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Supplementary Information

Quadruple metals-based layered structure as the photocatalyst for conversion of carbon dioxide into a value-added carbon monoxide with high selectivity and efficiency

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Table of Contents

Section S1. Experimental Details

Chemicals: All chemicals used in the synthesis of materials were purchased from Sigma Aldrich. Also, ethanol and distilled water were purchased from Duksan. In addition, all chemicals were used as received in air.

Synthesis of photocatalyts: A layered structure was synthesized in two steps using co-precipitation and hydrothermal methods. At first, an aqueous solution of sodium carbonate (1.0 M) and sodium hydroxide (1.0 M) was pre-heated in a one-neck flask at 60℃. The metal precursor aqueous solution (0.64 M) was added to a pre-heated solution in a drop-wise manner. For NMGA, the metal precursor solution was prepared by dissolving 0.24 M nickel nitrate hexahydrate, 0.24 M magnesium nitrate hexahydrate, 0.08 M gallium nitrate hydrate, and 0.08 M aluminum nitrate nonahydrate in DI water. Also, for NMG, the metal precursor solution was obtained by dissolving 0.24 M nickel nitrate hexahydrate, 0.24 M magnesium nitrate hexahydrate, and 0.16 M gallium nitrate hydrate in DI water. For NGA, the metal precursor solution was gained by dissolving 0.48 M nickel nitrate hexahydrate, 0.08 M gallium nitrate hydrate, and 0.08 M aluminum nitrate nonahydrate in DI water. For NG, the metal precursor solution was prepared by dissolving 0.48 M nickel nitrate hexahydrate and 0.16 M gallium nitrate hydrate in DI water.) The reaction was proceeded for 24 h with refluxing. After co-precipitation, the solution was crystalized in the Teflon-made vessel with a stainless steel autoclave for 24 h at 110 °C. The produced solution was centrifuged several times at 6000 rpm for 10 min with water and ethanol. Finally, the centrifuged powder was dried at 50℃ in a vacuum oven overnight. For Bulk-NMGA, we synthesized this material using traditional urea co-precipitation method. At first, the precursor solution was prepared by dissolving 14.06 mM nickel nitrate hexahydrate, 14.06 mM magnesium nitrate hexahydrate, 4.69 mM gallium nitrate hydrate, 4.69 mM aluminum nitrate nonahydrate and 87.5 mM urea in DI water. And then precursor solution was put in the Teflon-made vessel with a stainless steel autoclave for 24h at 180℃. The produced solution was centrifuged several times at 6000 rpm for 10 min with water and ethanol. Finally, the centrifuged powder was dried at 50℃ in a vacuum oven overnight.

Characterizations: The powder X-ray diffraction (PXRD) patterns were measured with a Smartlab diffractometer (Rigaku, Japan) using a Cu kα operating condition of 40 kV and 30 mA, where the diffraction patterns were scanned from 3° to 70° with a 0.02 step size. The *in-situ* Fourier transform-infrared (FT-IR) spectra were collected with the ATR using FT-TR-6100 from JASCO with a range of 600 cm^{-1} ~ 4000 cm^{-1}, which is also equipped with Praying Mantis accessory (HARRICK). It is notable that the Praying Mantis high temperature reaction chamber has been connected with the vacuum pump and the CO_2 gas barrel. Then, 100 mg KBr and 5 mg LDH were mixed and introduced in the chamber for analysis. Also, the IR beam is directed into the sample inside the chamber through KBr window and the spectrum is acquired with the TGS (Triglycine Sulfate) IR detector. In addition, we have used the multiple mirrors to eliminate the specular reflection effectively. The UV and visible lights using a 300 W xenon lamp has been also shined into the chamber through the optical fiber. The UV-Vis spectrum was gained using a V-570 UV-vis spectrometer (Jasco, Japan) and a Sigma Probe (Thermo VG Scientific, England) with a He-I light source. REELS spectra were measured using Auger electron spectroscopy (AES; VG microlab 350 system). And the TGA (Thermogravimetry analysis) was carried out by using TG209F3 of NETZSCH. Moreover, transmission electron microscopy (TEM) and high resolution-transmission electron microscopy (HR-TEM) images were obtained with a JEM-ARM200F model (JEOL Ldt., Japan) and the Cs-corrected scanning transmission electron microscopy (STEM) measurements have been performed on JEM-ARM200F for the energy dispersive X-ray spectrometer (EDS) mapping images using a BRUKER QUANTAX EDS. Furthermore, CO_2 and N_2 adsorption-desorption isotherm analyses were carried out using a Quadrasorp model from Quantachrome instruments. Additionally, the x-ray absorption near edge structure (XANES) measurements were conducted in a 7D beam line at the Pohang Accelerating Laboratory (PAL, Republic of Korea), where a calibration of each K-edge spectrum was accomplished by employing the reference spectrum from the corresponding metal foil while the calibration was performed using the reference spectrum of W foil in the case of Ga. The XPS spectra were gained by using the K-alpha instrument (Thermo Scientific) equipped with the Al Ka micro-focused X-ray monochromator (1487 eV). ^{13}C solid-state NMR was carried out by Varian 600 MHz with CP/MAS technique. Also, the inductively coupled plasma mass spectroscopy (ICP-MS) analysis was carried out using an Agilent ICP-MS 7700S (Agilent Technologies, United States) pre-treated by nitric acid and hydrochloric acid.

TPD experiments: All the samples were mounted in the measurement cell and purged with 20 cc/min flow of Ar gas for 30 min to remove a trace amount of other gases. The measurement cell was heated up to 130 ºC with a ramp rate of 10 ºC/min under a flow of Ar at 20 cc/min for 1 h for pre-treatment. For the TPD measurements using Micromeritics' AutoChem 2950 HP, the samples were cooled down via contact with a liquid nitrogen, and CO_2 (10% CO_2/He, 20cc/min) and CO (10% CO/He, 20 cc/min) gases were dosed into the measurement cell for 30min. To pump out residual CO or CO_2 gases from measurement cells, the carrier gas was changed to He at a flow rate of 20 cc/min. After stabilizing the baseline of the outgoing gas, the TPD measurement started from -120 to 120 ºC with a ramp rate of 1.5 ºC/s, and the amounts of outgoing gases were recorded by the attached gas chromatography. Throughout the entire TPD process, the amounts of released gases from the samples were calibrated by the real amounts of CO_2 and CO gases.

