal size rose as the post-treatment temperature rose, which was in good agreement with the SEM observations. **Figure S2b** (Supporting Information) displays the XRD pattern of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ fabricated from the hydrothermal route in the absence of NiTiO_3 nanofibers, which indicated that the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ (JCPDS No. 40-0836) was composed of hexagonal phases.

Figure 3. XRD patterns of samples CZ/NT-5, CZ/NT-6, and CZ/NT-7.

As illustrated in **Figure 3**, the new XRD peaks located at 25.3° (100), 26.9° (002), 28.6° (101), 44.4° (110) and 52.2° (200), belong to hexagonal $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ [42], which resembled the standard

patterns of $\text{Cd}_{0.72}\text{Zn}_{0.28}\text{S}$ (JCPDS No. 40-0836). Results revealed that the characterization peaks pertaining to NiTiO_3 remained intact without any detectable shift after the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ modification, suggested that the hydrothermal process was unable to undermine the NiTiO_3 nanofibers. The broaden as well as lower intensive $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ diffraction peaks demonstrated their small grain size due to the uniform dispersion on the surface of NiTiO_3 nanofibers. The small grain size was supposed to reduce the migration distance of the photoinduced e^-/h^+ pairs. Additionally, there was a small peak at 25.6° belonging to NiS_2 (JCPDS No. 65-3352) in sample CZ/NT-5, which is converted from the NiO during the hydrothermal process[43]. The crystallite size of the obtained samples could be calculated by well-known Scherrer's equation[44]:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

Where λ corresponding to wavelength of X-ray radiation source, β is full width at half-maximum in [FWHM] radians, θ is Bragg's diffraction angle. The average sizes of CZ/NT-5, CZ/NT-6 AND CZ/NT-7 were calculated to be around 26, 33 and 38 nm, respectively.

The XPS was performed to obtain the surface chemical composition and valence state of different samples (**Figure 4**). The XPS survey spectrum (**Figure 4a**) indicated that Zn, Cd, S, Ni, Ti and O elements coexisted in the sample CZ/NT-6, while only Ni, Ti and O signals could be detected from the substrate nanofibers. The C 1s peak was ascribed to extrinsic carbon. The high-resolution XPS spectra collected from Ni 2p (**Figure 4b**) for the sample NT-6 and CZ/NT-6 showed two major peaks with binding energies of 855.62 and 873.22 eV that related to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, which were characteristic peaks for the Ni^{2+} . The two peaks at 861.82 and 879.82 eV were typical Ni^{2+} shakeup satellite peaks of NiTiO_3 [45]. As **Figure 4c** displayed, the binding energy difference between the Ti 2p_{3/2} (458.22 eV) and Ti 2p_{1/2} (463.92 eV) peaks obtained from different samples was approximately 5.7 eV, implying that the oxidation state of Ti was +4[46]. XPS spectrum (**Figure 2d**)

1 of sample NT-6 for O 1s could be fitted into two types of contributions for oxygen species, one of
2 which was the crystal lattice oxygen (530.02 eV, O_{M-O}), corresponding to the $NiTiO_3$ phase, and the
3 other one indicated the presence of hydroxy species (531.32 eV, O_{H-O}) on the surfaces[47]. The
4 sample CZ/NT-6 possessed an additional O 1s peak at 533.02 eV which belongs to adsorbed water.
5 The O1s peak of hydroxyl oxygen exhibited an obvious shift from 531.28 eV to 531.84 eV because
6 of the formation of O-Zn and O-Cd bonds at the interface between CZ and NT. The slightly different
7 of the Cd and Zn XPS peaks between the pure $Cd_{1-x}Zn_xS$ and $Cd_{1-x}Zn_xS/NiTiO_3$ further verified the
8 bonds of O-Zn and O-Cd. It was notable that the binding energies of the Ni, Ti, and O acquired from
9 the sample CZ/NT-6 exhibited no obvious shift compared to those of sample NT-6, indicating that
10 the structure of $NiTiO_3$ remained intact after the hydrothermal process. However, the intensities of
11 the characteristic peaks of the Ni, Ti, and O became lower for the sample CZ/NT-6 due to the $Cd_{1-x}Zn_xS$
12 coating, as the XPS spectra only revealed the surface element properties with a depth of 3~10
13 nm[36].

14 The XPS spectrum in **Figure 4e** showed two peaks at 450.42 and 412.22 eV were assigned to Cd
15 $3d_{5/2}$ and Cd $3d_{3/2}$, respectively, which was a hallmark of Cd^{2+} in $Cd_{1-x}Zn_xS$. The binding energies of
16 Zn 2p observed at 1022.52 and 1045.62 eV were well ascribed to Zn $2p_{3/2}$ and Zn $2p_{1/2}$. The splitting
17 spin-orbit separation of these two peaks was 23.1 eV, inferring the presence of Zn^{2+} . The
18 deconvoluted S 2p peaks in sample CZ/NT-6 were observed at 161.92 (S $2p_{3/2}$) and 163.12 eV (S
19 $2p_{1/2}$), respectively, which was in accordance with the reference value for S^{2-} [48].

