

Supporting Information

Nitrogen Photofixation over III-Nitride Nanowires Assisted by Ruthenium Clusters of Low Atomicity

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Supporting Information

1. Growth of GaN and InGaN/GaN Nanowires.

The catalyst-free GaN and InGaN/GaN nanowires are grown on a Si (111) substrate using radio frequency plasma-assisted molecular beam epitaxy (MBE) in nitrogen rich conditions. Prior to loading into the MBE system, the Si substrates were cleaned by hydrofluoric acid and standard solvent solutions. Growth conditions include the following: a temperature of ~ 750 °C, nitrogen flow rate of 1 sccm, and a forward plasma power of ~ 400 W. The as-synthesized nanowires can be doped with tetravalent (Ge^{4+}) and divalent (Mg^{2+}) ions to make it n and p type, respectively. The doping density is controlled by tuning the effusion cell temperatures of Ge Mg and In. For n-type doping, the Ge effusion cell temperature is 1100 °C. For p-type doping, the Mg effusion cell temperature is 265 °C. For the incorporation of indium, the indium effusion cell temperature is varied from 705 °C to 795 °C. The electron and hole concentrations for the Si-doped n-type and Mg-doped p-type GaN NWs were estimated to be on the order of $n = 5 \times 10^{18} \text{ cm}^{-3}$ and $p = 1 \times 10^{18} \text{ cm}^{-3}$, respectively. Other growth parameters were kept constant.

2. The deposition of Ru co-catalyst.

Ruthenium loading was conducted via the impregnation of as-synthesized GaN NWs (0.35 mg) with a solution of $\text{Ru}_3(\text{CO})_{12}$ in dry THF (1.5 mL), followed by the complete loss of carbonyl groups in vacuum under a temperature program of 2 °C min^{-1} up to 200 °C, held for one hour, 1 °C min^{-1} up to 350 °C, held for two hours and then cooled to ambient temperature. The Ru content was further confirmed by using the XPS measurement before and after the decomposition process.

3. Photo-driven ammonia synthesis.

A slice of freshly prepared GaN or InGaN/GaN NWs with areas of 3.5 cm^2 (corresponding to 0.35 mg of GaN NWs) was placed on the bottom of an air-tight

quartz reactor in vacuum, followed by the introduction of 600 μmol hydrogen (75 %) and nitrogen (25 %) mixture (Figure S7). In the case of powdered samples, 0.35 mg of powders was spread evenly on the bottom of the reactor in vacuum, which was then evacuated at 250 $^{\circ}\text{C}$ for 2 h to remove water and other molecules adsorbed in the powders. The light intensity measured at wavelengths between 290 and 380 nm was ca. 7.5 mWcm^{-2} . The light intensity measured at wavelengths longer than 400 nm was ca. 20 mWcm^{-2} . The NH_3 product was identified by gas chromatography-mass spectrometry and quantified via a colorimetric method. Specifically, 1.5 mL of deionized water was injected into the chamber to fully dissolve the NH_3 (gas phase) formed after the reaction. Then, 80 μL of an aqueous solution of EDTA tetrasodium salt hydrate (1.3 M), 160 μL of an aqueous solution of sodium salicylate (1.46 M) and pyrazole (0.24 M), 520 μL of an aqueous solution of sodium hydroxide (1.25 M) and sodium hypochlorite (0.25 M) were added consequently. In the presence of NH_3 , a green color complex with absorption at 650 nm was measured by UV/vis spectrometer (Figure S8). Ammonium chloride was employed for making the calibration curve (Figure S9).

4. Quantitative determination of NH_3

The quantitative determination of NH_3 was using a colorimetric method.

- (1) 1.5 mL of deionized water was injected into the chamber to fully dissolve the NH_3 (gas phase) formed after the reaction (designated as solution A).
- (2) 80 μL of an aqueous solution of EDTA tetrasodium salt hydrate (1.3 M) was added into solution A.
- (3) 160 μL of an aqueous solution of sodium salicylate (1.46 M) and pyrazole (0.24 M) added into solution A.
- (4) 520 μL of an aqueous solution of sodium hydroxide (1.25 M) and sodium hypochlorite (0.25 M) were added into solution A.

In the presence of NH_3 , a green color complex with absorption at 650 nm was measured by UV/vis spectrometer (Figure S8). A series of ammonium chloride with known concentration were employed for making the calibration curve (Figure S9).