Photocatalytic activity test: A closed system for photocatalytic CO_2 conversion was achieved using a stainless steel (SS) gas phase reactor. 25 mg/ml concentration of aqueous solution photocatalysts were dropped onto 1 cm by 1 cm slide glass being finished UV-ozone treatment. Drop casted (15 µL of 25 mg/ml aqueous solution) thin film on 1 cm by 1 cm glass of the LDH photocatalysts was put in the SS reactor. The reactor was purged using the CO_2 gas for 30 min at 60 °C to remove all remaining gases and to fill the reactor with only CO_2. And then 54 µl of the deionized water was then injected into the reactor and fully vaporized for 30 minutes. After these process, the reactor was illuminated with a 300 W xenon lamp having the fitted IR blocking filter. The products formed in the dead volume of a reactor were extracted at regular intervals to analyze the chromatogram. The products were injected to a GC (Shimadzu, GC-2014A, carrier gas: He) equipped with the Hayesep Q column using an FID (Flame Ionized Detector) for measurements of evolved CO gas.

Isotope-labelling experiment: In addition, isotopically-labelled $^{13}CO_2$ and $H_2{}^{18}O$ experiments were performed to trace the source of CO on the half-oxidation reaction. Also, the similar conditions in the above have been used for the photocatalytic activity test. However, it is notable that $^{13}CO_2$ instead of $^{12}CO_2$ was purged in the $^{13}CO_2$ isotope experiment. The products formed in the dead volume of a reactor were extracted to inject in GC-MS (Agilent, GC-7890A and MS-5975C) equipped with a capillary column (Supleco, 30 m × 0.32 mm) and MSD (Mass selective detector, inert triple-axis detector) for identifying m/z 29. In the $H_2{}^{18}O$ isotope experiment, Drop casted thin film of the LDH photocatalysts was put in reactor with the $^{12}CO_2$ purging. And then with 54 µl $H_2{}^{18}O$ was introduced on the reactor. The products formed in the dead volume of a reactor were also extracted to inject in the GC-MS (Agilent, GC-7890A and MS-5975C) equipped with a capillary column (Supleco, 30 m × 0.32 mm) and the MSD (Mass selective detector, inert triple-axis detector) for identification of m/z 36.

Section S2. Supporting Figures

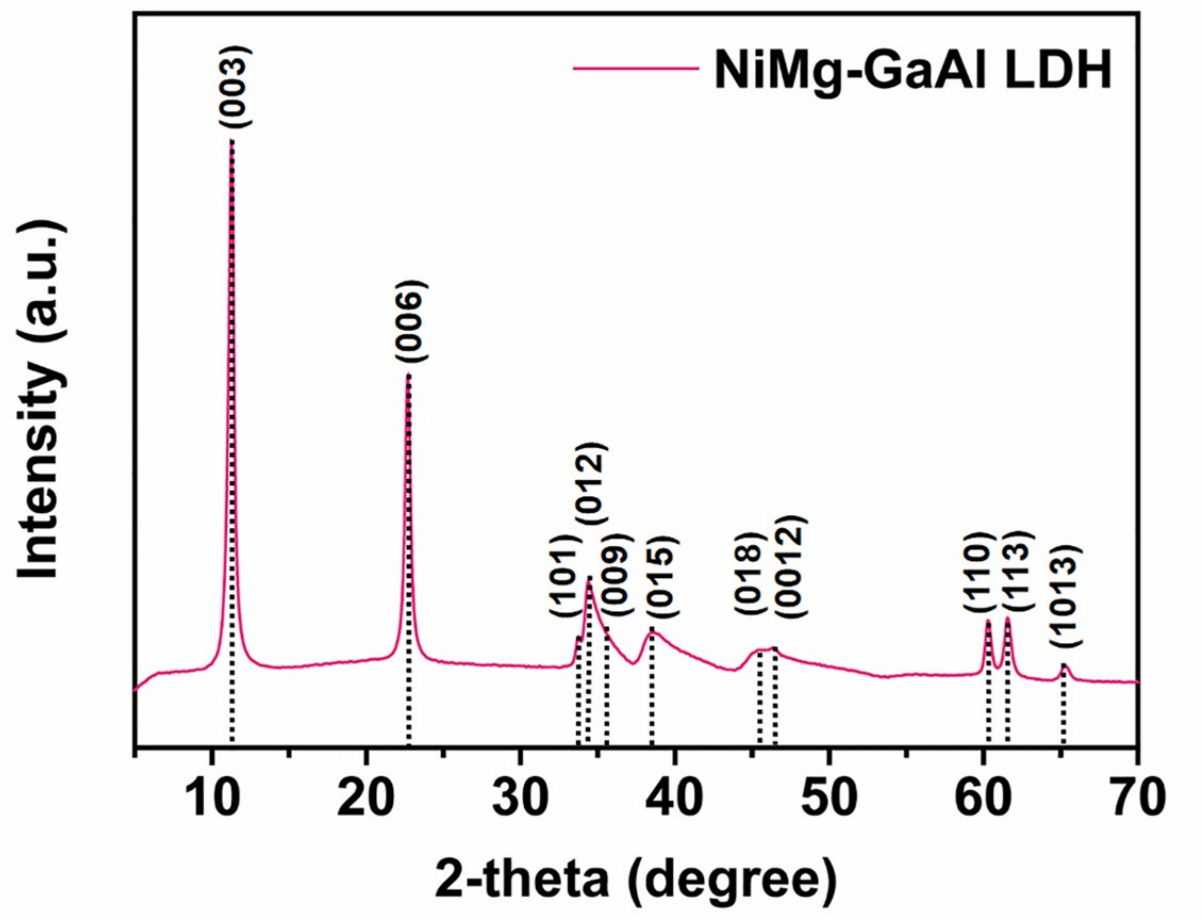

Figure S1. PXRD patterns of NMGA with indexed phase reflections.