20 The XPS information of $CdS/NiTiO_3$ (C/NT-6) and $ZnS/NiTiO_3$ (Z/NT-6) was also gathered to
21 verify the secondary structure in sample CZ/NT-6 was $Cd_{1-x}Zn_xS$ solid solution, rather than the
22 physical mixture of CdS and ZnS. As expected, **Figure S3a** (Supporting Information) exhibited that
23 the elements distributions were in accordance with the prescribed design in different samples. As

1 illustrated in **Figure S3b** (Supporting Information), the binding energy of Cd 3d_{5/2} peak of C/NT-6
2 was negatively shifted from 405.42 to 405.08 eV, as compared to the sample CZ/NT-6[49].
3 Additionally, element Zn in sample Z/NT-6 exhibited a Zn 2p_{3/2} peak at 1023.10 eV (**Figure S3c**,
4 Supporting Information), which was shifted by 0.58 eV slightly toward a higher binding energy, as
5 compared to the sample CZ/NT-6[50]. Meanwhile, **Figure S3d** (Supporting Information) manifested
6 that the binding energies of S 2p_{3/2} gradually rose from 161.48 to 161.92 and 162.53 eV for C/NT-6,
7 CZ/NT-6 and Z/NT-6, respectively. These XPS outcomes suggested the existence of the electronic
8 coupling between CdS and ZnS, and further demonstrated that the post-growth Cd_{1-x}Zn_xS possessed
9 a solid solution structure. Li *et al.* [51] reported that these chemical shifts were originated from the
10 Mulliken populations differences among CdS, ZnS and Cd_{1-x}Zn_xS solid solution. The solid solution
11 structure could promote the electron transformation from S to Zn and Cd, consequently increasing
12 the electron density of catalytically active sites, which was reported to facilitate the reactive of water
13 splitting.

Figure 4. (a) XPS fully scanned spectra of sample CZ/NT-6, High-resolution XPS spectrum for (b) Ni 2p, (c) Ti 2p, (d) O 1s, (e) Cd 3d, (f) Zn 2p and (g) S 2p.

The BET specific surface areas of different samples were characterized by N₂ adsorption-desorption isotherms. **Figure S4** (Supporting Information) gave the N₂ adsorption-desorption isotherms of NiTiO₃ calcined at different temperatures that presented type IV N₂ sorption isotherms attached with type H3 hysteresis loops. The specific area of sample NT-5 ($S_{\text{BET}} = 85.9 \text{ m}^2 \text{ g}^{-1}$) was obviously higher than those of NT-6 ($S_{\text{BET}} = 36.8 \text{ m}^2 \text{ g}^{-1}$) and NT-7 ($S_{\text{BET}} = 9.0 \text{ m}^2 \text{ g}^{-1}$). The increasing

crystal size may be the major reason why the S_{BET} decreased as the post-treatment temperature rise, which reportedly could deteriorate surface porosity. The surface areas of the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ coated samples experienced a similar trend with their substrates (**Figure 5a**). Particularly, the CZ/NT-5 possessed the highest specific areas of $59.6 \text{ m}^2 \text{ g}^{-1}$, while the sample CZ/NT-6 and CZ/NT-7 delivered surface areas with 17.9 and $12.6 \text{ m}^2 \text{ g}^{-1}$, respectively. It was easily observed that the surface areas of the hierarchically heterostructure nanofibers were manifestly lower than those of pristine nanofibers because the heterogeneous nucleation of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ preferentially anchor in the porous structures on the surface, while the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles failed to recruit as the plenty porous as the substrate nanofibers[52].

The optical properties of different samples were investigated by DRS. As shown in **Figure S5** (Supporting Information), the substrate NiTiO_3 nanofibers exhibited the similar characteristic absorption peaks, which possessed a broad UV absorption edge at about 410 nm assigned to the $\text{O}^{2-}/\text{Ti}^{4+}$ charge-transfer interaction. Two additional significant absorption peaks suited at the visible range around 451 and 512 nm were observed, which originated from that the 3d8 band associated with Ni^{2+} ions split up into two sub-bands in an octahedral environment, called the $\text{Ni}^{2+}/\text{Ti}^{4+}$ charge transfer bands[53]. Additionally, the 512 nm absorption peaks became more apparent as the firing temperature increased owing to the crystal field split up completely. As expected, the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ modified NiTiO_3 nanofibers displayed excellent visible-light response (**Figure 5b**). The absorption peaks at 512 nm of the NiTiO_3 nanofibers were enveloped by the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ absorption edge, implying guest $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ structures had better visible light absorption efficiency than that of the host NiTiO_3 nanofibers. To determine the band gap energy of the samples, the Kubelka–Munk function was applied to convert diffuse reflectance into equivalent absorption coefficient for powder samples[54, 55]:

$$F(R) = \frac{(1-R)^2}{2R} \quad (2)$$

Where $F(R)$ is the Kubelka–Munk function, R is the reflectance which can be calculated from $R = 10^{-A}$, A is the absorption. Therefore, the optical band gap can be determined by Tauc relation:

$$F(R)h\nu = C(h\nu - E_g)^n \quad (3)$$

Where $h\nu$ is light energy, C is constant, E_g is band gap energy. The value of n depended on the nature of the transition of the semiconductor, where $n = 1/2$ stood for direct band gap, and $n = 2$ referred to indirect band gap. In this work, $n = 1/2$ was selected to estimate the band gaps[56]. By the related curve of $(F(R)h\nu)^2$ versus photon energy $h\nu$ from the intersection of the extrapolated straight-line portion, the band gap energy could be obtained (inset in **Figure 5b**). The band gaps of the samples CZ/NT-5, CZ/NT-6 and CZ/NT-7 were measured to be approximately 2.28, 2.26 and 2.28 eV, respectively. The slight difference between CZ/NT-5 and CZ/NT-6 may be attributed to the Ni doping released from the NiO impurity[57]. The more Cd content lead to the little increase of the band gap for CZ/NT-7 compared to the sample CZ/NT-6, confirmed by the XRF investigations (**Table S1**, Supporting Information). The above outcomes indicated that the series of sample CZ/NT had the potential to be employed as photocatalysts under visible-light irradiation. To further study their electronic properties, the Mott-Schottky plots were conducted at 5 kHz in the dark. As shown in **Figure S6** (Supporting Information), all samples displayed the positive slopes in the linear region of the plots, indicating n-type semiconductors[15, 58, 59]. The observed smaller slope was indicative of a higher carrier density, which was responsible for high photocatalytic activities. From the plots, the valence band of samples can be obtained. At the same time, the conduction band could also be conducted combining with the DRS results. The values of valence band and conduction band were listed in **Table S2** (Supporting Information).