5. Generation Characterization.

The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced Diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) images were recorded using LASEM Hitachi S-4700. High resolution bright field transmission electron microscope (TEM) images were obtained using FEI Tecnai G2 F20 S/TEM at accelerating voltage of 200 kV. For STEM-HAADF imaging, a Hitachi HD2700 Cs-corrected STEM was used with a cold field emitter operated at 200 kV and with an electron beam diameter of $\sim 0.1 \text{ nm}$. STEM EDXS analysis was performed using a 60mm^2 silicon drift detector from Bruker. The UV-vis absorption spectra were measured with a Shimadzu UV-2450 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromated X-ray source (Al K α $h\nu = 1486.6 \text{ eV}$). The energy scale of the spectrometer was calibrated using Au 4f $_{7/2}$, Cu 2p $_{3/2}$, and Ag 3d $_{5/2}$ peak positions. The standard deviation for the binding energy (BE) values was 0.1 eV. The $E_F - E_V$ was estimated for each sample from XPS valence band spectrum. The PL measurement was performed with either a 405-nm laser or a 325-nm He-Cd laser (Kimmon Koha) as excitation source. The laser beam was focused on the sample through a $\times 60$ objective, with a circular beam size of $\sim 5 \text{ }\mu\text{m}$. The emitted light was collected by the same objective and spectrally resolved by a high-resolution spectrometer and detected by a photomultiplier tube.

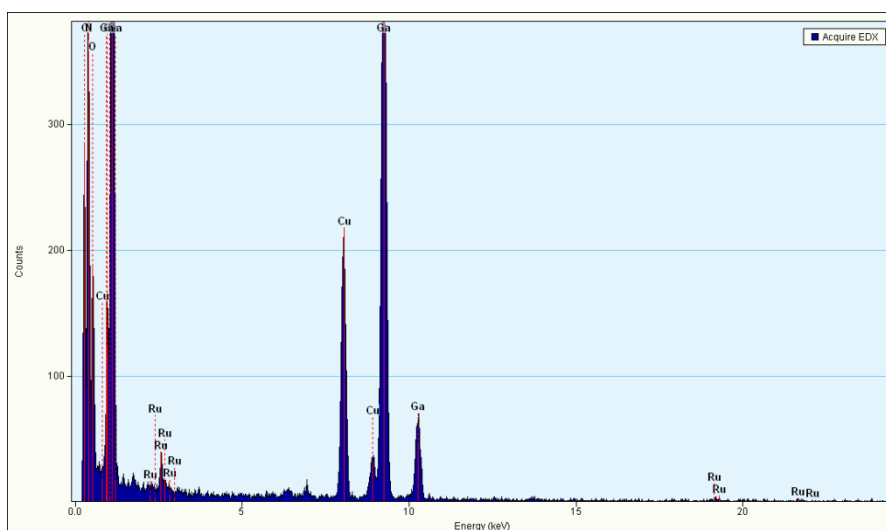


Figure S1. EDX spectrum of 5 wt% Ru modified GaN NWs.

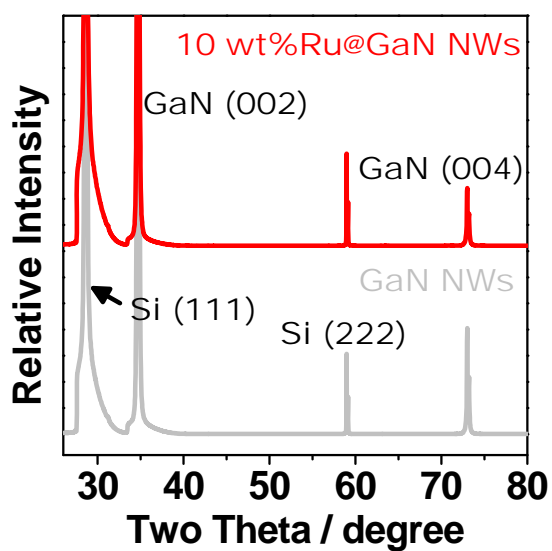


Figure S2. XRD patterns of GaN nanowires before (gray) and after (red) the deposition of Ru metal.



Figure S3. Reaction setup.

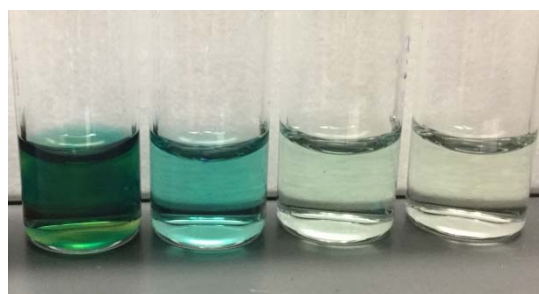


Figure S4. Photos of green complex obtained during the ammonia synthesis reaction, after performing the colorimetric treatment.