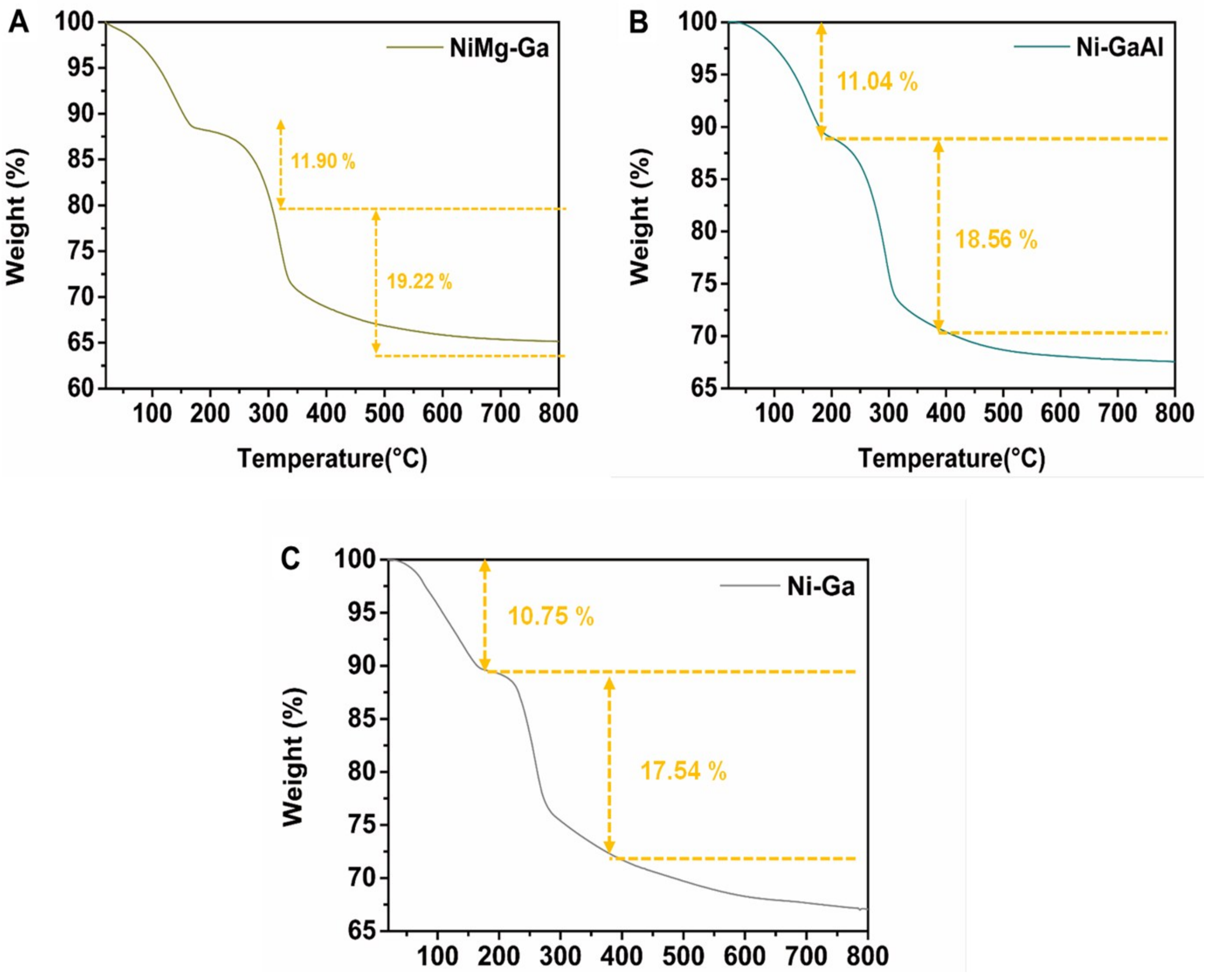

Figure S2. TGA curves of (A) NMG, (B) NGA and (C) NG, where all the curves are found to be on very similar shapes.