Figure 5. (a) Nitrogen adsorption-desorption isotherms of the samples CZ/NT-5, CZ/NT-6 and CZ/NT-7; (b) DRS of different samples, insert is the Tauc plot.

Figure 6a showed the H_2 evolution rate over different samples of $Cd_{0.7}Zn_{0.3}S/NiTiO_3$ with different $NiTiO_3$ nanofibers that calcined at different temperatures, which exhibited the highest H_2 evolution efficiency among samples with various x values (**Figure S7a, Supporting Information**). The photocatalytic activity of CZ/NT-6 with an H_2 production rate of $10.9 \text{ mmol g}^{-1} \text{ h}^{-1}$ obviously outperformed those of CZ/NT-5 ($7.18 \text{ mmol g}^{-1} \text{ h}^{-1}$) and CZ/NT-7 ($3.57 \text{ mmol g}^{-1} \text{ h}^{-1}$), and even much higher in many reported $NiTiO_3$ -based or $Zn_xCd_{1-x}S$ -based photocatalysts (**Table S3, Supporting Information**). In particular, although the CZ/NT-5 possessed the largest specific area, the uncontrolledly distributed impurity of NiS_2 acted as recombination sites for photogenerated e^-/h^+ pairs, which reduces the photocatalytic performance[60]. On the other side, the sample CZ/NT-7 not only displayed a smaller specific area, but also possessed the largest particle size for $Cd_{1-x}Zn_xS$ and $NiTiO_3$. Consequently, the sample CZ/NT-7 merely provided limited reaction sites, and prolonged the migration distance of the charge carriers, both of which retarded the photocatalytic activity[13]. In comparison, the CZ/NT-6 rendered a suitable surface area for photocatalytic reaction, while it was also impurity free. **Figure S7b (Supporting Information)** showed photocatalytic activity of the bare $NiTiO_3$, of which photocatalytic H_2 generation rates were obviously lower than those of hierarchical

heterostructures. Actually, the position of the conduction band of NiTiO_3 was not negative enough for H_2 generation over water splitting[61]. When the heterojunctions between $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and NiTiO_3 were formed, the Fermi energies in the boundary between the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and NiTiO_3 should be matched. This phenomenon inevitably promoted the potential of the conduction band in NiTiO_3 to be more negative, to meet the requirements of the hydrogen evolution reaction[58, 62, 63].

Figure 6. (a) Photocatalytic H_2 evolution efficiencies of CZ/NT-5, CZ/NT-6 and CZ/NT-7; (b) cycle experiments for CZ/NT-6; (c) EIS curves of different samples under visible light, the inset is the equivalent circuit.

It was noteworthy that the CZ/NT-6 exhibited sustainable photocatalytic activity after 6 cycles without obvious attenuation (**Figure 6b**), indicating that the electrospun product was stable and reusable. More importantly, **Figure S7c (Supporting Information)** showed that CZ/NT-6 delivered superior H_2 generation rate compared to the typical $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{TiO}_2$ composite photocatalyst, which was mainly by force of the excellent visible-light-responsive NiTiO_3 trunk. To further figure out the reason for the excellent photocatalytic performance of CZ/NT-6, EIS was executed. According to the Nyquist plots shown in **Figure 6c**, the CZ/NT-6 showed the smallest diameter of the semicircle in the high-medium frequency region, indicative of a lower charge-transfer resistance (R_{ct}) than those of other samples, which highlighted the more effective electron-transfer kinetics in sample CZ/NT-6[63]. The equivalent circuit model illustrated in the insert of **Figure 6c** was fitted to the experiment

1 data, where R_s , R_{ct} , and CPE referred to the solution resistance, charge-transfer resistance and double-
2 layer capacitance, respectively. **Table S4** (Supporting Information) showed the results which
3 confirmed that sample CZ/NT-6 presented the lowest R_{ct} . It could be attributed to the reasons as
4 follows: (1) the impurity free substrate guaranteed that the photoinduced e^- and h^+ efficiently
5 separated on the interface or migrated to the surface reactive site, rather than combining in the
6 bulk[60]; (2) the relatively smaller size of the $NiTiO_3$ and $Cd_{1-x}Zn_xS$ nanoparticles of CZ/NT-6, in
7 comparison with the sample CZ/NT-7, availably decreased the transition distance of the
8 photogenerated charge carriers, resultingly reducing the R_{ct} [64]; (3) the density loading of $Cd_{1-x}Zn_xS$
9 on the surface of $NiTiO_3$ imbued CZ/NT-6 with a large interfacial region, which improved the charge
10 carrier separation to a large extent[65].

