

Monodispersed Hierarchical ZnGa₂O₄ Microflowers Self-Assembled by Hexagonal Nanopetals for Self-Powered Solar-Blind Detection

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5 Experimental Section

Preparation of the ZG materials: In the preparation experiments, all the reagents were analytical grade and were used without further purification. In a typical synthesis of ZG-1, gallium chloride (0.253 g, 1.4 mmol) and dihydrate zinc acetate (0.157 g, 0.7 mmol) were dissolved in a water/ethanol solution (40 mL) with a volumetric ratio of water to ethanol (VRWE, 1:1.6). Then, 1.0 g of urea (17 mmol) was added to the solution under vigorous stirring for 1 h at room temperature. A homogeneous and clear solution was obtained. Subsequently, this solution was transferred into a Teflon-lined stainless steel autoclave, and a solvothermal treatment was performed at 473 K for 4 h. Finally, a white product (ZG-1, 0.154 g, yield 82%) was obtained by filtration and washing several times with ethanol and distilled water, and drying in vacuum. The series materials obtained at the same conditions but with different amounts of urea: 0.6 g (10 mmol), 0.75 g (13 mmol), 0.9 g (15 mmol), 1.2 g (20 mmol) and 1.5 g (25 mmol) were marked as ZG-1a, b, c, d and e, respectively. The materials obtained using VRWEs of 1:7 and 1:0.3 were marked as ZG-2 and 3, respectively.

Material characterization: XRD measurements were done with a Philips X'Pert Pro X-ray diffractometer using a monochromatized Cu K α radiation source (40 kV, 40 mA) with a wavelength of 0.1542 nm and analyzed in the range $10^\circ \leq 2\theta \leq 80^\circ$. FE-SEM and EDS images were performed by using a Supra 40 operated at 5 kV. The Zn and Ga contents of the ZG-1 sample were determined by flame atomic absorption spectrometry using a PerkinElmer AAnalyst 800. The results of elemental analysis (Anal. Calcd for ZG-1: Ga, 51.87; Zn, 24.32. Found: Ga, 51.71; Zn, 25.33) show that the molar ratio of Zn to Ga is 1:1.91. TEM images, HR-TEM images and SAED patterns were obtained in a JEF 2100F field-emission transmission electron microscope using an accelerating voltage of 200 kV. UV-Vis-NIR absorption spectra were recorded in a Shimadzu DUV-3700 spectrophotometer. Barium sulfate powder was used to adjust baseline parameters. PL measurements were acquired on a Perkin Elmer Luminescence spectrometer L550B at room temperature (excited at 260 nm).

Photoresponse Properties: The ZG samples in the presence of different amounts of PVB were coated on the ITO electrodes. The electrodes were immersed in 0.5 mol L⁻¹ Na₂SO₄ solution. Current-time curves were obtained by an electrochemical analyzer system, CHI760 (Chenhua, Shanghai, China) in a three-compartment cell with a working electrode, a platinum plate counter electrode and a saturated calomel electrode (SCE) reference electrode under a bias voltage of 0 V using the excitation light of a UV transilluminator (XS-T5, 6W) as the light source (254 nm).

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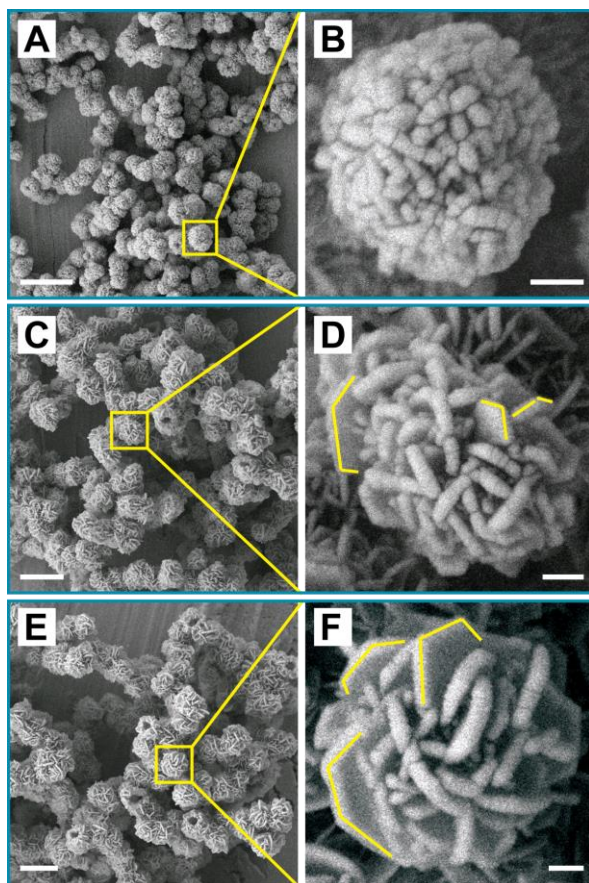