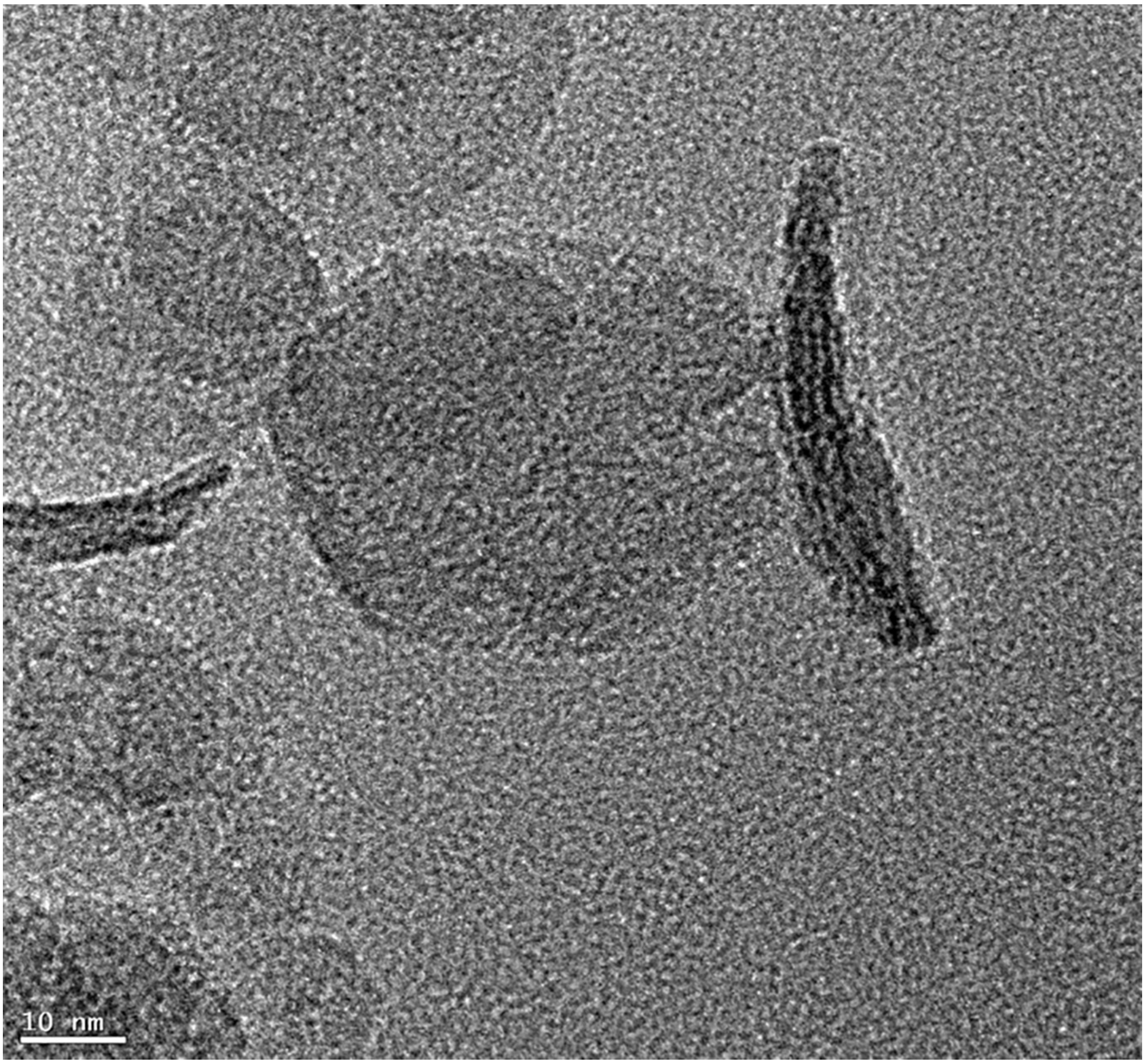

Figure S3. TEM images of NMGA nanoplates which were shown as front and lying shape.

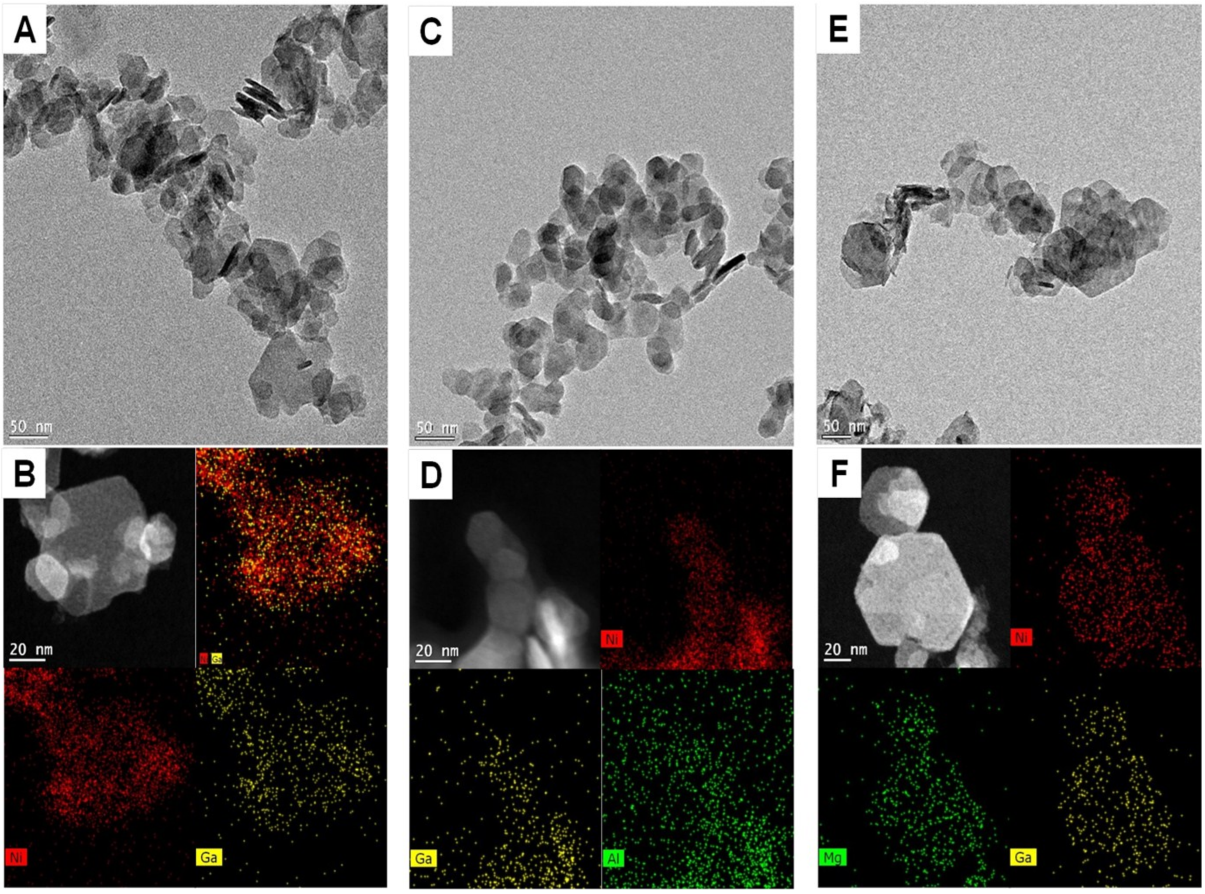

Figure S4. TEM images for (A) NG, (C) NGA, and (E) NMG along with the STEM-EDS mapping images of nickel, gallium for (B) NG, of nickel, gallium, aluminum for (D) NGA, and of nickel, magnesium, gallium for (F) NMG.

