

## Supporting Information: Electrochemical nitrogen reduction reaction over Gallium – a computational and experimental study

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### S1 Electrochemical Nitrogen Reduction Experiments

#### S1.1 Flow cell setup, membrane and electrode preparation

The membrane electrode assembly (MEA) for a home-made flow cell (Fig. S1) consists of Ga/KJ10 catalyst deposited on pretreated carbon paper as cathode gas diffusion electrode (GDE), a commercially available platinum on carbon paper (Pt/C, 0.2 mg cm<sup>-2</sup>) as anode GDE, and a pre-treated Nafion 117 cation exchange membrane (CEM). The electrodes had an active area of 1.9 cm × 1.9 cm. The catalytic ink was prepared via mixing synthesized Ga/KJ10 catalyst, 5 wt% Nafion (Sigma-Aldrich, USA), and 2-Isopropanol, which served as the catalyst, binder, and solvent, respectively. The ink was then dispersed in an ultrasonic bath for 30 min. It was subsequently dropped on the diffusion layer, i.e., pretreated carbon paper. The catalyst loading was 0.25 mg<sub>Ga</sub> cm<sup>-2</sup>. The anode and cathode carbon papers before use, were immersed in 0.5 M H<sub>2</sub>SO<sub>4</sub> overnight (at least 12 hours) to remove any contamination. Then, they were rinsed with MilliQ water several times and dried in an oven for 24 hours at 60°C. Nafion 117 membrane was cut to the designed area (3.5 cm × 3.5 cm) and sonicated for 20 minutes at room temperature in 5% H<sub>2</sub>O<sub>2</sub>. Next, Nafion was sonicated for 20 minutes at room temperature in MilliQ water before undergoing the same sonication step in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Then, it was sonicated again for 20 minutes at room temperature in MilliQ water to rinse the excessive acid from the previous step. At the final step, Nafion stored in MilliQ water at 80 °C overnight and kept at room temperature in water inside an amber glass until its application. Prior to use, the membrane was sonicated first in 0.05 M H<sub>2</sub>SO<sub>4</sub> and then in MilliQ water.<sup>1</sup>

#### S1.2 ENRR measurements

The electrochemical measurements were conducted in a home-made flow cell (Fig. S1). Two different electrolytes (pH=6) were used at anode side, MilliQ water and concentrated LiOTf. For the systems with MilliQ water as anolyte, 50 ml of anolyte was recirculated with a pump at a flow rate of 5 ml/min. For the systems with water in salts (LiOTf 9 m) as anolyte, 15 ml of anolyte was recirculated at a flow rate of 5 ml/min. A mini HydroFlex® hydrogen reference electrode (Gaskatel, gold plated connector, Palladium-Platinum gas diffusion electrode as sensor, replaceable hydrogen cell as hydrogen source) was used as the reference electrode. During

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the ENRR measurements, purified N<sub>2</sub> was continuously fed into the cathodic compartment at a flow rate of 50 sccm using mass flow controller (MKS, P-Series MFC3). An electrochemical workstation (ZIVE SP1, Korea) was used to control the applied current during the electrolysis process. Upon charging, the anolyte was fed into the anode by a HPLC pump (Gilson, model 305) at a flow rate of 5.0 mL min<sup>-1</sup>. An in-line acid trap of the cathode chamber filled with 0.01 M HCl was set to avoid volatilization of the produced ammonia. The anolyte from the anode side and acid trap from the cathode side were both collected and analysed for quantitative measurements.

The nitrogen or helium gas was supplied to the cathode through a cylinder at a flow rate of 50 sccm. The gas passed through a home-made copper cold trap (1/8 in copper tube with a length of approx. 1 meter immersed in liquid nitrogen at -196°C, Fig. S2) to clean the gas by removing contaminants such as NH<sub>3</sub> or NO<sub>x</sub> gases. According to freezing temperature of gases in Table S1, all gases including NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, NH<sub>3</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, NO, freeze in liquid nitrogen temperature and only N<sub>2</sub> gas passes through the cold trap and enters the cell. In this temperature Ar also freezes, therefore, we used He as background gas.

