Supporting Information

A novel Zn_2GeO_4 superstructure for effective photocatalytic hydrogen generation

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Experimental section

1. Synthesis

Preparation of bulk Zn_2GeO_4 particles. Bulk Zn_2GeO_4 particles were prepared by heating a stoichiometric mixture of GeO_2 and ZnO at 1473 K (ramp 5℃ •min^{-1}) for 15 h using a conventional solid state reaction method.

Preparation of Zn_2GeO_4 nanoribbons[1]. Zn_2GeO_4 nanoribbons were reproduced from a published solvothermal route in a binary ethylenediamine/H_2O solvent system. In a typical synthesis, 0.26 g (2.5 mmol) of GeO_2, and 1.10 g (5 mmol) of $Zn(CH_3COO)_2 \cdot 2H_2O$ were added to 15 mL of solvents which includes 10 mL of ethylenediamine and 5 mL of deionized water. The mixture was stirred for 1 h and then transferred to a 20 mL Teflon–lined stainless steel autoclave, sealed and maintained at 453 K for 24 h, followed by cooling naturally to room temperature. The resulted solid product was collected by centrifugation and washed several times with distilled water and absolute ethanol. The solid was dried in a vacuum oven at 343 K

for 12 h.

Preparation of Zn_2GeO_4 nanorods[2]. Zn_2GeO_4 nanorods were reproduced from a published surfactant-assisted hydrothermal method. In a typical synthesis, 0.10 g of cetyltrimethylammonium bromide (CTAB), 0.52 g of GeO_2, and 1.10 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ were added to 15 mL of deionized water. The pH value of the resulting mixture was adjusted to pH 8 by adding NaOH. The mixture was stirred for 1 h and then transferred to a 20 mL Teflon–lined stainless steel autoclave, sealed and maintained at 413 K for 24 h, followed by cooling naturally to room temperature. The resulted solid product was collected by centrifugation and washed several times with distilled water and absolute ethanol. The solid was dried in a vacuum oven at 343 K for 12 h.

Preparation of hexagonal Zn_2GeO_4 nanorods. A typical synthesis of hexagonal Zn_2GeO_4 nanorods was as following: 0.40 g of sodium dodecyl sulfate (SDS) was dissolved into 60 mL of deionized water under stirring. Then, 4.4 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ and 1.08 g of GeO_2 was added into the above solution in turn. Subsequently, appropriate amount of NaOH was added into the above solution (pH≈8.5). The mixture (ca. 80 mL) was stirred at room temperature for 2 h, followed by transferring the mixture into a 100 mL of Teflon–lined stainless steel autoclave, sealed and maintained at 453 K for 24 h. After cooling to room temperature, the resulted solid was collected by centrifugation and washed several times with distilled water and absolute ethanol. The solid was dried in a under vacuum oven at 343 K for 12 h.

2. *Characterization*

Table S0 Nitrogen adsorption−desorption isotherm linear plot of hexagonal Zn_2GeO_4 nanorod-bundles

Adsorption		Desorption	
Relative Pressure (P/Po)	Quantity Adsorbed (cm^2/g STP)	Relative Pressure (P/Po)	Quantity Adsorbed (cm^2/g STP)
0.009692	1.435966	0.995013	42.48768
0.034057	1.813242	0.98142	35.24321
0.068522	2.145649	0.96996	29.25792
0.079947	2.238565	0.944436	19.91699
0.100019	2.379155	0.926429	16.06034
0.119977	2.509629	0.902732	12.67688
0.140011	2.622452	0.87547	10.16946
0.159994	2.723494	0.851266	8.671963
0.180003	2.815764	0.825225	7.497806
0.200006	2.900293	0.800666	6.729816
0.249877	3.073511	0.750196	5.57846
0.300058	3.23663	0.699813	4.882758
0.349976	3.365725	0.65008	4.385743
0.399729	3.47037	0.599909	4.041821
0.450509	3.585565	0.549946	3.784258
0.499774	3.724347	0.500051	3.576381
0.549851	3.8779	0.450206	3.267416
0.599784	4.071802	0.381154	3.097994
0.650478	4.306419	0.330964	2.971086
0.700285	4.633008	0.280943	2.852724
0.750657	5.123839	0.230982	2.695177
0.8002	5.837914	0.18099	2.507891
0.820434	6.284572	0.124818	2.200435
0.850732	7.153326		
0.87552	8.199555		
0.900402	9.732702		
0.924801	12.10083		
0.949283	16.44265		
0.973036	24.65447		
0.982078	29.81453		
0.990331	36.34513		
0.995013	42.48768		