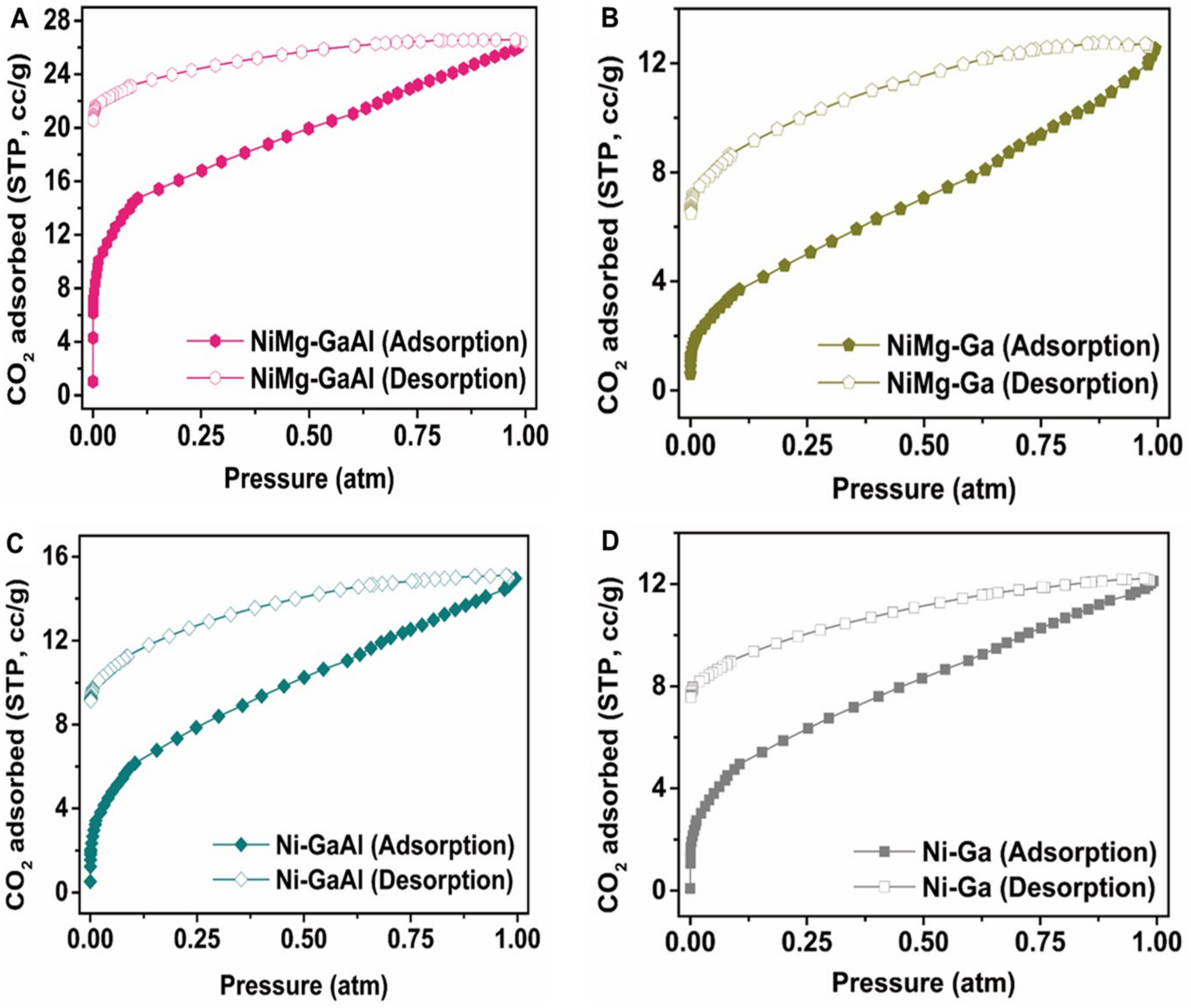

Figure S5. CO$_2$ adsorbed-desorbed isotherms of (A) NMGA, (B) NMG, (C) NGA and (D) NG.

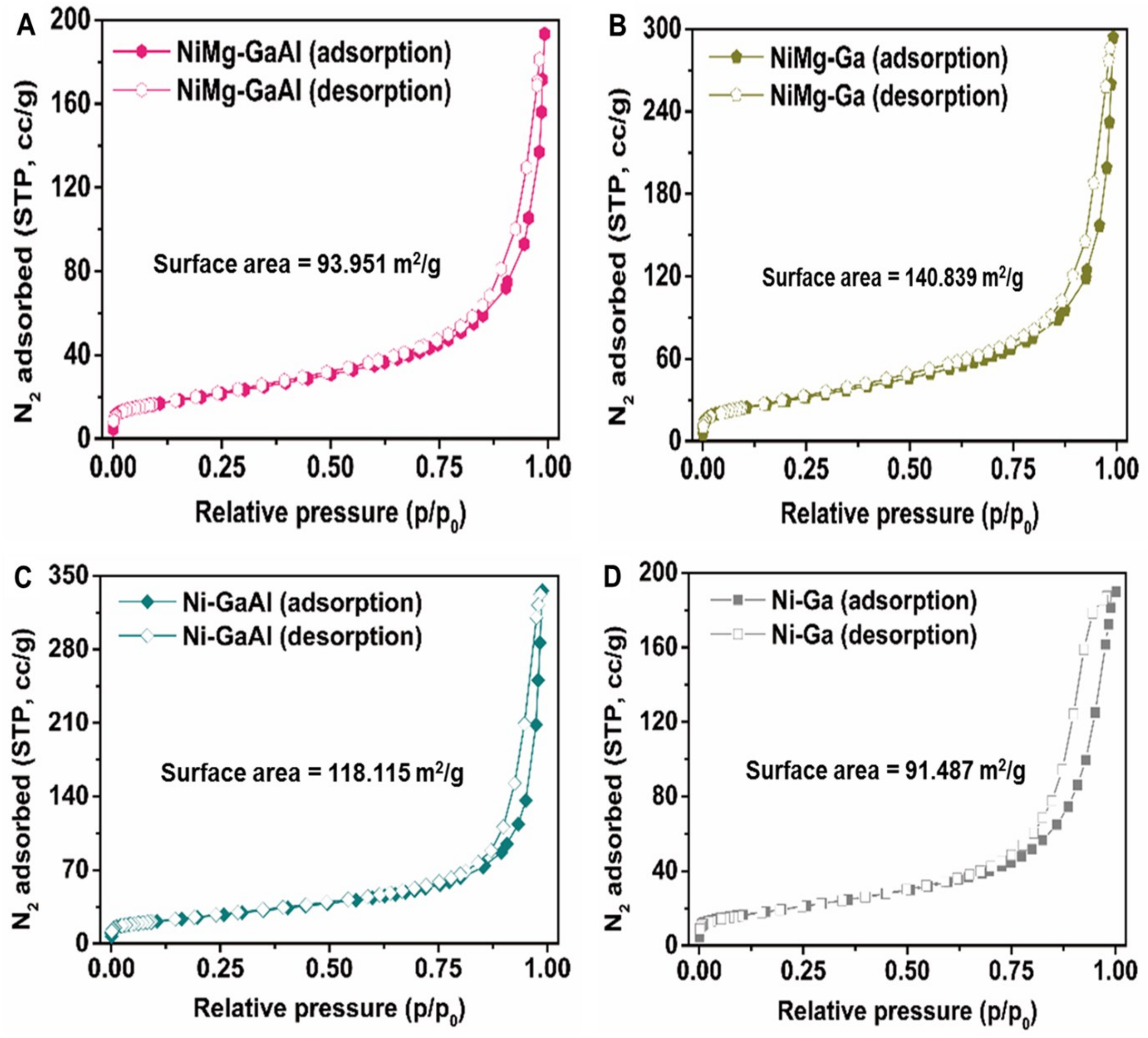

Figure S6. N_2 adsorbed-desorbed isotherms of (A) NMGA, (B) NMG, (C) NGA and (D) NG.