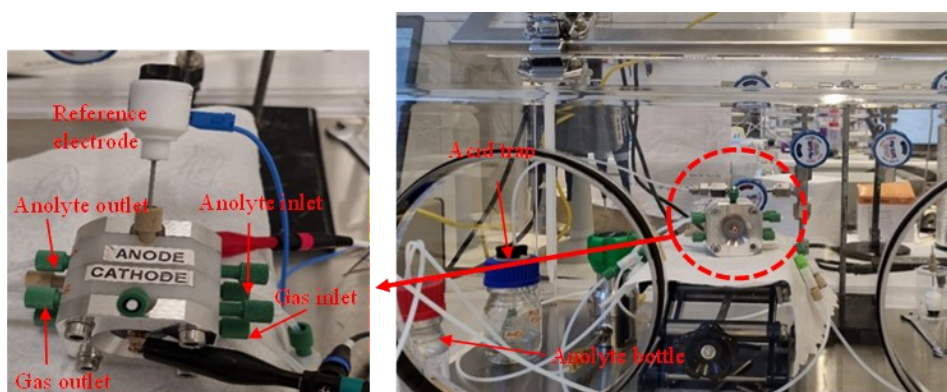


Figure S1- Gas-Liquid flow cell setup

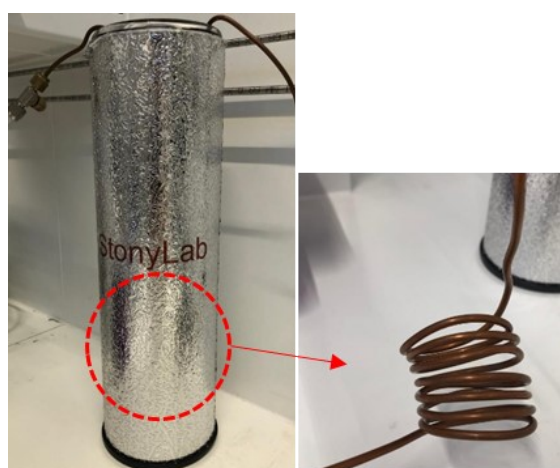


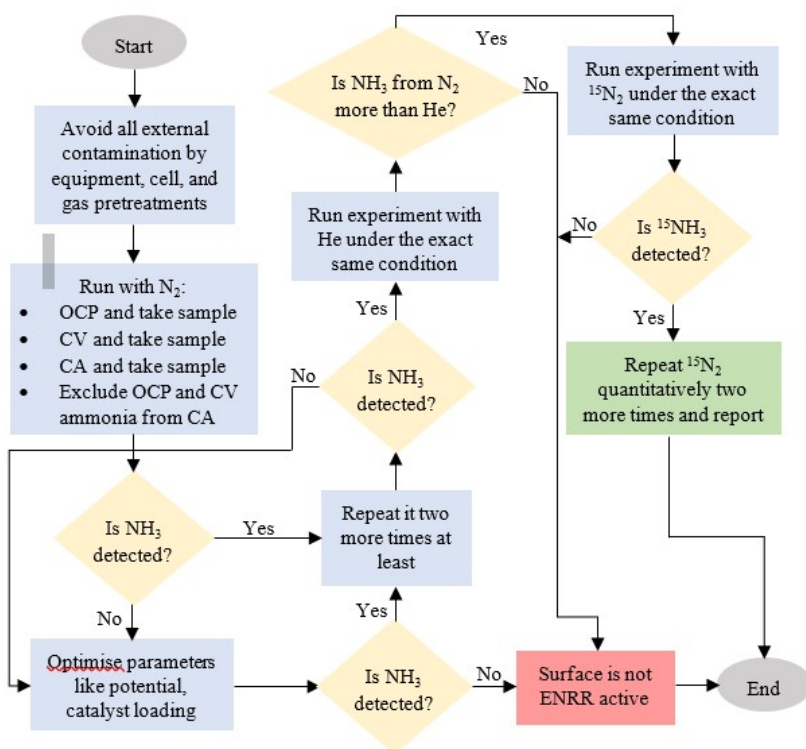
Figure S2-Copper cold trap - copper tube immersed in liquid nitrogen

Table S1- Freezing temperature of ammonia gas, NO<sub>x</sub> gases, He and Ar gases

Gas	NO <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>	NH <sub>3</sub>	N <sub>2</sub> O	N <sub>2</sub> O <sub>3</sub>	NO	Ar	N <sub>2</sub>	He
Freezing Temp. [°C]	-9.3	-11.2	-77.7	-90.9	-100.7	-164	-	-210	-272.2
							189.4		