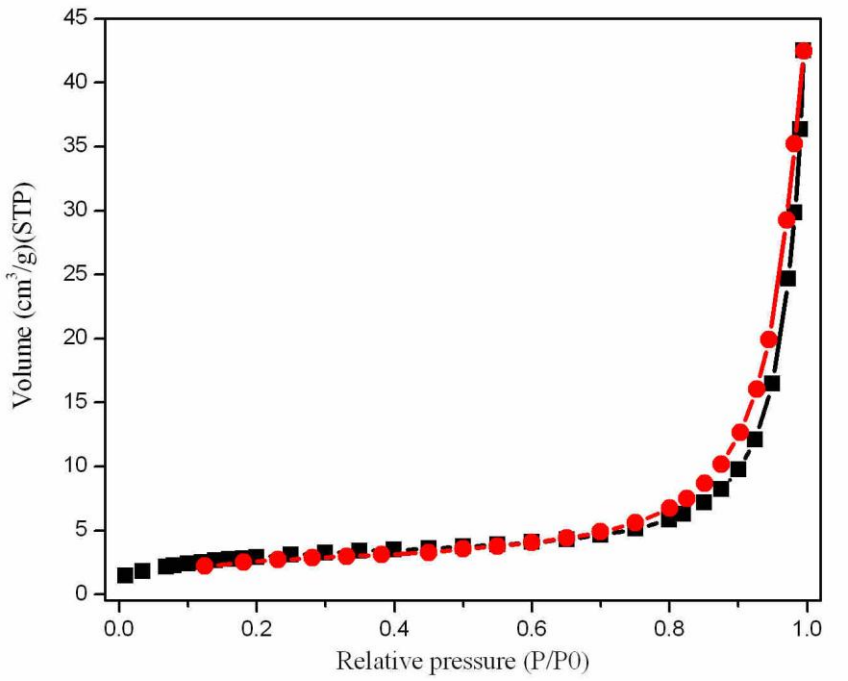


Figure S0. Nitrogen adsorption/desorption of the hexagonal Zn_2GeO_4 nanorod-bundles obtained at 473 K for 24 h.

Table S1. Textural, optical properties and hydrogen evolution results of the samples obtained.

Table S1

Catalyst	Shape	S_{BET} (m^2g^{-1})	Bandgap energy (eV)	H_2 gas evolved rate (mL/h • g^{-1})
Bulk Zn_2GeO_4	Particles	0.75	4.5	21
Zn_2GeO_4−En[1]	Nanoribbons	28.3	4.57	50
Zn_2GeO_4−CTAB[2]	Nanorods	36.0	4.67	62
Zn_2GeO_4−TEA	Bundles	9.7	4.61	109