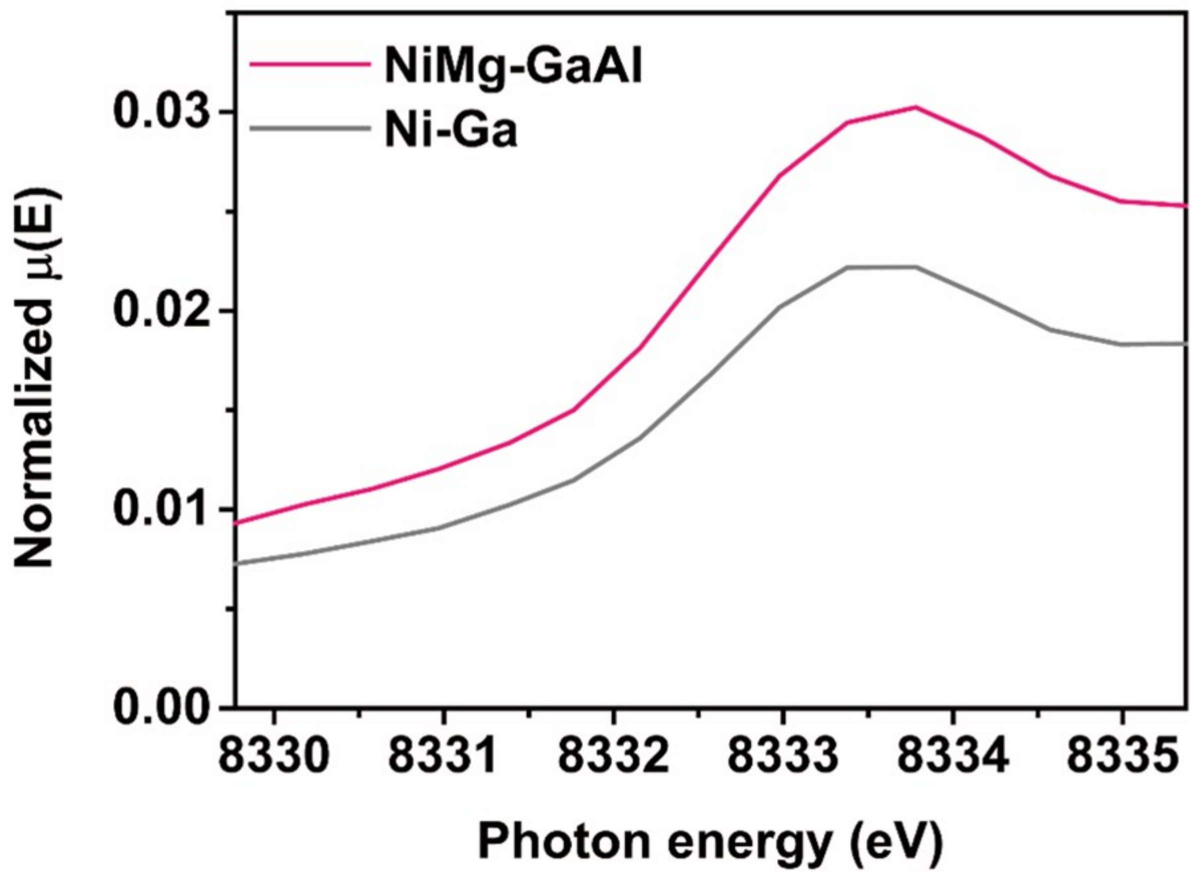

Figure S7. Ni K-edge XANES spectra magnified around 8333 eV of NMGA and NG.