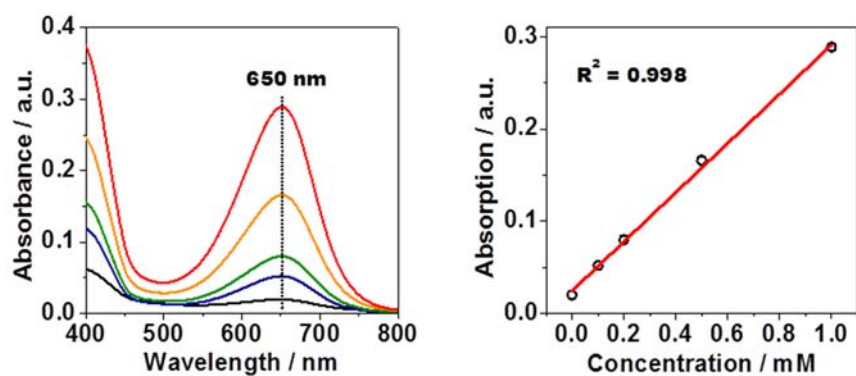


Figure S5. UV-vis spectroscopy calibration data for the quantitative determination of NH_3 at maximum absorbance peak of 650 nm (left) and the calibration curve (right).

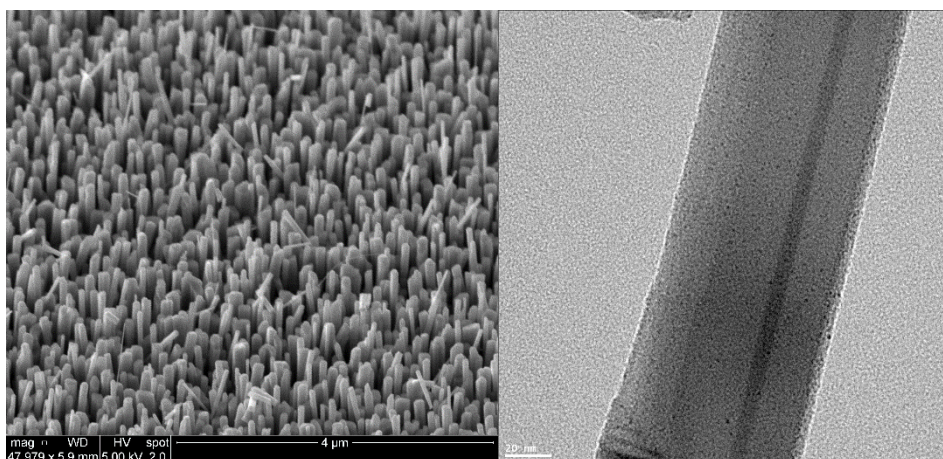


Figure S6. SEM (left) and TEM (right) images of the Ru@GaN NWs after 24h of photocatalytic reaction.

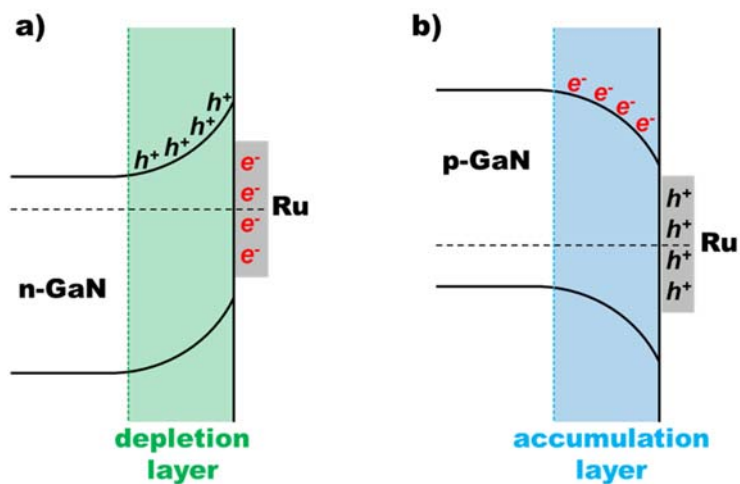


Figure S7. Energy band diagrams of Ru metal and GaN semiconductor contacts. (a) The formation of depletion layer between Ru and n-GaN NWs. (b) The formation of accumulation layer between Ru and p-GaN NWs.

