(Supporting Information)

Photochemical benzene to toluene methylation using methanol catalyzed by gallium nitride nanowire

Mingxin Liu[1,2‡], Zihang Qiu[1,‡], Roksana T. Rashid[3], Lu Li[4], Lida Tan[1], Sheng Chu[3], Yunen Cen[1], Rustam Khaliullin,[1] Zetian Mi*[2,3], and Chao-Jun Li*[1].

[1]Department of Chemistry and FRQNT Centre for Green Chemistry and Catalysts, McGill University, 801 Sherbrooke Ouest, Montreal, Quebec, H3A 0B8, Canada.

[2]Department of Electrical Engineering and Computer Science, University of Michigan, 1301 Beal Ave, Ann Arbor, MI, 48109, USA.

[3]Department of Electrical and Computer Engineering, McGill University, 3480 University, Montreal, Quebec, H3A 0E9, Canada.

[4]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Chemistry Department, Jilin University, Changchun, China.

[‡]These authors contributed equally.

Materials and methods

1. Growth of GaN Nanowires.

The catalyst-free GaN nanowires were grown on a Si (111) wafer using radio frequency plasma-assisted molecular beam epitaxy (MBE) in nitrogen rich conditions. The Si substrates were cleaned in clean room by absolute methanol, acetone, and essentially hydrofluoric acid prior to loading into the MBE system. Growth conditions: temperature ~750 ^{o}C, nitrogen flow rate 1 sccm, forward plasma power ~400 W. The as-synthesized nanowires can be doped with tetravalent (Si^{4+}) or divalent (Mg^{2+}) ions for making n- and p- type semiconductors, respectively. The doping density is controlled by tuning the effusion cell temperatures of Si and Mg. For n-type doping, the Si effusion cell temperature is 1350 °C. For p-type doping, the Mg effusion cell temperature is 265 °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 $n = 5 \times 10^{18}$ cm^{-3} and $p = 1 \times 10^{18}$ cm^{-3}, respectively. Other growth parameters were kept constant during the growth (typically 4 h).

2. Photo-driven benzene to toluene conversion

A 3.5 cm2 slice of a typical GaN NW grown for 4 h (equiv to 0.35 mg GaN) was then placed on the bottom of a 120 mL glass flange equipped with a sealing O-ring and an evacuation seal. The flange was capped with a 3'' quartz window and evacuated using vacuum oil pump until the internal pressure dropped below 5 × 10-2 mbar. 5 μL (equiv to 0.124 mmol) HPLC grade methanol and 10 μL (equiv to 0.112 mmol) HPLC grade benzene was then introduced through the evacuation seal to the flange before the flange was cooled to 4 oC in a chiller and shined with a 300 W full-arc xenon lamp for 12 h (Figure 3A). The gas phase inside the flange was analyzed using a valve syringe and gas chromatography mass spectrometer (GC-MS).

3. General Characterization.

Scanning electron microscopy (SEM) images were recorded using LASEM Hitachi S-4700. High resolution bright field transmission electron microscope. GC-MS was measured using Agilent G1701DA Gas Chromatography equipped with MSD5973 *inert* Mass Spectrometer.