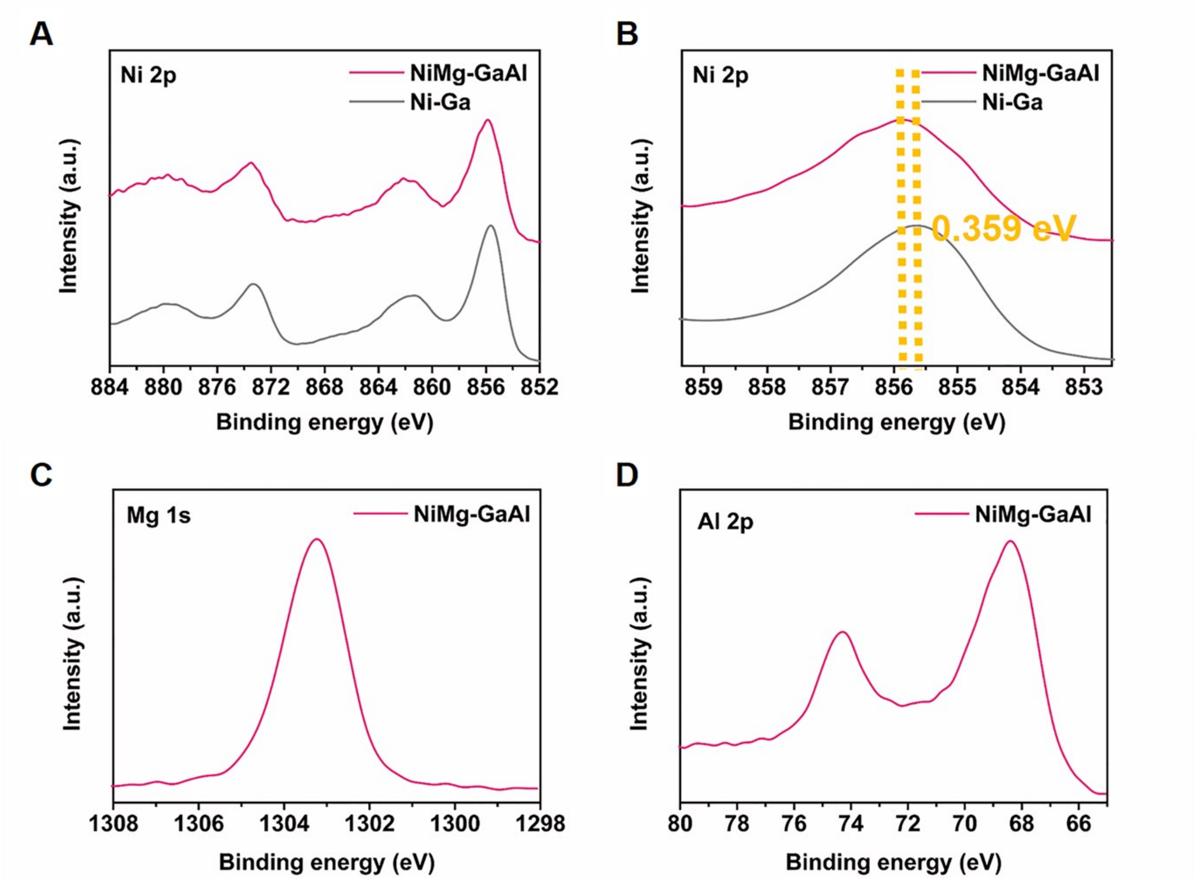

Figure S8. XPS spectra for (A) Ni 2p orbitals of NMGA and NG, (B) magnified region of Ni $2p_{3/2}$ orbitals of NMGA and NG (C) Mg 1s and (D) Al 2p orbitals of NMGA.

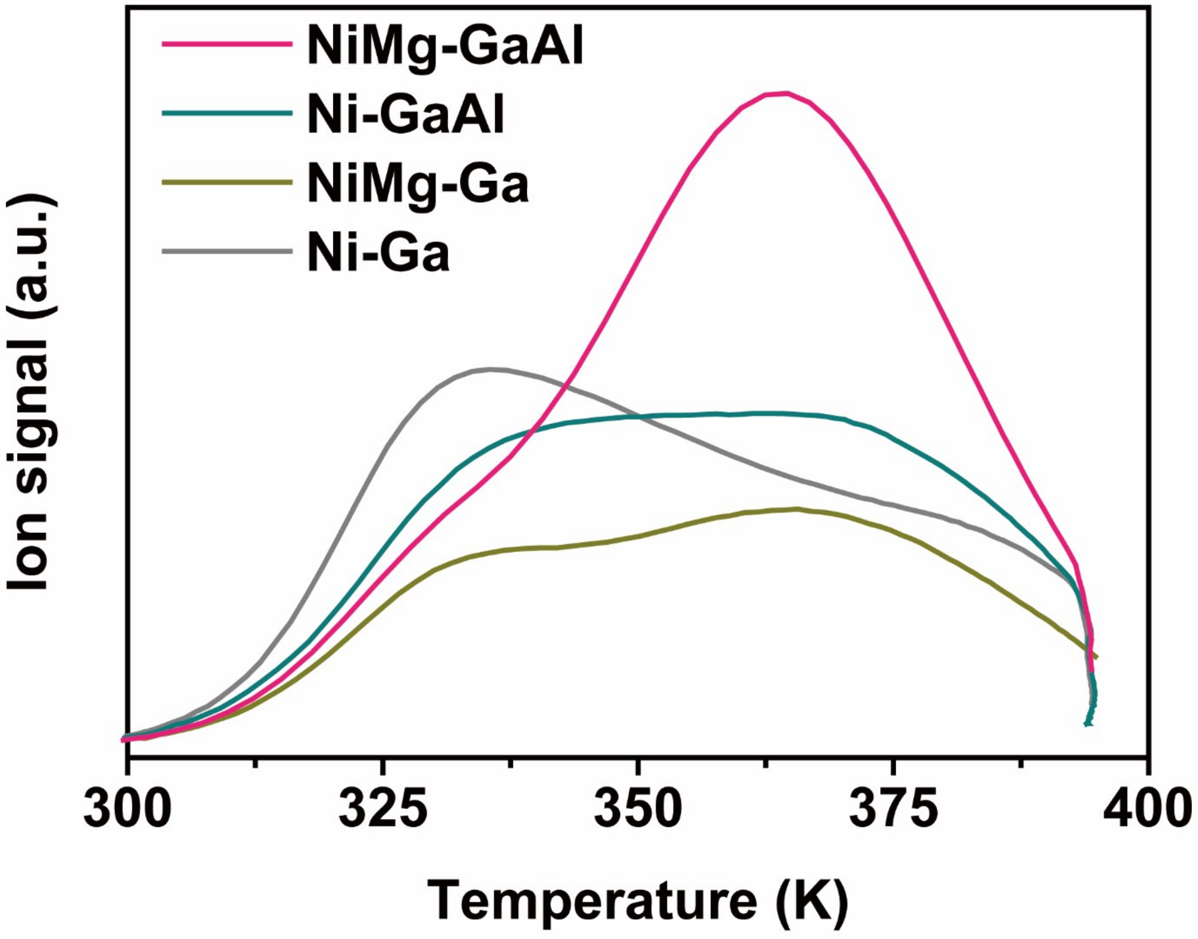

Figure S9. CO_2-TPD profiles of NMGA, NGA, NMG and NG.