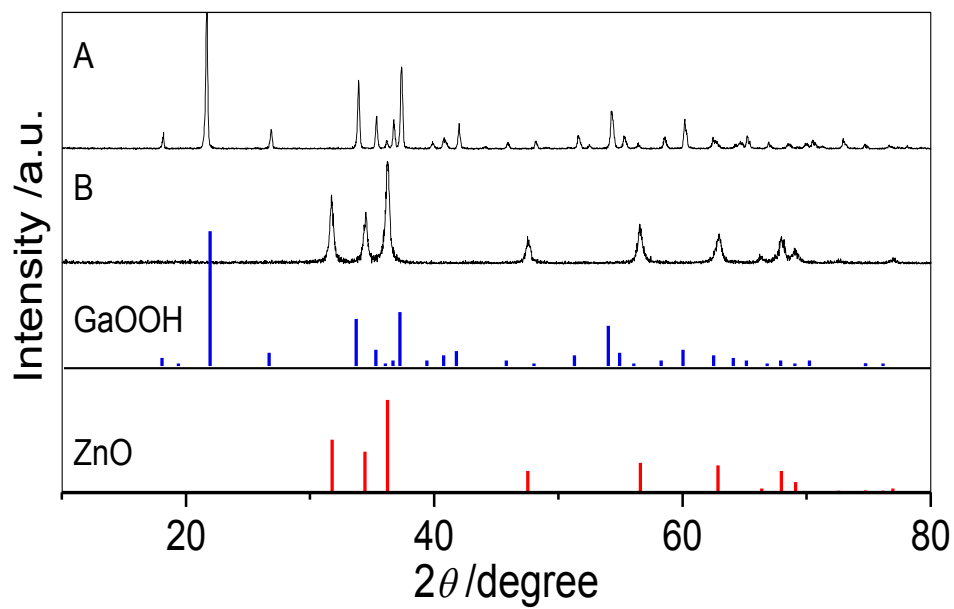
Figure S1. The FE-SEM images of the materials obtained using the same conditions as the ZG-1 but at 1 h (A, B), 2 h (C, D) and 3 h (E, F). The white bars in the left and right columns refer to 1 μm and 100 nm, respectively.

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Figure S2. The XRD patterns of the products obtained using the same conditions as the ZG-1 when urea was substituted by NaOH for adjusting pH: A, pH 5.1; B, pH 7.2.

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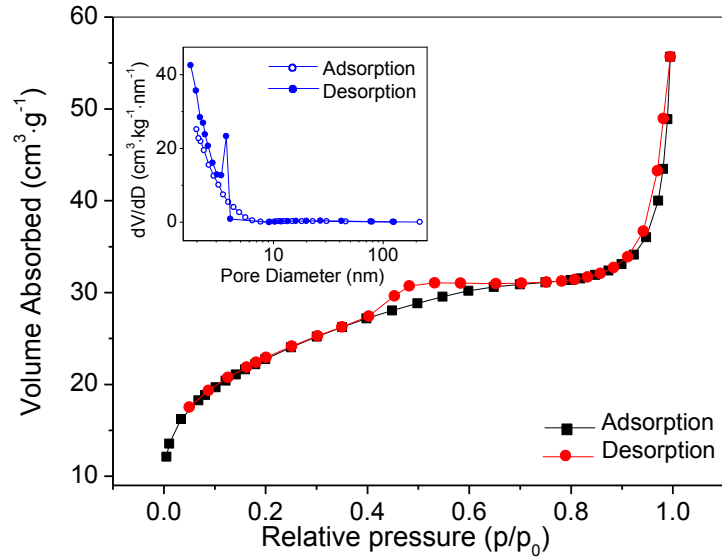


Figure S3. The N_2 adsorption-desorption isotherm and pore size distribution of the ZG-1.

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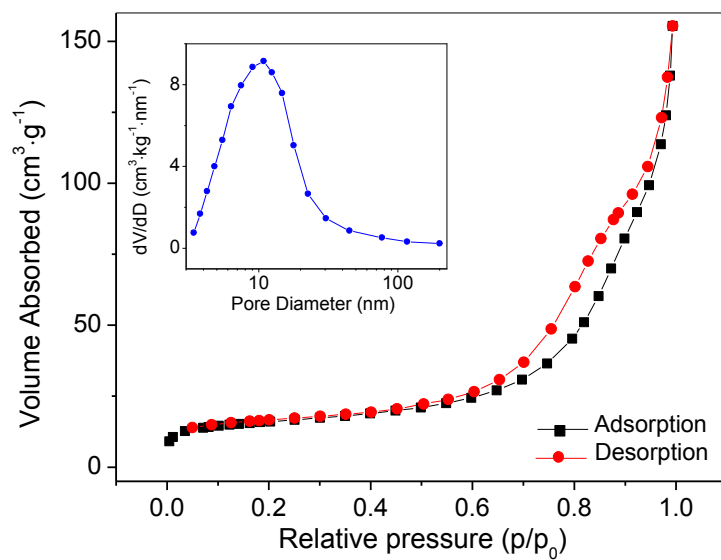