### S1.3 ENRR control experiments

The methodology of the control experiments is illustrated in Scheme S1. Before the experiments, we avoided all external contamination by performing several pretreatments including cleaning of gas, equipment, set up, electrode and membrane treatment. Before electrochemical experiments, open circuit potential (OCP) was applied for 1 hour. Then, cyclic voltammetry (CV) with a scan rate of 20 mV/s in the negative potential window (-1 V to -2 V vs. SHE) was recorded, to activate the catalyst in negative potential range. To study the electrochemical ammonia synthesis and calculate ammonia production rate and Faradaic efficiency, chronoamperometry (CA) technique was utilized with  $N_2$  gas for the same duration of OCP test. Samples were taken before the OCP experiment and after each step (OCP, CV, and CA) from acid trap solution and anolyte. The same procedure was applied with He gas to further exclude adventitious contamination, such as ammonia from atmosphere or human breath, trace on the equipment, or residues in the electrocatalyst.



Scheme S1-ENRR experimental protocol

### S1.4 Ammonia analysis

If ammonia is produced, this will happen at the cathode catalyst layer and thereafter it can either leave the cathode compartment via the nitrogen flow and reach the acid trap or (to a lesser extent) diffuse to anode compartment through CEM. To precisely collect the ammonia produced, an acid trap was therefore placed at the cathode outlet, the outflow anolyte was stored in a flask, and the cathode electrode and Nafion membrane were dipped in 0.05 M  $H_2SO_4$  solution overnight after the electrochemical tests. The water used was ultrapure and obtained from Milli-Q® Millipore (18.2 M $\Omega$  cm at 20 °C).

An [indophenol](#) blue method-based ammonium test kit (MQuant® 1.14423) was used to determine the produced ammonia. 5.0 mL sample solution was taken from the collected solutions and the pH was adjusted to the range 4-13. Then the reagents were added according to the procedure reported in the MQuant® user manual. The ammonium concentration in the final mixed solution was measured quantitatively by the UV-vis adsorption test (Thermo Scientific, Genesys 10S UV VIS Spectrophotometer) in 400-1000 nm wavelength range.

For the acid trap solutions and MilliQ water as anolyte, standard calibration curves were utilized, and for the LiOTf 9m as anolyte standard addition method was utilized.

## S2.1 Physicochemical Characterization

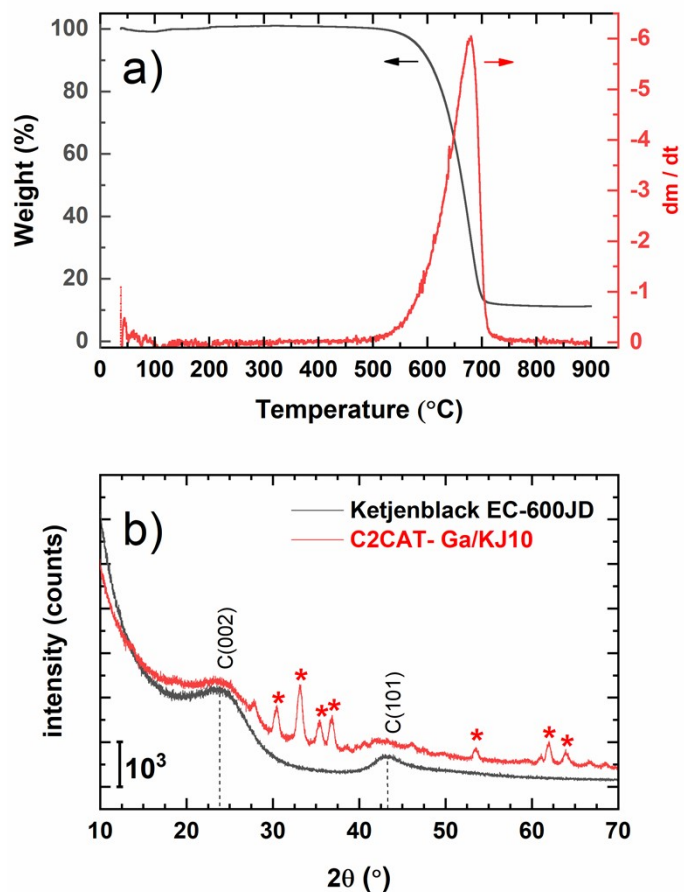


Figure S3. a) Thermogravimetric (TG) and differential thermal (DT) analyses curves at  $5\text{ }^{\circ}\text{C min}^{-1}$  linear temperature rate; and b) X-ray diffraction patterns of the as-prepared Ga/KJ10 and carbon material.

