(Supporting Information)

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

Mingxin Liu1,2‡, Zihang Qiu1,‡, Roksana T. Rashid3, Lu Li4, Lida Tan1, Sheng Chu3, Yunen Cen1, Rustam Khaliullin,1 Zetian Mi\*2,3, and Chao-Jun Li\*1.

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

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

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

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

‡These authors contributed equally.

**Materials and methods 2**

1. **Growth of GaN Nanowires 2**
2. **Photo-driven benzene to toluene conversion. 2**
3. **General Characterization. 3**

**Figures 4-6**

**Tables 7-9**

**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 oC, nitrogen flow rate 1 sccm, forward plasma power ~400 W. The as-synthesized nanowires can be doped with tetravalent (Si4+) or divalent (Mg2+) 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 × 1018 cm-3 and *p* = 1 × 1018 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 resulta.

|  |  |  |  |
| --- | --- | --- | --- |
| entry | catalyst | toluene yield / μmol | catalyst efficiency / μmol·gcat-1·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 NWb | not detected | N/A |
| 6 | no GaNc | not detected | N/A |
| 7 | *p-*GaN NWd | 39.0 | 9290 |
| 8 | *p-*GaN NWd | 38.8 | 9240 |
| 9 | *p-*GaN NWd | 38.3 | 9120 |
| 10 | *p-*GaN NWd | 38.7 | 9210 |
| 11 | *p-*GaN NWd | 37.6 | 8950 |
| 12 | *p-*GaN NWe | 38.0 | 18100 |
| 13 | *p-*GaN NWe,f | 860 | 421500 |
| 14 | GaN film | 9.4 | N/A |

aStd. cond.: time under light 12 h, 5μL MeOH, 10 μL benzene, 0.35 mg GaN (grown for 4 h).

bThe reaction was conducted without light.

cSi wafer with no GaN grown was used as catalyst.

dCatalyst recycled from previous experiments was used (for five consecutive recycles).

eGaN NW grown for 2 h instead of 4 h was used.

f1 mL MeOH and 2 mL benzene was loaded

TABLE S2. Kinetic experiments data formA.

|  |  |  |  |
| --- | --- | --- | --- |
| 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 | 30B | 0.8 | not detected |
| 6 | 60B | 1.4 | not detected |
| 7 | 90B | 1.9 | not detected |
| 8 | 120B | 2.5 | not detected |
| 9 | 30C | 1.8 | not detected |
| 10 | 60C | 2.6 | not detected |
| 11 | 90C | 3.1 | not detected |
| 12 | 120C | 4.4 | not detected |
| 13 | 30D | N/A | 0.9 |
| 14 | 60D | N/A | 2.1 |
| 15 | 90D | N/A | 3.0 |
| 16 | 120D | N/A | 3.8 |
| 17 | 30E | N/A | 0.2 |
| 18 | 60E | N/A | 0.5 |
| 19 | 90E | N/A | 0.7 |
| 20 | 120E | N/A | 1.0 |

AStd. cond.: 5μL MeOH, 10 μL benzene, 0.35 mg GaN (grown for 4 h).

BConducted with 2.5 μL MeOH and 10 μL benzene.

CConducted with 5 μL MeOH and 5 μL benzene

DConducted with 5 μL MeOH alone.

EConducted with 2.5 μL MeOH alone.

Table S3. Methanol to toluene conversion resultsα.

|  |  |  |  |
| --- | --- | --- | --- |
| entry | catalyst | toluene yield / μmol | catalyst efficiency / μmol·gcat-1·h-1 |
| 1 | *p-*GaN NW | 0.75 | 180 |
| 2 | *i-*GaN NW | 0.72 | 170 |
| 3 | *n-*GaN NW | 0.62 | 150 |

αStd. cond.: 0.1 mmol CH4, 2 μL MeOH, time under light 12 h, 0.35 mg GaN (grown for 4 h).