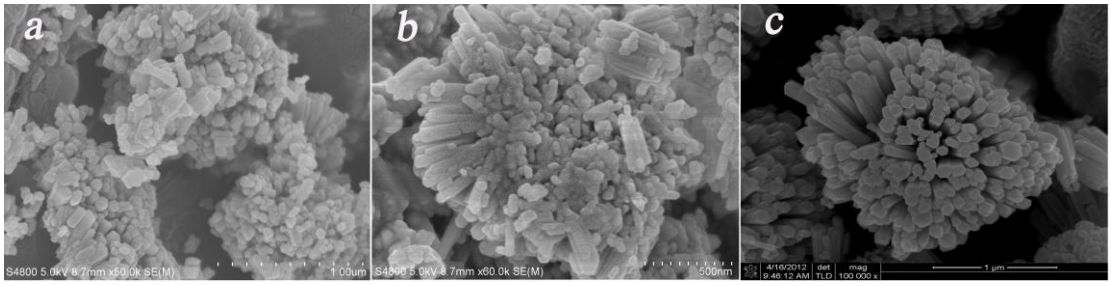


Figure S1. SEM images of the products obtained at 473 K with different solvothermal system: (a) H_2O-ethanolamine, (b) H_2O-diethanolamine, and (c) H_2O-triethanolamine.

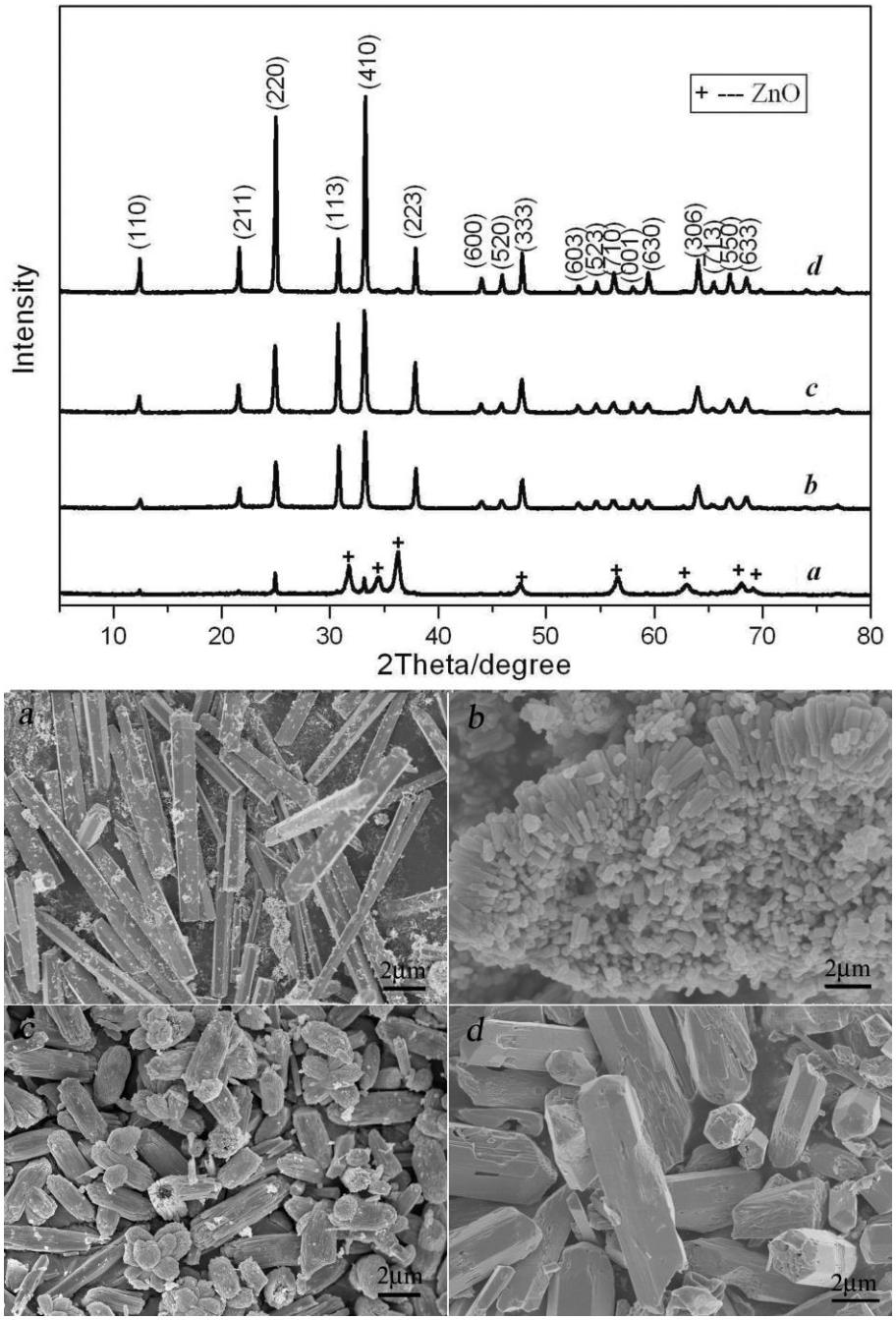
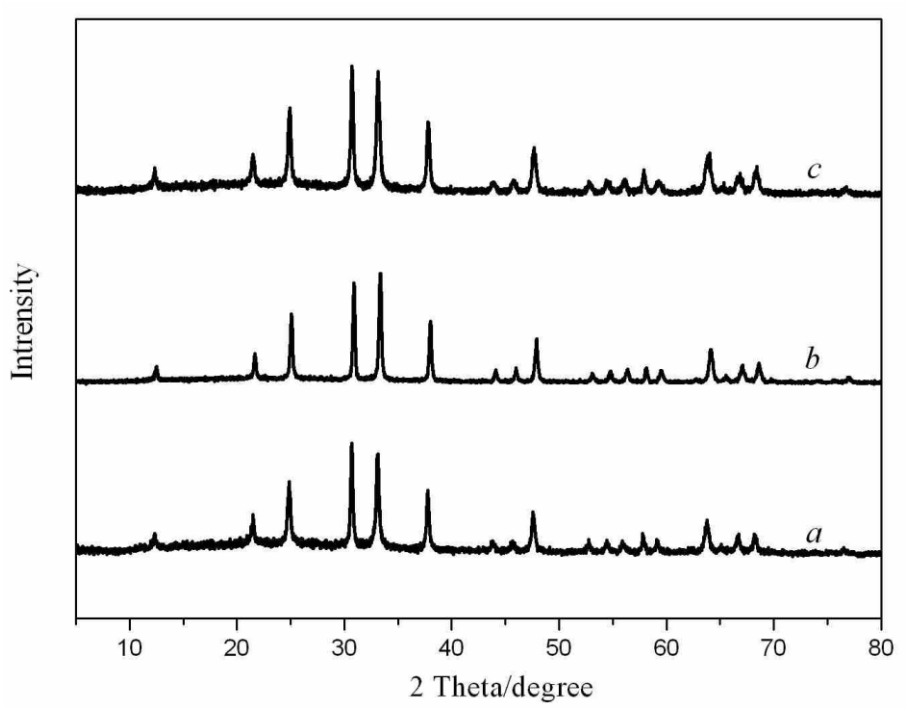