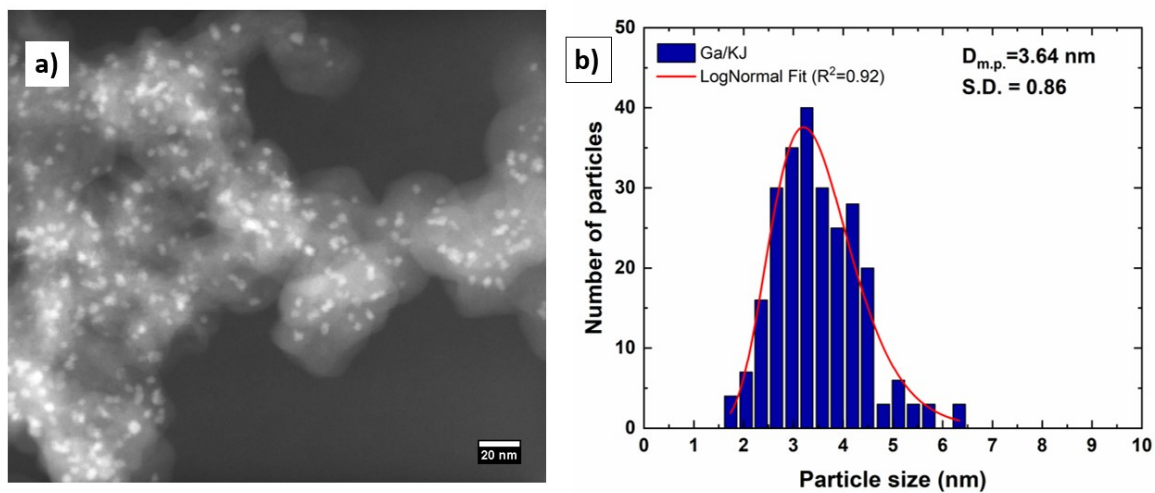


Figure S4. a) STEM micrograph of as-prepared Ga/KJ10 material and b) corresponding mean particle size distribution histogram.

To assess accurate metal loading of as prepared material, thermogravimetric (TG) analysis was employed with the NETZSCH Instrument TG 209F1 Libra<sup>®</sup> equipped with Netzsch-Proteus software. Simply, about 5.0 mg of catalyst powder in an alumina crucible was thermally heated under air flow of 20 mL min<sup>-1</sup> from 30 to 900 °C at a temperature scan rate of 5 °C min<sup>-1</sup>. As shown in Fig. S3a, the samples underwent to a small weight loss (about 1.17 wt.%) in the first interval between 30 and 545 °C. This is due to the elimination of adsorbed and intercalated species resulting from synthesis process. Afterward, the main loss weight about 87.7 wt.% starts at 545 °C accompanied by peak at around 679° on the  $dm/dt$  curve, which we assigned to complete removal of the Ketjenblack carbon substrate.<sup>2</sup> The accurate metal loading is found to be 11.13 wt.% in good agreement with the targeted 10 wt.% metal loading.

To learn about the crystal structure of the Ga/KJ10 material, X-ray diffraction (XRD) analysis was performed on AERIS PANalytical benchtop instrument. Copper tube powered at 45kV and 15mA (Cu-K $\alpha$ 1 =1.5406 Å and Cu-K $\alpha$ 2 =1.5444 Å). The diffraction angle (2 $\theta$ ) from 10 to 70° with steps of 0.05°. Fig. S3b presents XRD pattern of Ga/KJ10. The broad peaks at ca. 23.7° and 43.1° corresponding to (002) and (101) planes of Ketjenblack carbon, respectively. In this study, Ga is deposited onto the carbon substrate through impregnation process under supercritical CO<sub>2</sub> environment in a high-pressure autoclave (at 40 °C and 90 bar) followed two crucial steps (calcination under static air and reduction under pure H<sub>2</sub> flow at 400 °C). Note that phase transition tends to occur whereas no notable change in the morphology during heat treatment in the materials preparation processes. This is therefore, the peaks signed asterisk and centered at 30.5°, 33.2°, 35.3°, 36.9°, 53.5°, 61.9° and 63.9° correspond to the nanostructured Ga planes and its oxide phases in the Ga/KJ10 material.