Figure S4. The N_2 adsorption-desorption isotherm and pore size distribution of the ZG-2.

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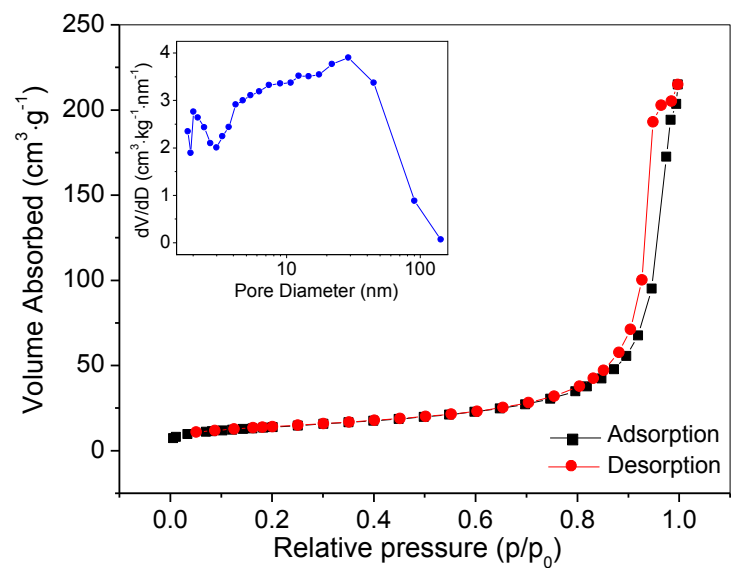


Figure S5. The N₂ adsorption-desorption isotherm and pore size distribution of the ZG-3.

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Table S1. Photoresponses of the ZGs for solar-blind photodetection.

ZGs	PVB [*] /μg·cm ⁻²	RT /s	DT /s	PC /μA	DC /nA	LDR
ZG-1	0.64	0.1	0.1	0.35	1.8	193
	1.28	0.1	0.1	0.68	4.4	153
	3.20	0.2	0.2	1.16	3.1	373
	4.80	0.2	0.3	2.32	2.1	1100
	9.60	0.3	0.3	2.73	34	80
	32.0	25	0.2	4.31	37	128
ZG-2	4.80	0.3	0.4	3.32	25	132
ZG-3	4.80	–	0.5	–	33	–

*The amount of PVB.

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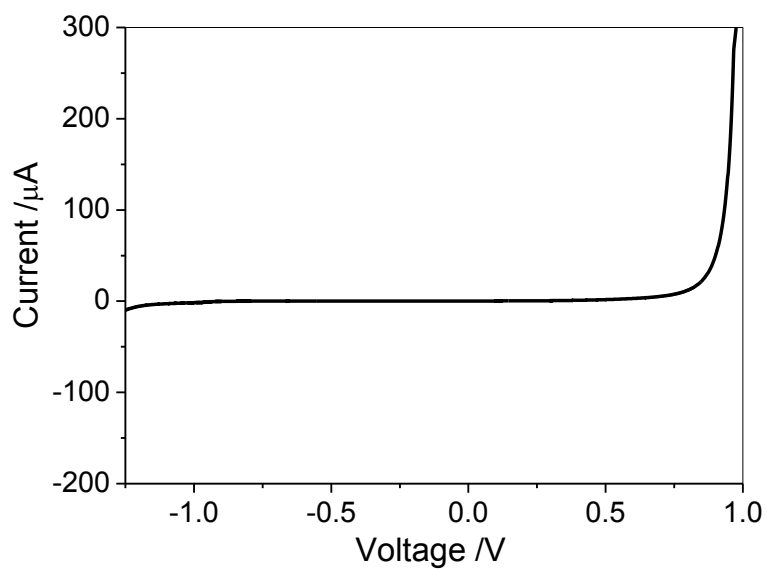
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Figure S6. The I–V characteristic of the heterojunctions in the ZG-1/PVB in absence of UV light illumination.

