Supplementary Information

Nano-flower S-scheme heterojunction NiAl-LDH/MoS_2 for enhance photocatalytic hydrogen production

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1. Detail of material characterization and performance measurements

1.1 Material characterization

The crystal structure characteristics of the samples were obtained by X-ray diffraction (XRD). Field emission scanning electron microscopy (SEM) was used to obtain the morphological characteristics of the samples. In order to investigate the elemental composition and valence state of the samples, the X-ray spectrometer (XPS, ESCALAB) was used to detect them. The specific surface area (S_{BET}) and pore size of the sample were obtained by N_2 adsorption–desorption instrument (ASAP 2020 M) test. In order to explore the response degree of the samples to visible light, the samples were detected by ultraviolet spectrophotometer (Lambda 750 S). The samples Photoluminescence (PL) spectra was obtained by spectrophotometer (Fluoromax-4). Photochemical measurements were made in a three-electrode system using the CHI 660D (electrochemical workstation). Preparation of working electrode: ITO (conductive glass, 1×2 cm^2) was cleaned with dilute hydrochloric acid solution. Then, under the action of ultrasound, the conductive glass sheets were immersed in diluted sodium hydroxide solution, acetone solution, ethanol and distilled water respectively for about 30min. The catalyst was added to the anhydrous ethanol, which was dispersed by ultrasound to form a suspension. Then, the suspension was uniformly dropped on the treated conductive glass sheet with pipetting gun, and the smear area was controlled at 1×1cm^2. The electrode coated with catalyst was dried under natural conditions to obtain the working electrode. The Pt electrode was used as the counter electrode, the saturated calomel electrode (SCE) was used as the reference electrode. A 300-watt xenon lamp (λ≥420nm) was used as the incident light source, and Na_2SO_4 solution (0.2 mol/ L) was used as the electrolyte.

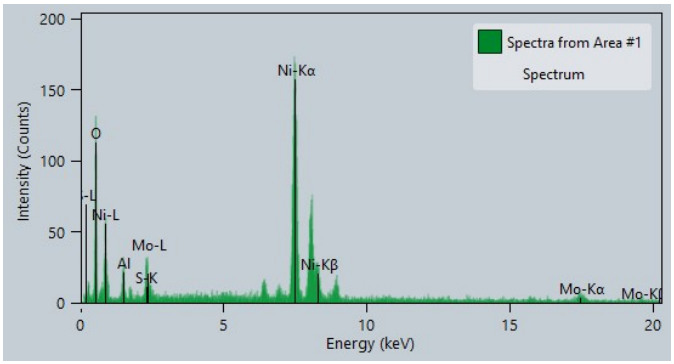
1.2 Hydrogen production condition

The photocatalytic production hydrogen was carried out in an airtight quartz bottle, which

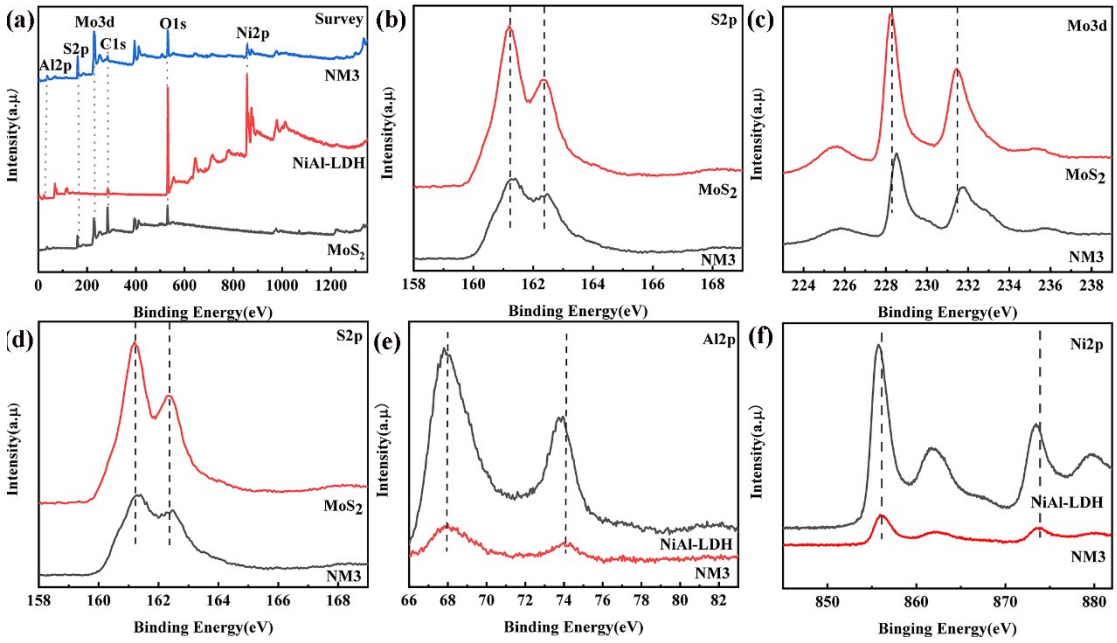
could be degassed and sampled. Usually, 10mg of catalytic material, 20mg of Eosin Y (EY), and 30 mL of TEOA solution containing 10%were weighed and added into a quartz flask. Before the solution was illuminated by visible light, the reactant system was degassed by vacuuming to remove excess gas from the solution. The amount of hydrogen evolution was analyzed by online gas chromatograph (SP 2100, N_2 as carrier).