11 To acquire the actual transformation process of the $Cd_{1-x}Zn_xS/NiTiO_3$ heterostructured nanofibers,
12 the time-dependent experiments were conducted using sample CZ/NT-6 as an example. **Figure S8a-**
13 **e (Supporting Information)** panels showed the SEM and EDS observations of the intermediate solids
14 collected stepwise after 1, 5, 10, 30, and 60 min of reaction. These sequential images revealed an
15 evolutionary route of the morphology and compositions from the substrate $NiTiO_3$ nanofibers to Cd_{1-}
16 $xZn_xS /NiTiO_3$ hierarchical nanofibers. Obviously, there was no visible changes detected in the
17 original $NiTiO_3$ nanofibers at the initial stage (1 and 5 min). However, the EDS results indicated that
18 Cd^{2+} was absorbed on the surfaces of the $NiTiO_3$ nanofibers after 5 min of hydrothermal treatment
19 (inset of **Figure S8b, Supporting Information**). When the reaction time was extended to 10 min,
20 although most $NiTiO_3$ nanofibers appeared to be bare, a few CdS nanoparticles, which could be
21 deduced from the EDS, had already formed on the surface of the substrate nanofibers (**Figure S8c,**
22 **Supporting Information**). As the reaction time prolonged to 30 min, the continuous growth resulted
23 in the tiny nanoparticle coating nanofibers. It was notable that $Cd_{1-x}Zn_xS$ was formed at this step

(insert in **Figure S8d, Supporting Information**). By further increasing the reaction time to 60 min, the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanoparticles uniformly and densely grew on the surface of the NiTiO_3 nanofibers (**Figure S8e, Supporting Information**), which exhibited a similar morphology to the final sample CZ/NT-6.

Scheme 1 Possible formation mechanism of hierarchical nanofibers.

A possible mechanism was proposed to disclose the formation of the hierarchical nanofibers, based on the time-dependent experiments. As the **Scheme 1** illustrated, the NiTiO_3 nanofibers firstly absorbed Cd^{2+} due to the negative charges on their surface, which had been demonstrated by the negative zeta potential (**Figure S9, Supporting Information**), as the pH value of this reaction system was 6.47. It was well known that the Cd^{2+} ions had higher outer electron density than that of Zn^{2+} , so the substrate nanofibers were inclined to arrest the Cd^{2+} . Then, the thioacetamide started to release H_2S that reacted with the Cd^{2+} to produce CdS . It had been reported that surface porous structures were able to reduce the energy barrier of heterogeneous nucleation. Considering the different solubility products of CdS and ZnS , which were 8.0×10^{-27} and 2.5×10^{-22} , respectively, the nuclei of CdS was formed firstly in the system due to the lower solubility[51]. Furthermore, heterogeneous nucleation was favored compared to homogeneous nucleation[66]. Therefore, the CdS had grown preferentially on the rough surface of NiTiO_3 nanofibers rather than in the solution. In other words, NiTiO_3 nanofibers could guide the secondary nanoparticles self-assembling growth in aqueous solution. The **Scheme 1** step 3 displayed this stage, supported by the abovementioned EDS and SEM observations. At the next step, Zn^{2+} entered the crystal lattice of CdS to form the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ [66]. In

1 addition, as the temperature increasing, the TAA decomposition was triggered and started to release
2 plenty of S^{2-} [67], which could react with Cd^{2+} and Zn^{2+} to fabricate $Cd_{1-x}Zn_xS$ tiny nanoparticles
3 depositing on the rough surface of $NiTiO_3$ nanofibers. As **Scheme 1** step 4 shown, with the
4 hydrothermal reaction proceeding, the precursors were consumed for the oriented growth to dense
5 shell layer surrounding the $NiTiO_3$ nanofibers. Finally, the hierarchically heterostructure Zn_xCd_{1-x}
6 $S/NiTiO_3$ nanofibers were obtained.

8 **4. Conclusion**

9 In summary, hierarchical $Zn_xCd_{1-x}S/NiTiO_3$ nanofibers were successfully prepared via the facile
10 electrospinning method followed by a hydrothermal process. The $Zn_xCd_{1-x}S/NiTiO_3$ nanofibers
11 demonstrated better photocatalytic activities over water splitting under visible-light than that of
12 $Zn_xCd_{1-x}S/TiO_2$, owing to that $NiTiO_3$ could absorb visible-light and provide photoinduced e^- for H_2
13 generation. Particularly, the sample CZ/NT-6 with $NiTiO_3$ nanofibers annealed at 600 °C as substrate
14 exhibited the highest H_2 evolution rate of among different samples, which could contribute to its
15 excellent properties that could synergistically improve the photocatalytic performance, including pure
16 phase, plenty interfaces and suitable grain sizes. Remarkably, electrospun nanofibers have been
17 extensively employed as a substrate for direct growth of secondary nanostructures benefitting from
18 their porous surface and good self-supporting property. $NiTiO_3$ nanofibers prepared in this work are
19 anticipated to be favorable for assembling more efficient photocatalysts in future.

21 **Acknowledgements**

22 This work was supported by the Natural science fund of Jiangsu Province (BK20170416), National
23 Science Foundation of China (51978569, 51908458) and China Postdoctoral Science Foundation

1 (2019M650264, 2018M643635).