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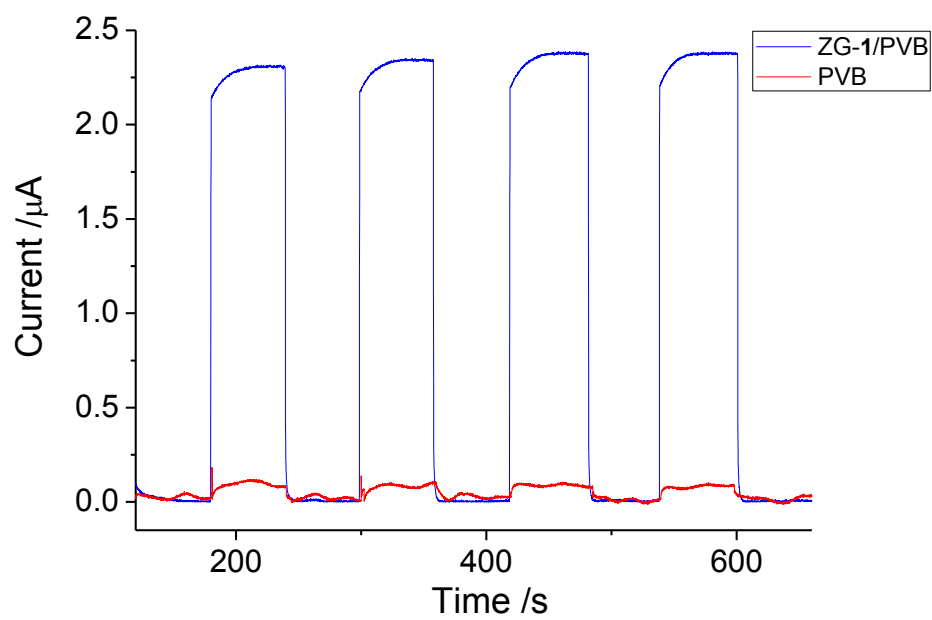


Figure S7. Current-time curves of PVB ($4.8 \mu\text{g}\cdot\text{cm}^{-2}$) on ITO and the ZG-1/PVB ($4.8 \mu\text{g}\cdot\text{cm}^{-2}$) on ITO.

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Table S2. Photoresponses of different materials for solar-blind photodetection.

Nanomaterials	RT /s	LDR	Bias voltage /V	Power density / $\mu\text{W cm}^{-2}$	Wavelength /nm	Reference
ZnGa ₂ O ₄ microflowers	0.2	1100	0	28.4	254	the present work
ZnGa ₂ O ₄ microspheres	0.3	132	0	28.4	254	the present work
ZnGa ₂ O ₄ bulks	–	–	0	28.4	254	the present work
ZnGa ₂ O ₄ nanowires	~2	200	30	–	254	1
γ -Ga ₂ O ₃ nanoflowers	< 0.1	220	0.5	–	254	2
β -Ga ₂ O ₃ nanowires	0.22	666	8	–	254	3
β -Ga ₂ O ₃ nanowires	0.5	21	20	–	254	4
β -Ga ₂ O ₃ nanowires	–	10 ⁴	50	2000	254	5
β -Ga ₂ O ₃ nanobelts	< 0.3	10 ³	20	98.3	250	6
β -Ga ₂ O ₃ nanobelts	91	100	30	65	250	7
Zn ₂ GeO ₄ nanowires	12	10 ⁴	8	50.2	245	8
MgZnO film	–	200	150	–	254	9

References

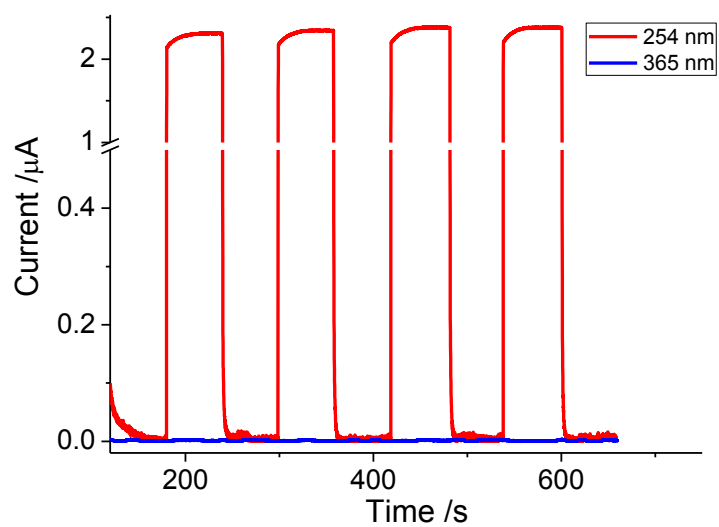
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Figure S8. Current-time curves of the ZG-1 under 254 (red line) and 365 (blue line) nm illumination.

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