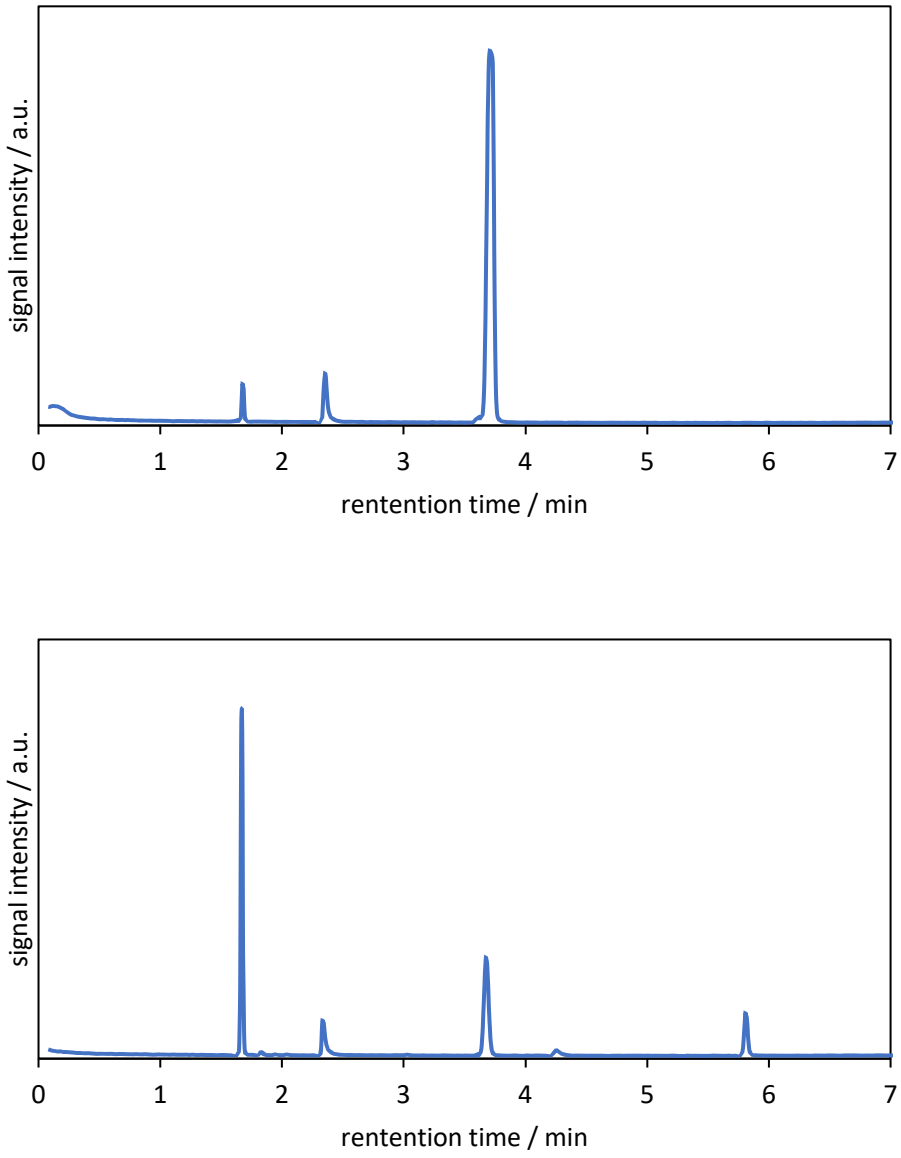

Figure S1. Chromatography of the reaction mixture before (above) and after (below) light irradiation: 1.7 min: dead volume; 2.2 min: methanol; 3.7 min: benzene; 5.8 min: toluene.

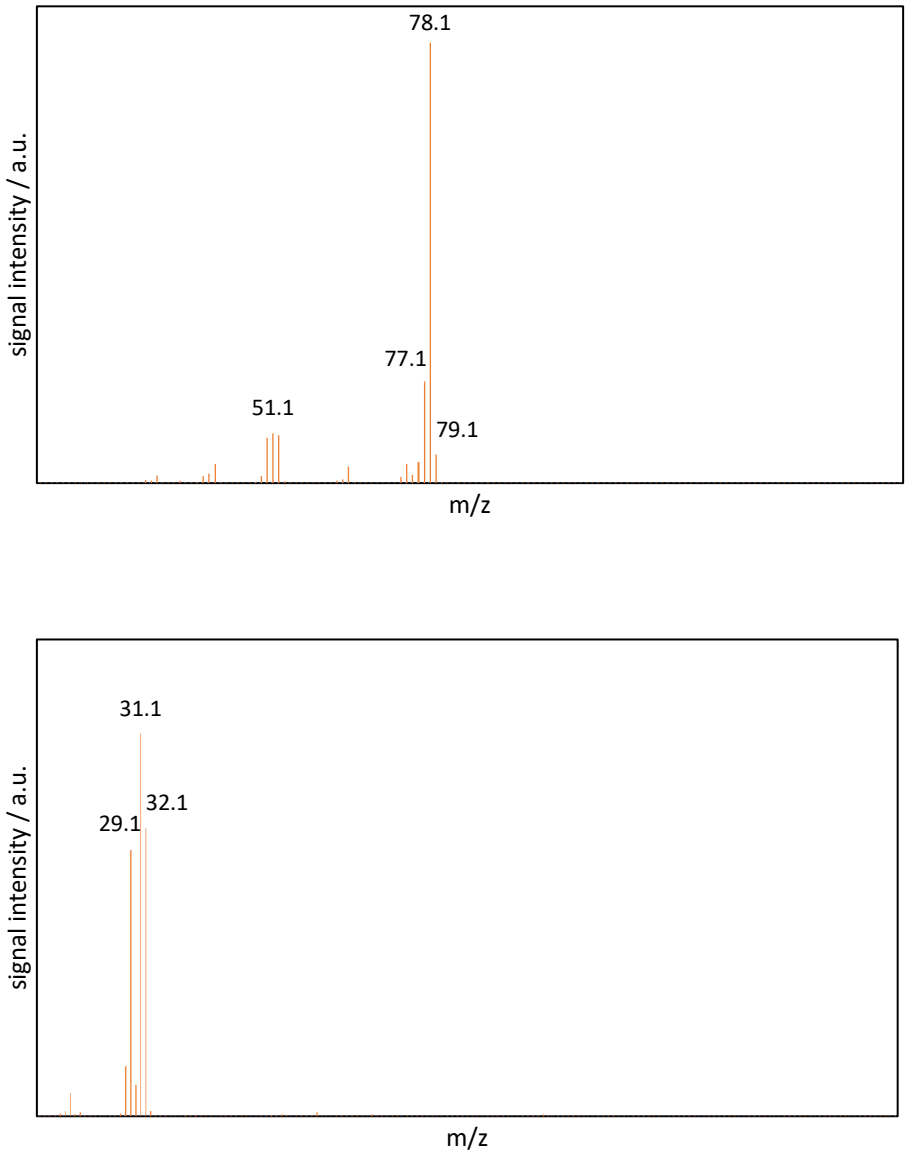

Figure S2. Mass spectra of the starting material benzene (above) and methanol (below) found at retention time 2.2 min and 3.7 min after GC-MS injection, respectively.