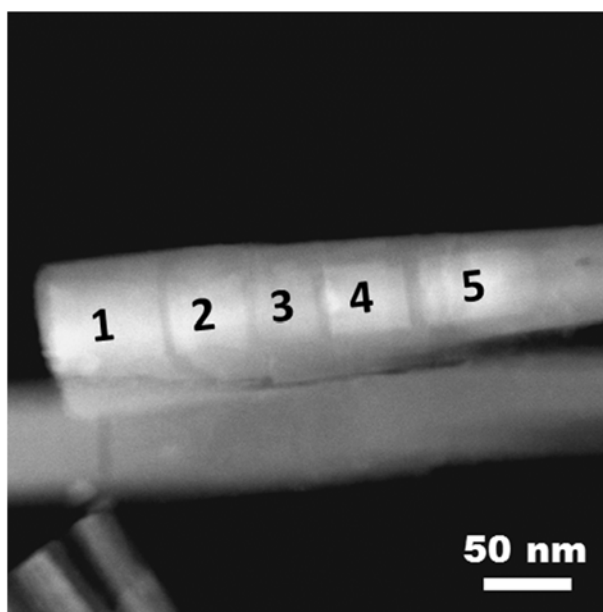


Figure S8. STEM-HAADF image of the as-synthesized InGaN/GaN NWs with five InGaN segments.

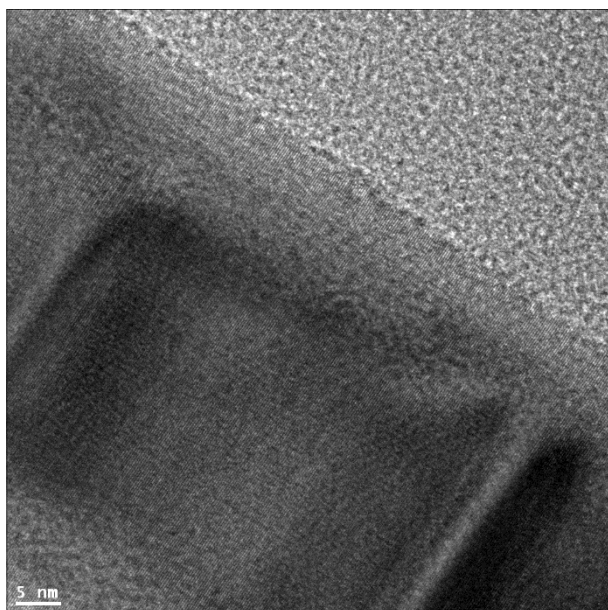


Figure S9. TEM image of 5 wt % Ru modified InGaN/GaN NWs.

Table S1. Results of various samples for the photocatalytic ammonia synthesis.^[a]

Entry	Substrates	Time (h)	Wavelength (nm)	NH ₃ yield (μmol/g)
1	i-GaN NWs	24	> 290 nm	30
2	n-GaN NWs	24	> 290 nm	57
3	p-GaN NWs	24	> 290 nm	23
4	GaN powder	24	> 290 nm	4
5	0.5 wt%Ru@n-GaN NWs	24	> 290 nm	162
6	2 wt%Ru@n-GaN NWs	24	> 290 nm	348
7	5 wt%Ru@n-GaN NWs	24	> 290 nm	514
8	10 wt%Ru@n-GaN NWs	24	> 290 nm	390
9	5 wt%Ru@n-GaN NWs	24	Dark	n.d.
10	5 wt%Ru@n-GaN NWs	2	> 290 nm	241
11	5 wt%Ru@n-GaN NWs	4	> 290 nm	301
12	5 wt%Ru@n-GaN NWs	12	> 290 nm	423
13	5 wt%Ru@n-GaN NWs	48	> 290 nm	473
14	5 wt%Ru@n-GaN NWs	72	> 290 nm	348
15	5 wt%Ru ₃ (CO) ₁₂ @n-GaN NWs	24	> 290 nm	62
16	5 wt%Ru*@n-GaN NWs	24	> 290 nm	213
17	5 wt%Ru@i-GaN NWs	24	> 290 nm	291
18	5 wt%Ru@p-GaN NWs	24	> 290 nm	144
19	5 wt%Ru@Si substrate	24	> 290 nm	trace
20	n-InGaN/n-GaN NWs	24	> 400 nm	41
21	i-InGaN/i-GaN NWs	24	> 400 nm	32
22	p-InGaN/p-GaN NWs	24	> 400 nm	15
23	5 wt%Ru@n-InGaN/n-GaN NWs	24	> 400 nm	65
24	n-GaN NWs	24	> 400 nm	n.d. ^b
25	5 wt%Ru@n-GaN NWs	24	> 400 nm	n.d.

^[a]Reaction conditions were as follows: reaction temperature, 10 °C; reactant, 600 μmol of H₂ (75%) and N₂ (25%); irradiation source, 290-380 nm UV irradiation at an intensity of 7.5 mWcm⁻²; irradiation time, 2-72 h. After the reaction. ^[b]Not detectable