Supplementary Information (ESI):

An Ultraviolet-Induced Ostwald Ripening Strategy towards Mesoporous Ga_2O_3/GaOOH Heterojunction Composite with Controllable Structures for Enhanced Photocatalytic Hydrogen Evolution

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1. Experimental procedure

1.1. Materials

Gallium(III) nitrate hydrate (Sinopharm Chemical Reagent Co., Ltd.), isopropanol, Ethanol and glycerol (Beijing Chemical Factory), Deionized water (18.2 MΩ·cm resistivity) was obtained via a PALL PURELAB Plus system in laboratory.

1.2. Preparation of gallium alkoxide (Ga-gly) microsphere

Firstly, 0.328 g gallium nitrate hydrate and 10 g glycerol were dissolved in isopropanol (30 mL)，forming a homogeneous solution. Next, the solution was transferred into a Teflon-lined autoclave and heated at 180 ℃ for 3 h. After cooling down, the white precipitate was separated and washed several by ethanol and finally dried at 65 ℃ for 12 h in an oven.

1.3. Preparation of mesoporous Ga_2O_3 microspheres

In order to obtain mesoporous Ga_2O_3 microspheres, the Ga-gly was calcined at different temperatures (450, 600 or 700 ℃, respectively) for 3 h in a muffle furnace in air with a heating rate of 2 ℃/min, labelled as Meso-Ga_2O_3-*X*, where *X* was the calcination temperature.

1.4. Preparation of mesoporous Ga_2O_3/GaOOH heterojuction composite and GaOOH sample

40 mg of the Meso-Ga_2O_3-*600* sample was dispersed in 50 mL deionized water and then irradiated under UV light for 3 h at room temperature. The UV-light source was a 500 W mercury-arc lamp. After UV irradiation, the result sample was washed with ethanol and dried in an oven at 65 ◦C for 12 h. This resulting powdered sample was denoted as Ga_2O_3/GaOOH heterojuction composite. While the Meso-Ga_2O_3-*450* was irradiated for 4h at identical condition, the fusiform GaOOH sample was obtained.

1.5 Preparation of bulk Ga_2O_3

0.5 g gallium nitrate hydrate was directly calcined in air at 900 ℃ for 3h with 2 ℃/min.

2. Characterization

Powder X-ray diffraction (XRD) results were collected on a Rigaku 2550 (Japan) diffractometer with Cu Kα radiation (λ = 1.5418 Å). The morphologies and structures of the samples were characterized by SEM (JEOL JSM 6700F), TEM, high resolution TEM, EDX (Philips-FEI Tecnai G2S-Twin microscope equipped with a field emission gun operating at 200 kV) and STEM (Talos F200x). N_2 adsorption/desorption isotherms and pore size distribution curves were determined by Brunauer-Emmett-Teller (BET) measurement by using a Quanta 4200e surface area analyzer. The X-ray photoelectron spectroscopy (XPS) results were obtained by ESCALAB 250 X-ray photoelectron spectrometer with a monochromatic X-ray source (Al Kα radiation). And the Shimadzu UV-2450 spectrometer, Renishaw, Perkin-Elmer 580B and Hitachi F-7000 spectrophotometer were applied to obtained UV-vis spectra, Raman spectra, Fourier transform infrared spectra (FT-IR) and Photoluminescence spectra (PL) results, respectively.

2.1 Photocatalytic and photoelectrochemical activity test

The photocatalytic H_2 production experiments were performed in a Pyrex reaction cell with a top quartz window and a 500 W mercury-arc lamp as a light source. A total of 40 mg photocatalyst was suspended in a 50 mL solution including 40 mL H_2O and 10 mL methanolas sacrificial agents. Before the irradiation, the reactor was evacuated several times to remove air dissolved in the water. The generated hydrogen was analyzed by an online gas chromatograph. Cycling experiments were carried out under the same condition.