2 **References**

- 3 [1] Thanh Truc NT, Tran DT, Hanh NT, Pham T-D. Novel visible light-driven Nb-doped Ta₃N₅
4 sensitized/protected by PPy for efficient overall water splitting. Int. J. Hydrogen Energy
5 2018;43:15898-906. <https://doi.org/10.1016/j.ijhydene.2018.06.128>.
- 6 [2] Le Chi NTP, Dieu Cam NT, Van Thuan D, Truong TT, Thanh Truc NT, Van Hoang C, Thu Phuong
7 TT, Pham T-D, Thanh Tung MH, Minh Thu NT, Phuong NM, Nguyen VN. Synthesis of vanadium
8 doped tantalum oxy-nitride for photocatalytic reduction of carbon dioxide under visible light. Appl.
9 Surf. Sci. 2019;467-468:1249-55. <https://doi.org/10.1016/j.apsusc.2018.10.260>.
- 10 [3] Christoforidis KC, Fornasiero P. Photocatalytic Hydrogen Production: A Rift into the Future
11 Energy Supply. ChemCatChem 2017;9:1523-44. <https://doi.org/10.1002/cctc.201601659>.
- 12 [4] Thanh Truc NT, Thi Hanh N, Nguyen DT, Trang HT, Nguyen VN, Ha MN, Nguyen TDC, Pham
13 T-D. Novel overall photocatalytic water splitting of tantalum nitride sensitized/protected by
14 conducting polymers. J. Solid State Chem. 2019;269:361-6.
15 <https://doi.org/10.1016/j.jssc.2018.10.005>.
- 16 [5] Wang Z, Li C, Domen K. Recent developments in heterogeneous photocatalysts for solar-driven
17 overall water splitting. Chem. Soc. Rev. 2019;48:2109-25. <https://doi.org/10.1039/c8cs00542g>.
- 18 [6] Kozlova EA, Parmon VN. Heterogeneous semiconductor photocatalysts for hydrogen production
19 from aqueous solutions of electron donors. Russian Chemical Reviews 2017;86:870-906.
20 <https://doi.org/10.1070/rcr4739>.
- 21 [7] Wang XY, Chen LJ, Chong SY, Little MA, Wu YZ, Zhu WH, Clowes R, Yan Y, Zwiijnenburg MA,
22 Sprick RS, Cooper AI. Sulfone-containing covalent organic frameworks for photocatalytic hydrogen
23 evolution from water. Nat. Chem. 2018;10:1180-9. <https://doi.org/10.1038/s41557-018-0141-5>.

- 1 [8] Puga AV. Photocatalytic production of hydrogen from biomass-derived feedstocks. *Coord. Chem.*
2 *Rev.* 2016;315:1-66. <https://doi.org/10.1016/j.ccr.2015.12.009>.
- 3 [9] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature*
4 1972;238:37-8. <https://doi.org/https://doi.org/10.1038/238037a0>.
- 5 [10] Lewis NS. Research opportunities to advance solar energy utilization. *Science* 2016;351:1920.
6 <https://doi.org/10.1126/science.aad1920>.
- 7 [11] Le Minh Tri N, Trung DQ, Van Thuan D, Dieu Cam NT, Al Tahtamouni T, Pham T-D, Duc DS,
8 Thanh Tung MH, Van Ha H, Anh Thu NH, Trang HT. The advanced photocatalytic performance of
9 V doped CuWO_4 for water splitting to produce hydrogen. *Int. J. Hydrogen Energy*
10 2019;<https://doi.org/10.1016/j.ijhydene.2019.06.132>.
- 11 [12] Dao V-D, Le Chi NTP, Van Thuan D, Pham T-D, Tran D-T, Nguyen MP, Thao P, Nguyen MV,
12 Dieu Cam NT, Tuong NM, Dang NM, Choi H-S. Superior stability and photocatalytic activity of
13 Ta_3N_5 sensitized/protected by conducting polymers for water splitting. *J. Alloys Compd.*
14 2019;775:942-9. <https://doi.org/10.1016/j.jallcom.2018.10.188>.
- 15 [13] Zhang LS, Wang WZ, Yang J, Chen ZG, Zhang WQ, Zhou L, Liu SW. Sonochemical synthesis
16 of nanocrystallite Bi_2O_3 as a visible-light-driven photocatalyst. *Appl. Catal. A-Gen.* 2006;308:105-
17 10. <https://doi.org/10.1016/j.apcata.2006.04.016>.
- 18 [14] Lu Y, Yin WJ, Peng KL, Wang K, Hu Q, Selloni A, Chen FR, Liu LM, Sui ML. Self-hydrogenated
19 shell promoting photocatalytic H_2 evolution on anatase TiO_2 . *Nat. Commun.* 2018;9:2752.
20 <https://doi.org/10.1038/s41467-018-05144-1>.
- 21 [15] Cheng X, Zhang YJ, Bi YP. Spatial dual-electric fields for highly enhanced the solar water
22 splitting of TiO_2 nanotube arrays. *Nano Energy* 2019;57:542-8.
23 <https://doi.org/10.1016/j.nanoen.2018.12.079>.

- [16] Zhao Y, Hoivik N, Wang KY. Recent advance on engineering titanium dioxide nanotubes for photochemical and photoelectrochemical water splitting. *Nano Energy* 2016;30:728-44. <https://doi.org/10.1016/j.nanoen.2016.09.027>.
- [17] Ma Y, Wang XL, Jia YS, Chen XB, Han HX, Li C. Titanium dioxide-based nanomaterials for photocatalytic fuel generations. *Chem. Rev.* 2014;114:9987-10043. <https://doi.org/10.1021/cr500008u>.
- [18] Herlihy DM, Waeghele MM, Chen XH, Pemmaraju CD, Prendergast D, Cuk T. Detecting the oxyl radical of photocatalytic water oxidation at an n-SrTiO₃/aqueous interface through its subsurface vibration. *Nat. Chem.* 2016;8:549-55. <https://doi.org/10.1038/nchem.2497>.
- [19] Yang GR, Yan W, Wang JN, Zhang Q, Yang HH. Fabrication and photocatalytic activities of SrTiO₃ nanofibers by sol-gel assisted electrospinning. *J. Sol-Gel Sci. Technol.* 2014;71:159-67. <https://doi.org/10.1007/s10971-014-3346-0>.
- [20] Xu JJ, Ding W, Zhao WL, Zhao W, Hong ZL, Huang FQ. In situ growth enabling ideal graphene encapsulation upon mesocrystalline MTiO₃ (M = Ni, Co, Fe) nanorods for stable lithium storage. *ACS Energy Lett.* 2017;2:659-63. <https://doi.org/10.1021/acsenergylett.7b00018>.
- [21] Inamdar AI, Kalubarme RS, Kim J, Jo Y, Woo H, Cho S, Pawar SM, Park C-J, Lee Y-W, Sohn JI, Cha S, Kwak J, Kim H, Im H. Nickel titanate lithium-ion battery anodes with high reversible capacity and high-rate long-cycle life performance. *J. Mater. Chem. A* 2016;4:4691-9. <https://doi.org/10.1039/c5ta10528e>.
- [22] Li YY, Wang JG, Sun HH, Wei BQ. Heterostructured TiO₂/NiTiO₃ nanorod arrays for inorganic sensitized solar cells with significantly enhanced photovoltaic performance and stability. *ACS Appl. Mater. Inter.* 2018;10:11580-6. <https://doi.org/10.1021/acsami.7b17044>.
- [23] Dong CL, Liu XY, Wang X, Yuan XT, Xu ZW, Dong WJ, Riaz MS, Li GB, Huang FQ.