Under the same reaction conditions and reaction time, apparent quantum efficiency (AQE) experiments were performed using different narrow-band filters. The number of hydrogen evolution of the system at 420 nm, 450 nm, 475 nm, 500 nm, and 520 nm was measured, and AQE in the corresponding band was obtained according to formula[1, 2].

AQE= [2×number of H_2 molecules evolved in 1h/ number of incident photons in 1h]×100



S1. EDX spectrum of NM3



S2. electron transfer contrast

Table 1. Comparison of the H_2 production activity of NiAl-LDH/MoS_2 photocatalyst and the recently reported photocatalyst.

Photocatalyst	Catalyst dosage(mg)	Scavenger	Light source	H_2 evolution rate (μmol g^{-1} h^{-1})	Ref
NiAl-LDH/MoS_2	10	10% TEOA	5 W LED	4590	This work
MoS_2/RGO/$CaTiO_3$	10	25% lactic acid	sunlight	808	[3]
ZnO-MoS_2-RGO	5	0.1M Na_2S/Na_2SO_3	sunlight	28.616	[4]
ZnO–MoS_2-PANI	10	0.3M Na_2S/Na_2SO_4	sunlight	29.57	[5]
N-ZnO and MoS_2	10	0.3M Na_2S/Na_2SO_4	sunlight	17.363	[6]
P-LDH/CN	30	10%TEOA	300 W xenon	1678.6	[7]
$Mn_{0.05}Cd_{0.95}S$/NiAl-LDH	15	0.3M Na_2S/Na_2SO_3	5 W LED	7500	[8]
g-C_nH_{2n-2}/ NiAl-LDH	10	10% TEOA	5 W LED	649	[9]
NiAl-LDH/g-C_3N_4/Ag_3PO_4	50	10% methanol	250W quartz tungsten halogen lamp	4330	[10]

References

[1] A. Kumar, A. Kumar, V. Krishnan, Perovskite Oxide Based Materials for Energy and Environment-Oriented Photocatalysis, Acs Catalysis 10(17) (2020) 10253-10315.

[2] A. Kumar, V. Krishnan, Vacancy Engineering in Semiconductor Photocatalysts: Implications in Hydrogen Evolution and Nitrogen Fixation Applications, Advanced Functional Materials 31(28) (2021).

[3] A. Kumar, V.N. Rao, A. Kumar, M.V. Shankar, V. Krishnan, Interplay between Mesocrystals of CaTiO3 and Edge Sulfur Atom Enriched MoS2 on Reduced Graphene Oxide Nanosheets: Enhanced Photocatalytic Performance under Sunlight Irradiation, Chemphotochem 4(6) (2020) 427-444.

[4] S. Kumar, N.L. Reddy, H.S. Kushwaha, A. Kumar, M.V. Shankar, K. Bhattacharyya, A. Halder, V. Krishnan, Efficient Electron Transfer across a ZnO-MoS2-Reduced Graphene Oxide Heterojunction for Enhanced Sunlight-Driven Photocatalytic Hydrogen Evolution, Chemsuschem 10(18) (2017) 3588-3603.

[5] V. Sharma, V. Maivizhikannan, V.N. Rao, S. Kumar, A. Kumar, A. Kumar, M.V. Shankar, V. Krishnan, Sea urchin shaped ZnO coupled with MoS2 and polyaniline as highly efficient photocatalysts for organic pollutant decomposition and hydrogen evolution, Ceramics International 47(7) (2021) 10301-10313.

[6] S. Kumar, A. Kumar, V.N. Rao, A. Kumar, M.V. Shankar, V. Krishnan, Defect-Rich MoS2 Ultrathin Nanosheets-Coated Nitrogen-Doped ZnO Nanorod Heterostructures: An Insight into in-Situ-Generated ZnS for Enhanced Photocatalytic Hydrogen Evolution, Acs Applied Energy Materials 2(8) (2019) 5622-5634.

[7] J.-Y. He, D. Zhang, X.-J. Wang, J. Zhao, Y.-P. Li, Y. Liu, F.-T. Li, Phosphorylation of NiAl-layered double hydroxide nanosheets as a novel cocatalyst for photocatalytic hydrogen evolution, International Journal of Hydrogen Energy 46(36) (2021) 18977-18987.

[8] Y. Wang, X. Hao, G. Wang, Z. Jin, Rational Design of a Core-Shell-Shaped Flowerlike Mn0.05Cd0.95S@NiAl-LDH Structure for Efficient Hydrogen Evolution, Catalysis Letters 151(3) (2021) 634-647.

[9] Z.-L. Jin, Y.-P. Wang, Strategy of Graphdiyne (g-Cn H2n-2) Preparation Coupling with the Flower-Like NiAl-LDH Heterojunctions for Efficient Photocatalytic Hydrogen Evolution*, Chemistry (Weinheim an der Bergstrasse, Germany) 27(49) (2021) 12649-12658.

[10] S. Megala, P. Ravi, P. Maadeswaran, M. Navaneethan, M. Sathish, R. Ramesh, The construction of a dual direct Z-scheme NiAl LDH/g-C3N4/Ag3PO4 nanocomposite for enhanced photocatalytic oxygen and hydrogen evolution, Nanoscale Advances 3(7) (2021) 2075-2088.