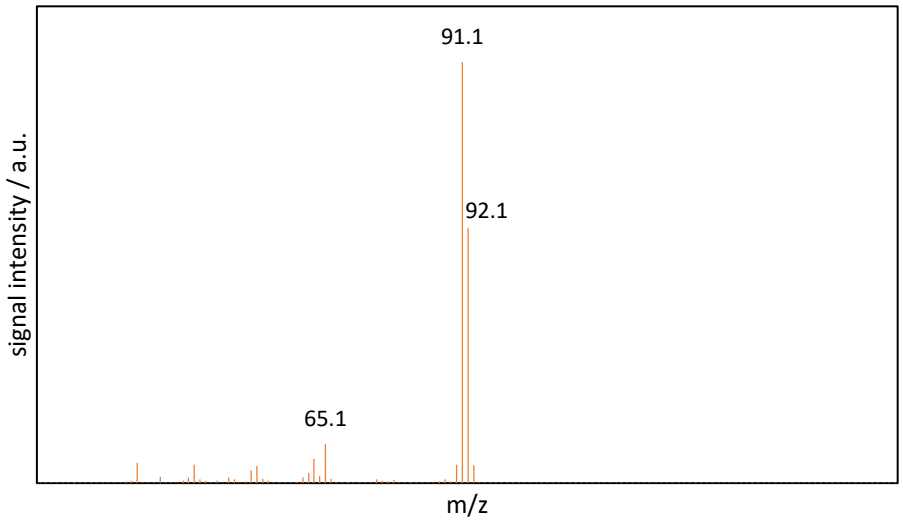

Figure S3. Product mass spectrum obtained at retention time 5.8 min after GC-MS injection.

TABLE S1. Benzene to toluene conversion result[a].

entry	catalyst	toluene yield / μmol	catalyst efficiency / $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$
1	*p*-GaN NW	38.0	9050
2	*i*-GaN NW	9.4	2240
3	*n*-GaN NW	6.9	1640
4	GaN Powder	2.3	550
5	p-GaN NW[b]	not detected	N/A
6	no GaN[c]	not detected	N/A
7	*p*-GaN NW[d]	39.0	9290
8	*p*-GaN NW[d]	38.8	9240
9	*p*-GaN NW[d]	38.3	9120
10	*p*-GaN NW[d]	38.7	9210
11	*p*-GaN NW[d]	37.6	8950
12	*p*-GaN NW[e]	38.0	18100
13	*p*-GaN NW[e,f]	860	421500
14	GaN film	9.4	N/A

[a]Std. cond.: time under light 12 h, 5μL MeOH, 10 μL benzene, 0.35 mg GaN (grown for 4 h).
[b]The reaction was conducted without light.
[c]Si wafer with no GaN grown was used as catalyst.
[d]Catalyst recycled from previous experiments was used (for five consecutive recycles).
[e]GaN NW grown for 2 h instead of 4 h was used.
[f]1 mL MeOH and 2 mL benzene was loaded

TABLE S2. Kinetic experiments data form[A].

entry	time / min	toluene yield / μmol	ethanol yield / μmol
1	30	3.4	not detected
2	60	6.1	not detected
3	90	7.4	not detected
4	120	9.0	not detected
5	30[B]	0.8	not detected
6	60[B]	1.4	not detected
7	90[B]	1.9	not detected
8	120[B]	2.5	not detected
9	30[C]	1.8	not detected
10	60[C]	2.6	not detected
11	90[C]	3.1	not detected
12	120[C]	4.4	not detected
13	30[D]	N/A	0.9
14	60[D]	N/A	2.1
15	90[D]	N/A	3.0
16	120[D]	N/A	3.8
17	30[E]	N/A	0.2
18	60[E]	N/A	0.5
19	90[E]	N/A	0.7
20	120[E]	N/A	1.0

[A]Std. cond.: 5μL MeOH, 10 μL benzene, 0.35 mg GaN (grown for 4 h).
[B]Conducted with 2.5 μL MeOH and 10 μL benzene.
[C]Conducted with 5 μL MeOH and 5 μL benzene
[D]Conducted with 5 μL MeOH alone.
[E]Conducted with 2.5 μL MeOH alone.

Table S3. Methanol to toluene conversion results[α].

entry	catalyst	toluene yield / μmol	catalyst efficiency / $\mu mol \cdot g_{cat}^{-1} \cdot h^{-1}$
1	*p*-GaN NW	0.75	180
2	*i*-GaN NW	0.72	170
3	*n*-GaN NW	0.62	150

[α]Std. cond.: 0.1 mmol CH_4, 2 μL MeOH, time under light 12 h, 0.35 mg GaN (grown for 4 h).