High resolution scanning transmission electron microscopy (STEM) analysis was employed by using TALOS F200X microscope working at 200 kV. The STEM sample was dispersed in absolute ethanol (99.98%, AnalaR NORMAPUR VWR Chemicals) and then a drop of solution was deposited onto the Cu grid. The size distribution and mean particle size was determined by measuring the diameter of isolated particles using ImageJ<sup>®</sup> free software. Fig. S4a depicts typical STEM image of Ga/KJ10 nanoparticles represented by the white spots. The STEM analyses confirmed that Ga nanoparticles are well-dispersed as well as solely agglomerated particles on the surface of the carbon substrate. Moreover, the STEM studies revealed that the mean particle size ( $D_{m,p}$ ) was evaluated by considering the >250 isolated nanoparticles and fitting the histogram using Log-Normal function. The histogram in Fig. S4b exhibits the mean particle size is found to be 3.6 nm.

### S3.1 Computational modelling and mechanism

The binding energies for elementary steps were computed as follow:

$$A^* + (H^+ + e^-) \rightarrow AH^*, \Delta E_{AH^*} = E(AH^*) - E(A^*) - 0.5E(H_2)$$

The free energies for elementary steps were computed as:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

Here,  $\Delta ZPE$  and  $T\Delta S$  refer to the change in the zero-point energy and entropy upon the elementary reaction. Hessian calculations were performed to compute the vibrational frequencies of the adsorbed species. The vibrations frequencies were used to obtain the ZPE and the vibrational entropy corrections.<sup>2,3</sup>

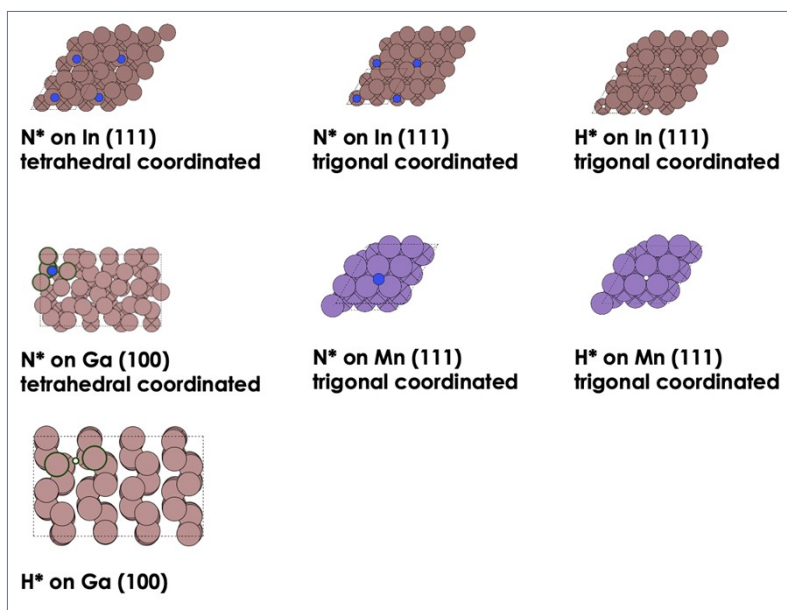


Figure S4. Snapshots of N and H adatom coordinated on In, Mn and Ga surfaces. For Ga the trigonal coordinated N\* is shown in the main text, and therefore only the tetrahedral coordinated geometry is shown here.

Table S2: DFT computed potential energies and ZPE-TΔS corrections in eV for intermediates in the ENRR over the bare Ga slab.

Complex	E	ZPE-TΔS
Ga	-283.959852	
N <sub>2</sub> *	-299.85	0.493
N <sub>2</sub> H*	-301.802	0.8845
NHNH*	-305.5083049	1.354
N-NH <sub>2</sub> *	-305.6813891	1.325
N*	-290.942	0.286
NH*	-295.0995232	0.6095
NH <sub>2</sub> *	-299.6936377	0.973
NH-NH <sub>2</sub> *	-310.0250089	1.7105
NH <sub>2</sub> -NH <sub>2</sub> *	-313.6950461	2.059
H*	-287.145793	0.2165

Table S3: DFT computed potential energies and ZPE-TΔS corrections in eV for intermediates in the ENRR over the Ga slab with L(H<sub>2</sub>O)<sub>4</sub>/Cl.

Complex	E	ZPE-TΔS
Ga-Li(H <sub>2</sub> O) <sub>4</sub> -Cl	-349.058194	
N <sub>2</sub> *	-365.004	-0.07
N <sub>2</sub> H*	-367.287	0.354
N-NH <sub>2</sub> *	-371.068	0.666
N*	-356.352	0.027
NH*	-360.38	0.207
NH <sub>2</sub> *	-364.22	0.503

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