2.2 Photoelectrochemical Performance

The photoelectrochemical performance of samples were carried out by using a three-electrode CHI 660E electrochemical workstation with the mesoporous Ga_2O_3/GaOOH heterojunction composite, Ga_2O_3 and GaOOH respectively used as working electrodes, saturated calomel electrode (SCE) as reference electrode, and Pt foil as counter electrode in a 0.5 M Na_2SO_4 electrolyte. The working electrode was prepared by dropping the catalyst mixture containing 20 mg of powder and 200 μL of ethanol onto fluoride-tin oxide (FTO) glass (0.5 cm × 0.5 cm), then dried in air. And a 500 W mercury-arc lamp was employed as light source.

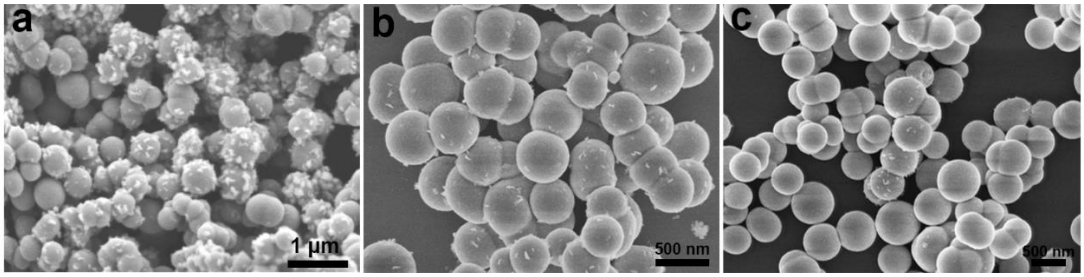

Figure S1. SEM images of Meso-Ga_2O_3-*450*; Meso-Ga_2O_3-*600 and* Meso-Ga_2O_3-*700* microspheres.

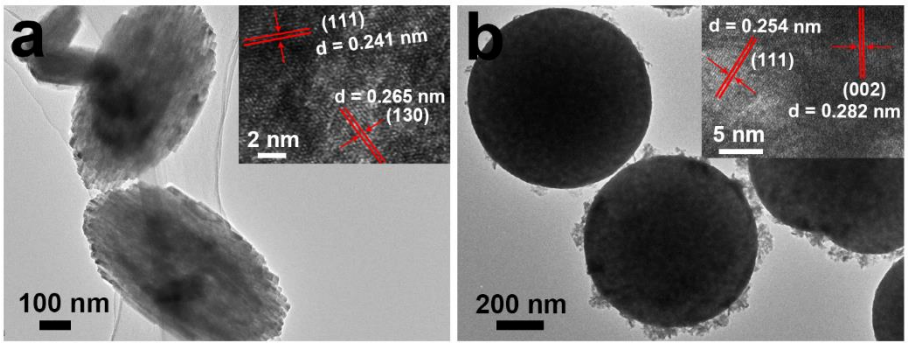

Figure S2. TEM images of GaOOH and Ga_2O_3. Insets are high magnification TEM images of them.

Table S1. The detailed pore structural data for samples.

Sample	S_{BET}[a] ($m^2 g^{-1}$)	Pore size (nm)	V_T[b] ($cm^3 g^{-1}$)
Meso-Ga_2O_3-*450*	**89.015**	**8.145**	**0.301**
Meso-Ga_2O_3-*600*	**89.223**	**6.794**	**0.149**

Meso-Ga_2O_3-*700*	**51.173**	**9.416**	**0.149**
GaOOH	**106.932**	**4.887**	**0.158**
mesoporous Ga_2O_3/GaOOH heterojunction composite	**111.493**	**6.079**	**0.202**
Ga_2O_3	**51.173**	**9.416**	**0.149**

[a] S_{BET}: specific surface area obtained from N_2 adsorption data in the P/P_0 range from 0.05 to 0.20. [b] $V_{T:}$ total pore volume calculated from adsorption isotherm at P/P_0 = 0.99.

