Supplementary Information (ESI):

An Ultraviolet-Induced Ostwald Ripening Strategy towards Mesoporous Ga$_2$O$_3$/GaOOH Heterojunction Composite with Controllable Structures for Enhanced Photocatalytic Hydrogen Evolution

Yuenan Zheng,$^{[a]}$ Meihong Fan,$^{[a]}$ Kaiqian Li,$^{[a]}$ Rui Zhang,$^{[a]}$ Xuefeng Li,$^{[c]}$ Ling Zhang,$^{[b]}$ and Zhen-An Qiao$^{[a]}$

$^{a}$ State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Joint Research Laboratory of Nano-Micro Architecture Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

$^{b}$ State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

$^{c}$ Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

E-mail: qiaozhenan@jlu.edu.cn
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 °C for 3 h. After cooling down, the white precipitate was separated and washed several by ethanol and finally dried at 65 °C for 12 h in an oven.

1.3. Preparation of mesoporous Ga$_2$O$_3$ microspheres
In order to obtain mesoporous Ga$_2$O$_3$ microspheres, the Ga-gly was calcined at different temperatures (450, 600 or 700 °C, respectively) for 3 h in a muffle furnace in air with a heating rate of 2 °C/min, labelled as Meso-Ga$_2$O$_3$-X, where X was the calcination temperature.

1.4. Preparation of mesoporous Ga$_2$O$_3$/GaOOH heterojunction composite and GaOOH sample
40 mg of the Meso-Ga$_2$O$_3$-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 at 65 °C for 12 h. This resulting powdered sample was denoted as Ga$_2$O$_3$/GaOOH heterojunction composite. While the Meso-Ga$_2$O$_3$-450 was irradiated for 4h at identical condition, the fusiform GaOOH sample was obtained.

1.5 Preparation of bulk Ga$_2$O$_3$
0.5 g gallium nitrate hydrate was directly calcined in air at 900 °C for 3h with 2 °C/min.

2. Characterization
Powder X-ray diffraction (XRD) results were collected on a Rigaku 2550 (Japan) diffractometer with Cu Kα radiation ($\lambda = 1.5418$ 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\textsubscript{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\textsubscript{2}O and 10 mL methanol as 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\textsubscript{2}O\textsubscript{3}/GaOOH heterojunction composite, Ga\textsubscript{2}O\textsubscript{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\textsubscript{2}SO\textsubscript{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](image1)

**Figure S1.** SEM images of Meso-Ga\textsubscript{2}O\textsubscript{3}-450; Meso-Ga\textsubscript{2}O\textsubscript{3}-600 and Meso-Ga\textsubscript{2}O\textsubscript{3}-700 microspheres.

![Figure S2](image2)

**Figure S2.** TEM images of GaOOH and Ga\textsubscript{2}O\textsubscript{3}. Insets are high magnification TEM images of them.

**Table S1.** The detailed pore structural data for samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) \textsuperscript{a} ((\text{m}^2 \text{ g}^{-1}))</th>
<th>Pore size ((\text{nm}))</th>
<th>(V_f) \textsuperscript{b} ((\text{cm}^3 \text{ g}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meso-Ga\textsubscript{2}O\textsubscript{3}-450</td>
<td>89.015</td>
<td>8.145</td>
<td>0.301</td>
</tr>
<tr>
<td>Meso-Ga\textsubscript{2}O\textsubscript{3}-600</td>
<td>89.223</td>
<td>6.794</td>
<td>0.149</td>
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</tbody>
</table>
Table S2. The oxygen species and percentages of each peak in fitting results of O 1s XPS spectra of samples.

<table>
<thead>
<tr>
<th></th>
<th>Relative percentage (%)</th>
<th>O(^2)-</th>
<th>O(_x)</th>
<th>O(_{OH})</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaOOH</td>
<td></td>
<td>33.545</td>
<td>14.875</td>
<td>51.579</td>
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<tr>
<td>Mesoporous GaOOH/Ga(_2)O(_3) heterojunction composite</td>
<td></td>
<td>27.185</td>
<td>36.672</td>
<td>36.143</td>
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<tr>
<td>Ga(_2)O(_3)</td>
<td></td>
<td>37.837</td>
<td>62.163</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) 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 \(P/P_0 = 0.99\).

Figure S3. The XRD patterns of mesoporous Ga\(_2\)O\(_3\)/GaOOH heterojunction composite before (fresh) and after (after catalysis) photocatalytic H\(_2\) evolution test.
Figure S4. Bandgap energies of GaOOH and Ga$_2$O$_3$ estimated from the UV/Vis diffuse reflectance spectra by the Kubelka-Munk method.