Figure S2. XRD patterns and SEM images of the products obtained at 473 K with different NaOH amount: (a) 0.1 g, (b) 0.25 g, (c) 0.4 g, and (d) 0.6 g.



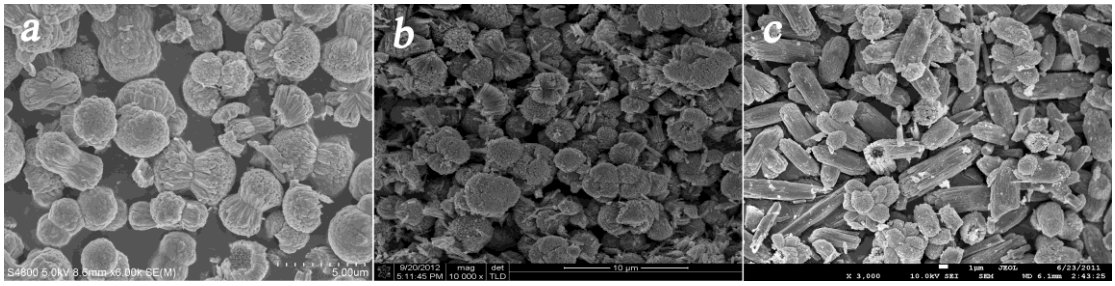


Figure S3. XRD patterns and SEM images of the products obtained at 473 K with different solvothermal treatment times of (a) 30 min, (b) 12 h, and (c) 24 h.

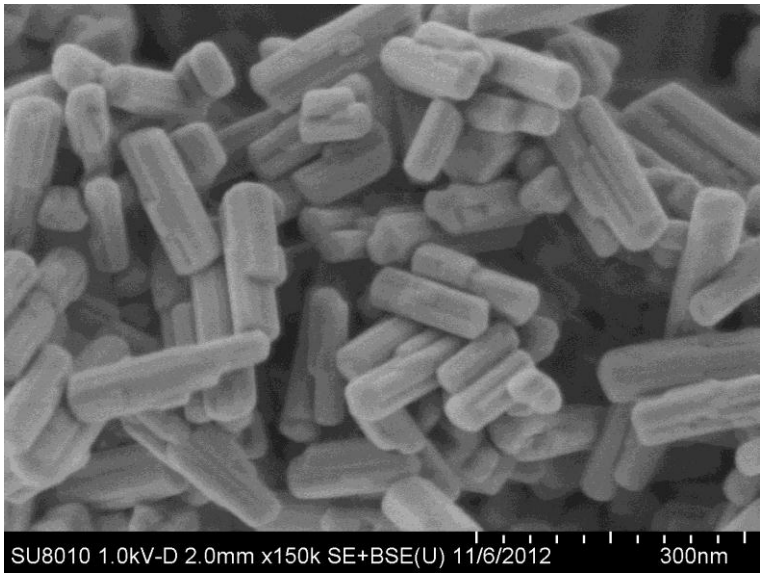


Figure S4. SEM images of the hexagonal Zn_2GeO_4 nanorods prepared by a hydrothermal method.

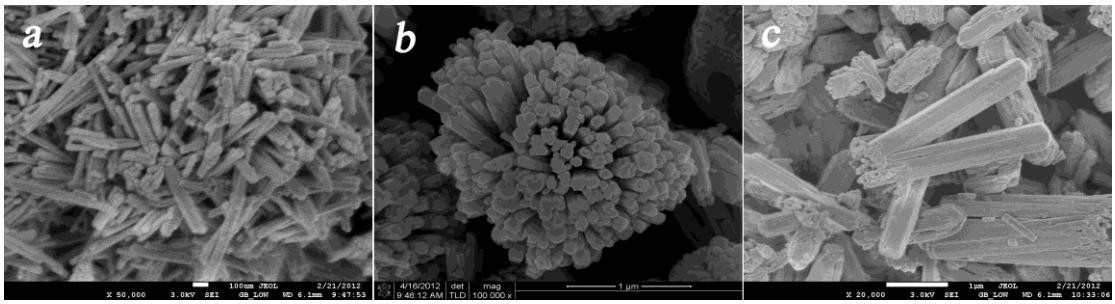


Figure S5. SEM images of the products obtained at 473 K with different mass ratio of H_2O to TEA: (a) 18:2, (b) 15:5, and (c) 10:10.

References

(1) Q. Liu, Y. Zhou, J. H. Kou, X. Y. Chen, Z. P. Tian, J. Gao, S. C. Yan and Z. G. Zou, *J. Am. Chem. Soc.*, 2010, **132**, 14385.

(2) J. Huang, K. Ding, Y. Hou, X. X. Wang and X. Z. Fu, *ChemSusChem*, 2008, **1**, 1011.