1 Hierarchical Ni-NiTiO₃ derived from NiTi LDHs: a bifunctional electrocatalyst for overall water
 2 splitting. *J. Mater. Chem. A* 2017;5:24767-74. <https://doi.org/10.1039/C7TA08440D>.

3 [24] Della Gaspera E, Pujatti M, Guglielmi M, Post ML, Martucci A. Structural evolution and
 4 hydrogen sulfide sensing properties of NiTiO₃-TiO₂ sol-gel thin films containing Au nanoparticles.
 5 *Mater. Sci. Eng. B* 2011;176:716-22. <https://doi.org/10.1016/j.mseb.2011.02.027>.

6 [25] Mi LQ, Huang YL, Qin L, Seo HJ. Improved photo-degradation of dyes over Ag-loaded
 7 NiTiO₃:V nanorods on visible-light-irradiation. *Mater. Res. Bull.* 2018;102:269-76.
 8 <https://doi.org/10.1016/j.materresbull.2018.02.043>.

9 [26] Jin YM, Shen XF, Liu ZX, Wang ZJ, Zhu B, Xu PF, Luo L, Zhang LS. Synthesis of NiTiO₃-
 10 Bi₂MoO₆ core-shell fiber-shaped heterojunctions as efficient and easily recyclable photocatalysts.
 11 *New J. Chem.* 2018;42:411-9. <https://doi.org/10.1039/c7nj03367b>.

12 [27] Pham T-T, Shin EW. Thermal formation effect of g-C₃N₄ structure on the visible light driven
 13 photocatalysis of g-C₃N₄/NiTiO₃ Z-scheme composite photocatalysts. *Appl. Surf. Sci.* 2018;447:757-
 14 66. <https://doi.org/10.1016/j.apsusc.2018.04.051>.

15 [28] Pham T-T, Shin EW. Influence of g-C₃N₄ precursors in g-C₃N₄/NiTiO₃ composites on
 16 photocatalytic behavior and the Interconnection between g-C₃N₄ and NiTiO₃. *Langmuir*
 17 2018;34:13144-54. <https://doi.org/10.1021/acs.langmuir.8b02596>.

18 [29] Diab KR, El-Maghrabi HH, Nada AA, Youssef AM, Hamdy A, Roualdes S, Abd El-Wahab S.
 19 Facile fabrication of NiTiO₃/Graphene nanocomposites for photocatalytic hydrogen generation. *J.*
 20 *Photoch. Photobio. A* 2018;365:86-93. <https://doi.org/10.1016/j.jphotochem.2018.07.040>.

21 [30] Wang ZY, Peng JW, Feng X, Ding ZX, Li ZH. Wide spectrum responsive CdS/NiTiO₃/CoS with
 22 superior photocatalytic performance for hydrogen evolution. *Catal. Sci. Technol.* 2017;7:2524-30.
 23 <https://doi.org/10.1039/c7cy00476a>.

- 1 [31] Lakhera SK, Hafeez HY, Veluswamy P, Ganesh V, Khan A, Ikeda H, Neppolian B. Enhanced
2 photocatalytic degradation and hydrogen production activity of in situ grown TiO₂ coupled NiTiO₃
3 nanocomposites. Appl. Surf. Sci. 2018;449:790-8. <https://doi.org/10.1016/j.apsusc.2018.02.136>.
- 4 [32] Inceesungvorn B, Teeranunpong T, Nunkaew J, Suntalelat S, Tantraviwat D. Novel
5 NiTiO₃/Ag₃VO₄ composite with enhanced photocatalytic performance under visible light. Catal.
6 Commun. 2014;54:35-8. <https://doi.org/10.1016/j.catcom.2014.05.015>.
- 7 [33] Pham T-T, Nguyen-Huy C, Shin EW. NiTiO₃/reduced graphene oxide materials synthesized by
8 a two-step microwave-assisted method. Mater. Lett. 2016;184:38-42.
9 <https://doi.org/10.1016/j.matlet.2016.07.136>.
- 10 [34] Zhang Y, Gu J, Murugananthan M, Zhang YR. Development of novel α -Fe₂O₃/NiTiO₃
11 heterojunction nanofibers material with enhanced visible-light photocatalytic performance. J. Alloys
12 Compd. 2015;630:110-6. <https://doi.org/10.1016/j.jallcom.2014.12.193>.
- 13 [35] Kumar Challa K, Goswami SK, Oh E, Kim E-T. Effect of CdS film thickness on the photoexcited
14 carrier lifetime of TiO₂/CdS core-shell nanowires. Appl. Phys. Lett. 2011;99:153111.
15 <https://doi.org/10.1063/1.3651340>.
- 16 [36] Yang GR, Zhang Q, Chang W, Yan W. Fabrication of Cd_{1-x}Zn_xS/TiO₂ heterostructures with
17 enhanced photocatalytic activity. J. Alloys Compd. 2013;580:29-36.
18 <https://doi.org/10.1016/j.jallcom.2013.05.083>.
- 19 [37] Yuan YJ, Chen DQ, Yu ZT, Zou ZG. Cadmium sulfide-based nanomaterials for photocatalytic
20 hydrogen production. J. Mater. Chem. A 2018;6:11606-30. <https://doi.org/10.1039/c8ta00671g>.
- 21 [38] Song JG, Zhao HT, Sun RR, Li XT, Sun DJ. An efficient hydrogen evolution catalyst composed
22 of palladium phosphorous sulphide (PdP_{~0.33}S_{~1.67}) and twin nanocrystal Zn_{0.5}Cd_{0.5}S solid solution
23 with both homo- and hetero-junctions. Energ. Environ. Sci. 2017;10:225-35.