Table S2. The oxygen species and percentages of each peak in fitting results of O 1s XPS spectra of samples.

Sample / **oxygen species**	**Relative percentage (%)**		
	O^{2-}	**O_c**	**O_{OH-}**
GaOOH	**33.545**	**14.875**	**51.579**
Mesoporous GaOOH/Ga_2O_3 heterojunction composite	**27.185**	**36.672**	**36.143**
Ga_2O_3	**37.837**	**62.163**	——

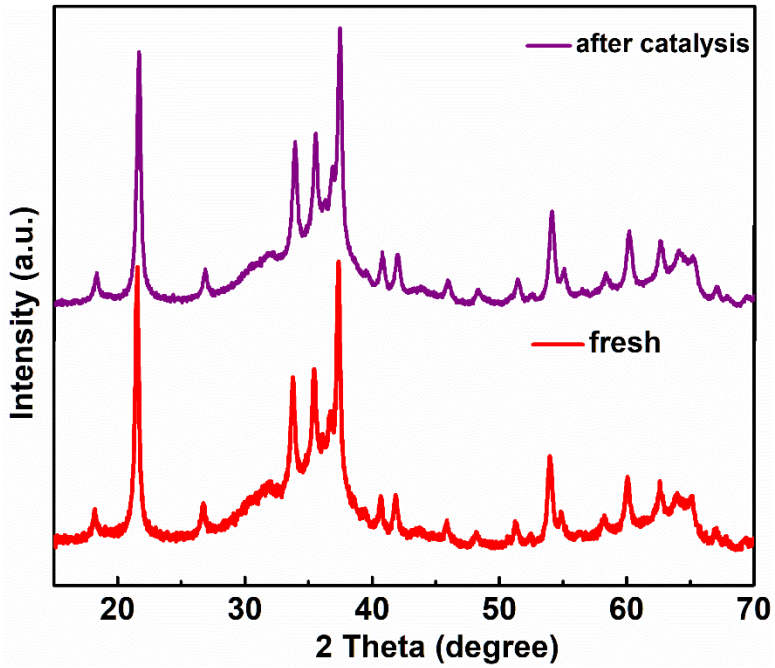

Figure S3. The XRD patterns of mesoporous Ga_2O_3/GaOOH heterojunction composite before (fresh) and after (after catalysis) photocatalytic H_2 evolution test.

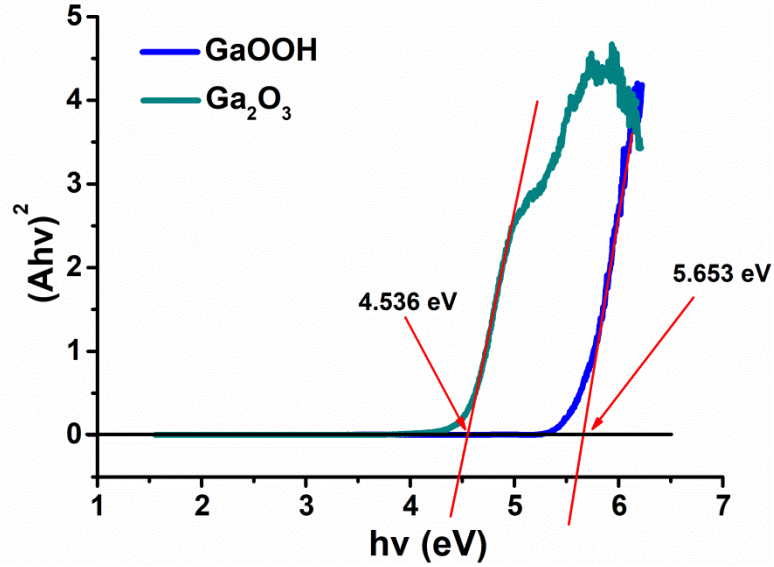

Figure S4. Bandgap energies of GaOOH and Ga_2O_3 estimated from the UV/Vis diffuse reflectance spectra by the Kubelka-Munk method.