Supplementary Information

Ge modified GaN-ZnO wurtzite solid solutions with high Zn content for efficient photocatalytic H₂ evolution from water under visible light illumination

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Material synthesis

Ge modified GaN-ZnO solid solutions (denoted as GGZ) were prepared by moistureassisted high temperature ammonolysis. In brief, ZnO (Aladdin, 99.9%), Ga₂O₃ (Aladdin, 99.99%) and GeO₂ (Aladdin, 99.999%) powders were mixed up in a molar ratio Zn/Ga/Ge = 5/1.25/1 with an aid of agate mortar and pestle. The mixtures were transferred into an alumina boat and were mounted in a tube furnace. The temperature of the furnace was ramped to 1173 K at 7 K/min. Subsequently, ultrapure ammonia gas (Jiaya Chemicals, 99.999%) was directed through a bubbler containing saturated ammonia solution and was then introduced into the tube furnace. This treatment was named as moisture-assisted ammonolysis as water vapor (ca. 13 kPa at 298 K) was introduced into tube furnace along with ammonia gas (flow rate 250 mL/min)¹. The ammonolysis temperature was kept at 1173 K with duration of 10 h. After that, the furnace was cooled down naturally and the product powders were washed by deionized water, dried in an oven and collected for further analysis. GaN-ZnO solid solutions (denoted as GZ) was prepared in a similar procedure using ZnO and Ga₂O₃ (Aladdin, 99.99%) with a molar ratio Zn/Ga = 5/2.25 as the starting materials.

Material analysis

Phase identification and structure analysis of sample powders were carried out by Xray powder diffraction (XRD) technique. A Bruker D8 Focus diffractometer with incident radiation Cu K_{a1} radiation ($\lambda = 1.5405$ Å) and Cu K_{a2} radiation ($\lambda = 1.5444$ Å) was used. The step size for data collection was 0.01 ° and duration of 10 s was used for each step. Structure information was explored using the General Structure Analysis System (GSAS) to perform Rietveld refinements on XRD data collected². UV-Vis light absorption of sample powders was collected on a UV-vis spectrophotometer equipped with an integrating sphere (JASCO-750, Japan). The spectrophotometer was operated in diffuse reflectance mode. Collected data were analyzed using JASCO software suite. The non-absorbing reference material is BaSO₄. Sample powders were also inspected by field emission scanning electron microscope (FESEM, Hitachi S4800, Japan) and transmission electron microscope (TEM, JEOL JEM-2100F, Japan) equipped with a Mica energy dispersive X-ray spectroscopy (EDS) analytic system. The Brunauer-Emmett-Teller (BET) surface area was measured using a TRISTAR 3020 adsorption analyzer. X-ray photoelectron spectroscopy (Thermo Esclab 250Xi, a monochromatic Al Ka X-ray source) was used to investigate the surface state of sample powders. All data are referenced to the C 1s peak $(284.7 \text{ eV})^3$. The nitrogen and oxygen content in the sample powders were determined by an oxygen-nitrogen-hydrogen analyzer (ONH836, LECO Co., USA).

Photocatalytic activity

The photocatalytic activity of sample powders was evaluated by monitoring their H₂ evolution in the presence of oxalic acid aqueous solution (0.025 M) as sacrificial agent under visible light illumination ($\lambda \ge 420$ nm). A top irradiation-type glass reactor connected to a gas-closed circulation and evacuation system (Perfect Light, Labsolar-IIIAG, China) was used to perform the experiment. For a typical experiment,

100 mg sample powders were deposited with Pt as a co-catalyst according to previous report⁴: sample powders were immersed into appropriate amounts of H₂PtCl₆ aqueous solution to form slurry. The slurry was heated at 353 K in an oven until dry and further calcined on a hot plate at 523 K. Pt deposited sample powders and 100 mL oxalic acid aqueous solution (0.025 M) were sealed in the reactor and was evacuated for 45 min to remove air dissolved. A 300 W Xeon lamp (Perfect Light, PLX-SXE300, China) was used as the light source. Visible light illumination was produced by filtering the output of the lamp with a UV-cutoff filter ($\lambda \ge 420$ nm). Monochromatic light was used to determine the apparent quantum efficiency of photocatalytic activity. Band pass filter (Perfect light, China) at 420 nm, 450 nm, 500 nm, 550 nm and 600 nm was used to filter the Xeon lamp, respectively. A quantum meter (Apogee MP-300, USA) was used to determine accurate photon flux at individual wavelength. H₂ produced in the reactor were analyzed by an on-line gas chromatograph (TECHCOMP, GC7900, China). The gas chromatograph was equipped with 5 Å molecular sieve columns and a thermal conductivity detector and was operated using Ar as the carrier gas. The apparent quantum efficiency (AQE) at each monochromatic wavelength was evaluated according to following formula:

Apparent quantum efficiency (AQE)

 $=\frac{2 \times moles \ of \ H_2 \ production \ per \ hour}{moles \ of \ photon \ flux \ per \ hour} \times 100\%$



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Table S1 Unit cell parameters, band gap and BET surface area of Ge modified GaN-ZnO solid solutions (denoted as GGZ) and GaN-ZnO solid solutions (denoted as GZ), standard deviations are included in the parenthesis.

	Space	<i>a</i> / Å	<i>c</i> / Å	V / Å ³	Band	BET Surface
	group				gap / eV	area / $m^2 \cdot g^{-1}$
GGZ	P6 ₃ mc	3.1913(1)	5.1782(2)	45.673(2)	2.75(1)	4.2(1)
GZ	P6 ₃ mc	3.1980(1)	5.1877(2)	45.950(3)	2.89(1)	4.1(1)

Table S2 Nitrogen and oxygen content determined by an oxygen-nitrogen-hydrogen analyzer.

Sample	Nitrogen content (wt%)	Oxygen content (wt%)
GGZ	9.0	9.2
GZ	1.8	15.3

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