1 <https://doi.org/10.1039/c6ee02414a>.

2 [39] Liu MC, Chen YB, Su JZ, Shi JW, Wang XX, Guo LJ. Photocatalytic hydrogen production using
 3 twinned nanocrystals and an unanchored NiS_x co-catalyst. Nat. Energy
 4 2016;1:<https://doi.org/10.1038/nenergy.2016.151>.

5 [40] Li SJ, Hu SW, Jiang W, Liu YP, Zhou YT, Liu Y, Mo LY. Hierarchical architectures of bismuth
 6 molybdate nanosheets onto nickel titanate nanofibers: Facile synthesis and efficient photocatalytic
 7 removal of tetracycline hydrochloride. J. Colloid Interface Sci. 2018;521:42-9.
 8 <https://doi.org/10.1016/j.jcis.2018.03.033>.

9 [41] Qu Y, Zhou W, Ren ZY, Du SC, Meng XY, Tian GH, Pan K, Wang GF, Fu HG. Facile preparation
 10 of porous NiTiO₃ nanorods with enhanced visible-light-driven photocatalytic performance. J. Mater.
 11 Chem. 2012;22:<https://doi.org/10.1039/c2jm32044d>.

12 [42] Kaur M, Nagaraja CM. Template-free synthesis of Zn_{1-x}Cd_xS nanocrystals with tunable band
 13 structure for efficient water splitting and reduction of nitroaromatics in water. ACS Sustain. Chem.
 14 Eng. 2017;5:4293-303. <https://doi.org/10.1021/acssuschemeng.7b00325>.

15 [43] Zhang DM, Zhou XB, Ye K, Li YJ, Song CY, Cheng K, Cao DX, Wang GL, Li Q. Synthesis of
 16 honeycomb-like NiS₂/NiO nano-multiple materials for high performance supercapacitors.
 17 Electrochim. Acta 2015;173:209-14. <https://doi.org/10.1016/j.electacta.2015.05.070>.

18 [44] Kanjwal MA, Sheikh FA, Barakat NAM, Li X, Kim HY, Chronakis IS. Zinc oxide's hierarchical
 19 nanostructure and its photocatalytic properties. Appl. Surf. Sci. 2012;258:3695-702.
 20 <https://doi.org/10.1016/j.apsusc.2011.12.008>.

21 [45] Yang GR, Wang L, Zhao YM, Peng SJ, Wang JN, Ji DX, Wang Z, Yan W, Ramakrishna S. One-
 22 dimensional Mg_xTi_yO_{x+2y} nanostructures: general synthesis and enhanced photocatalytic performance.
 23 Appl. Catal. B-Environ. 2018;225:332-9. <https://doi.org/10.1016/j.apcatb.2017.11.062>.

- [46] Rawool SA, Pai MR, Banerjee AM, Arya A, Ningthoujam RS, Tewari R, Rao R, Chalke B, Ayyub P, Tripathi AK, Bharadwaj SR. *pn* Heterojunctions in NiO:TiO₂ composites with type-II band alignment assisting sunlight driven photocatalytic H₂ generation. Appl. Catal. B-Environ. 2018;221:443-58. <https://doi.org/10.1016/j.apcatb.2017.09.004>.
- [47] Garaje SN, Apte SK, Naik SD, Ambekar JD, Sonawane RS, Kulkarni MV, Vinu A, Kale BB. Template-free synthesis of nanostructured Cd_xZn_{1-x}S with tunable band structure for H₂ production and organic dye degradation using solar light. Environ. Sci. Technol. 2013;47:6664-72. <https://doi.org/10.1021/es3045955>.
- [48] Xu Y, Gong YY, Ren H, Liu WB, Li C, Liu XJ, Niu LY. Insight into enhanced photocatalytic H₂ production by Ni(OH)₂-decorated Zn_xCd_{1-x}S nanocomposite photocatalysts. J. Alloys Compd. 2018;735:2551-7. <https://doi.org/10.1016/j.jallcom.2017.11.388>.
- [49] Mei ZW, Zhang M, Schneider J, Wang W, Zhang N, Su YT, Chen BK, Wang SF, Rogach AL, Pan F. Hexagonal Zn_{1-x}Cd_xS (0.2 ≤ x ≤ 1) solid solution photocatalysts for H₂ generation from water. Catal. Sci. Technol. 2017;7:982-7. <https://doi.org/10.1039/c6cy02572b>.
- [50] Li Q, Meng H, Zhou P, Zheng YQ, Wang J, Yu JG, Gong JR. Zn_{1-x}Cd_xS solid solutions with controlled bandgap and enhanced visible-light photocatalytic H₂-production activity. ACS Catal. 2013;3:882-9. <https://doi.org/10.1021/cs4000975>.
- [51] Chen JM, Chen JY, Li YW. Hollow ZnCdS dodecahedral cages for highly efficient visible-light-driven hydrogen generation. J. Mater. Chem. A 2017;5:24116-25. <https://doi.org/10.1039/C7TA07587A>.
- [52] Wang HG, Ma DL, Huang XL, Huang Y, Zhang XB. General and controllable synthesis strategy of metal oxide/TiO₂ hierarchical heterostructures with improved lithium-ion battery performance. Sci. Rep. 2012;2:701. <https://doi.org/10.1038/srep00701>.

- [53] Lin Y-J, Chang Y-H, Yang W-D, Tsai B-S. Synthesis and characterization of ilmenite NiTiO_3 and CoTiO_3 prepared by a modified pechini method. *J. Non-Cryst. Solids* 2006;352:789-94. <https://doi.org/10.1016/j.jnoncrysol.2006.02.001>.
- [54] Tangcharoen T, T-Thienprasert J, Kongmark C. Effect of calcination temperature on structural and optical properties of MAl_2O_4 (M = Ni, Cu, Zn) aluminate spinel nanoparticles. *Journal of Advanced Ceramics* 2019;8:352-66. <https://doi.org/10.1007/s40145-019-0317-5>.
- [55] Kim D, Lee E, Ha D, Lee J, Bae J-S, Ahn SI, Chung I, Kim S-J, Park J-C. Highly luminous and green-emitting Eu^{2+} activated $\text{Eu}_{1-x}\text{Sr}_x\text{Al}_2\text{O}_4$ ($0 \leq x \leq 1$) materials for NUV-LEDs. *Mater. Chem. Phys.* 2019;233:185-93. <https://doi.org/10.1016/j.matchemphys.2019.05.052>.
- [56] Du H, Xie X, Zhu Q, Lin L, Jiang YF, Yang ZK, Zhou X, Xu AW. Metallic MoO_2 cocatalyst significantly enhances visible-light photocatalytic hydrogen production over $\text{Mo}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ heterojunction. *Nanoscale* 2015;7:5752-9. <https://doi.org/10.1039/c4nr06949h>.
- [57] Zhang XH, Jing DW, Liu MC, Guo LJ. Efficient photocatalytic H_2 production under visible light irradiation over Ni doped $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ microsphere photocatalysts. *Catal. Commun.* 2008;9:1720-4. <https://doi.org/10.1016/j.catcom.2008.01.032>.
- [58] Liu Y, Yu YX, Zhang WD. MoS_2/CdS heterojunction with high photoelectrochemical activity for H_2 evolution under visible light: the role of MoS_2 . *J. Phys. Chem. C* 2013;117:12949-57. <https://doi.org/10.1021/jp4009652>.
- [59] Zhang N, Qu Y, Pan K, Wang GF, Li YD. Synthesis of pure phase $\text{Mg}_{1.2}\text{Ti}_{1.8}\text{O}_5$ and MgTiO_3 nanocrystals for photocatalytic hydrogen production. *Nano Research* 2016;9:726-34. <https://doi.org/10.1007/s12274-015-0951-3>.
- [60] Zhang N, Zhang KF, Zhou W, Jiang BJ, Pan K, Qu Y, Wang GF. Pure phase orthorhombic MgTi_2O_5 photocatalyst for H_2 production. *RSC Adv.* 2015;5:106151-5.

1 <https://doi.org/10.1039/c5ra20992g>.

2 [61] Xu Y, Schoonen MAA. The absolute energy positions of conduction and valence bands of
3 selected semiconducting minerals. Am. Mineral. 2000;85:543-56.
4 <https://doi.org/https://doi.org/10.2138/am-2000-0416>.

5 [62] Xu X, Yang GR, Liang J, Ding SJ, Tang CL, Yang HH, Yan W, Yang GD, Yu DM. Fabrication
6 of one-dimensional heterostructured TiO₂@SnO₂ with enhanced photocatalytic activity. J. Mater.
7 Chem. A 2014;2:116-22. <https://doi.org/10.1039/c3ta12863f>.

8 [63] Lei FC, Sun YF, Liu KT, Gao S, Liang L, Pan BC, Xie Y. Oxygen vacancies confined in ultrathin
9 indium oxide porous sheets for promoted visible-light water splitting. J. Am. Chem. Soc.
10 2014;136:6826-9. <https://doi.org/10.1021/ja501866r>.

11 [64] Rothenberge G, Moser J, Grätzel M, Serpone N, Sharma DK. Charge carrier trapping and
12 recombination dynamics in small semiconductor particles. J. Am. Chem. Soc. 1985;107:8054-9.
13 <https://doi.org/10.1021/ja00312a043>.

14 [65] Yang GR, Yan W, Zhang Q, Shen SH, Ding SJ. One-dimensional CdS/ZnO core/shell nanofibers
15 via single-spinneret electrospinning: tunable morphology and efficient photocatalytic hydrogen
16 production. Nanoscale 2013;5:12432-9. <https://doi.org/10.1039/c3nr03462c>.

17 [66] Li K, Chen R, Li SL, Xie SL, Dong LZ, Kang ZH, Bao JC, Lan YQ. Engineering Zn_{1-x}Cd_xS/CdS
18 heterostructures with enhanced photocatalytic activity. ACS Appl. Mater. Inter. 2016;8:14535-41.
19 <https://doi.org/10.1021/acsami.6b02765>.

20 [67] Wang L, Wang WZ, Shang M, Yin WZ, Sun SM, Zhang L. Enhanced photocatalytic hydrogen
21 evolution under visible light over Cd_{1-x}Zn_xS solid solution with cubic zinc blend phase. Int. J.
22 Hydrogen Energy 2010;35:19-25. <https://doi.org/10.1016/j.ijhydene.2009.10.084>.