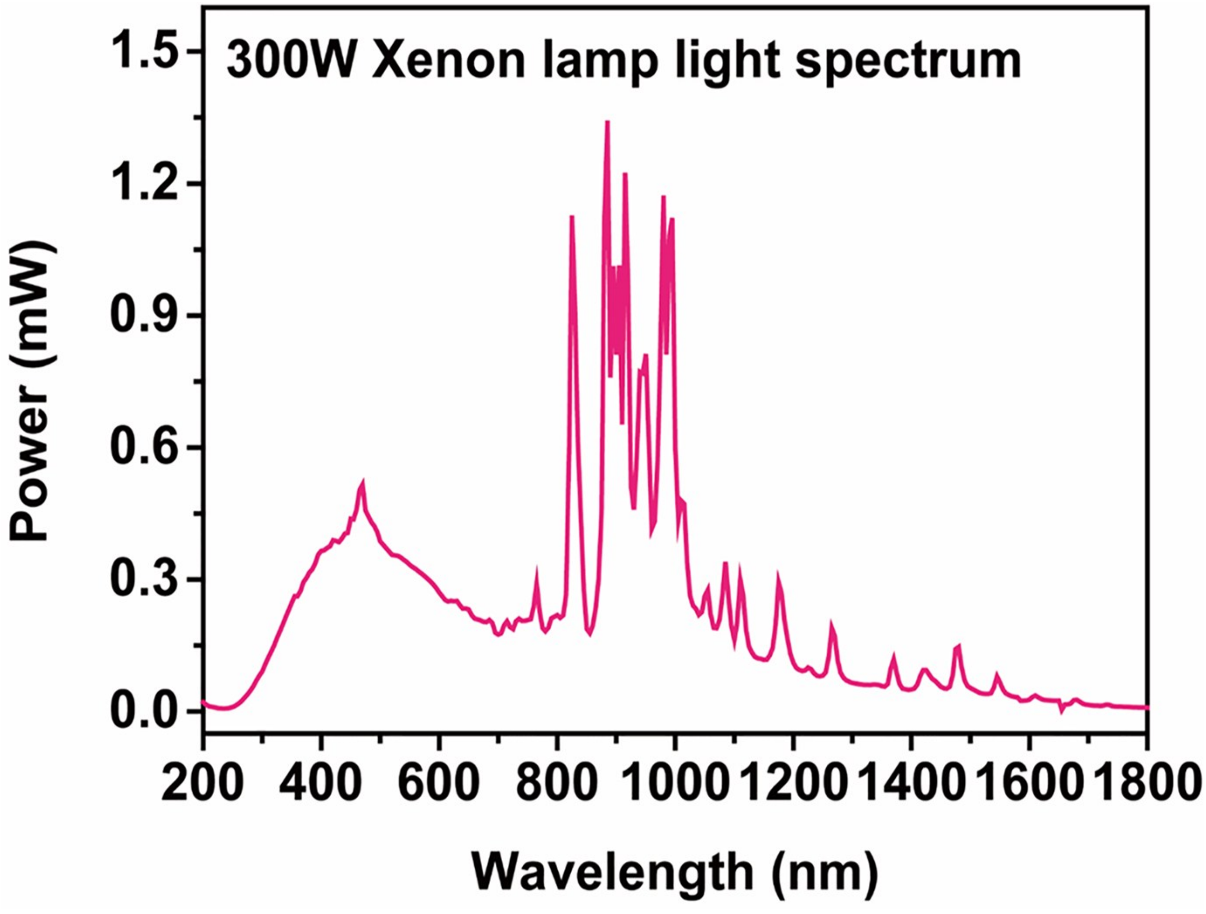

Figure S10. 300 W Xenon lamp spectrum.

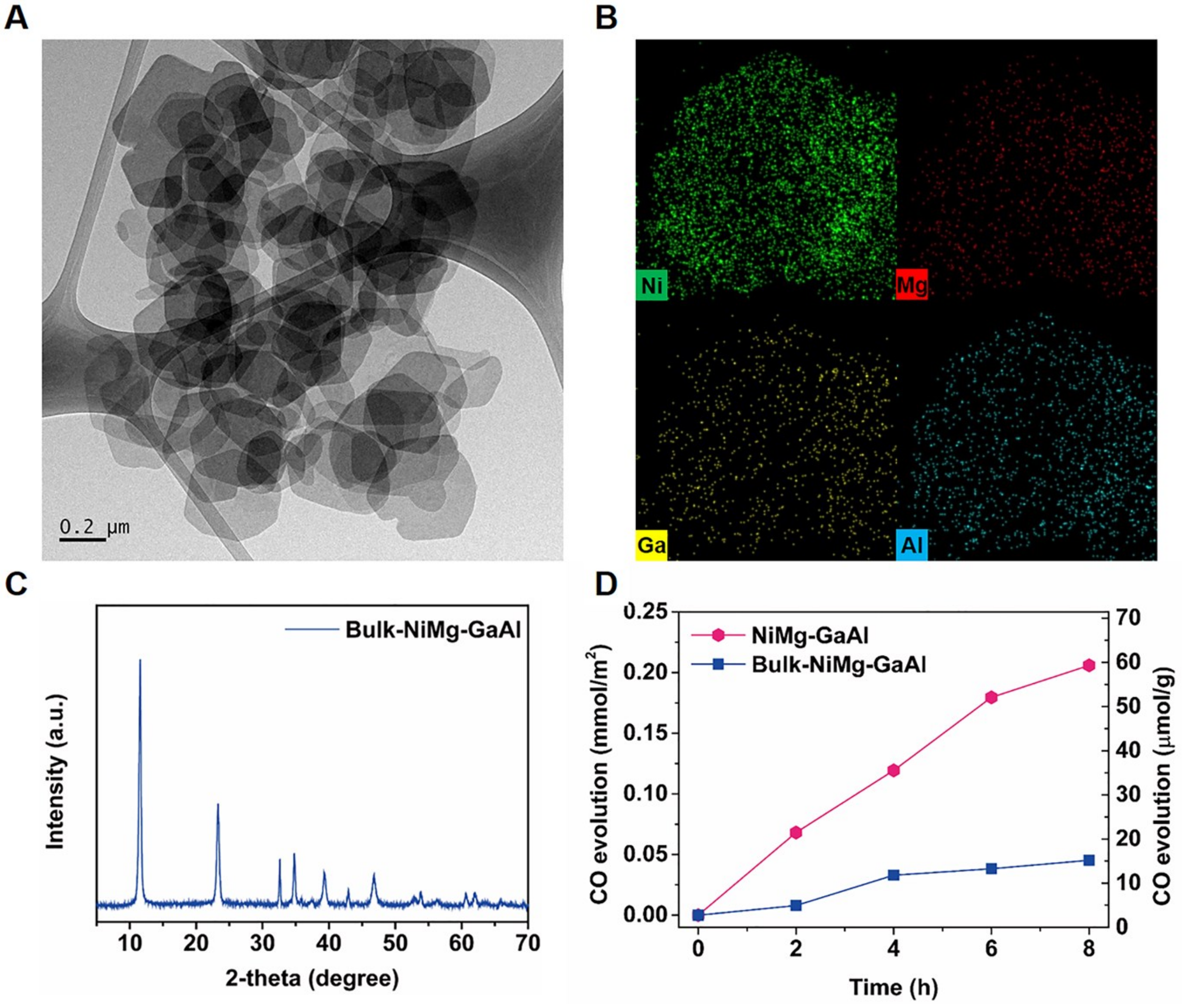

Figure S11. TEM images of (A) Bulk-NMGA, (B) STEM-EDS mapping images for nickel, magnesium, gallium, aluminum of Bulk-NMGA, (C) PXRD patterns of Bulk-NMGA, and (D) Time-dependent evolved CO per the unit surface as well as the unit gram for NMGA and Bulk-NMGA.

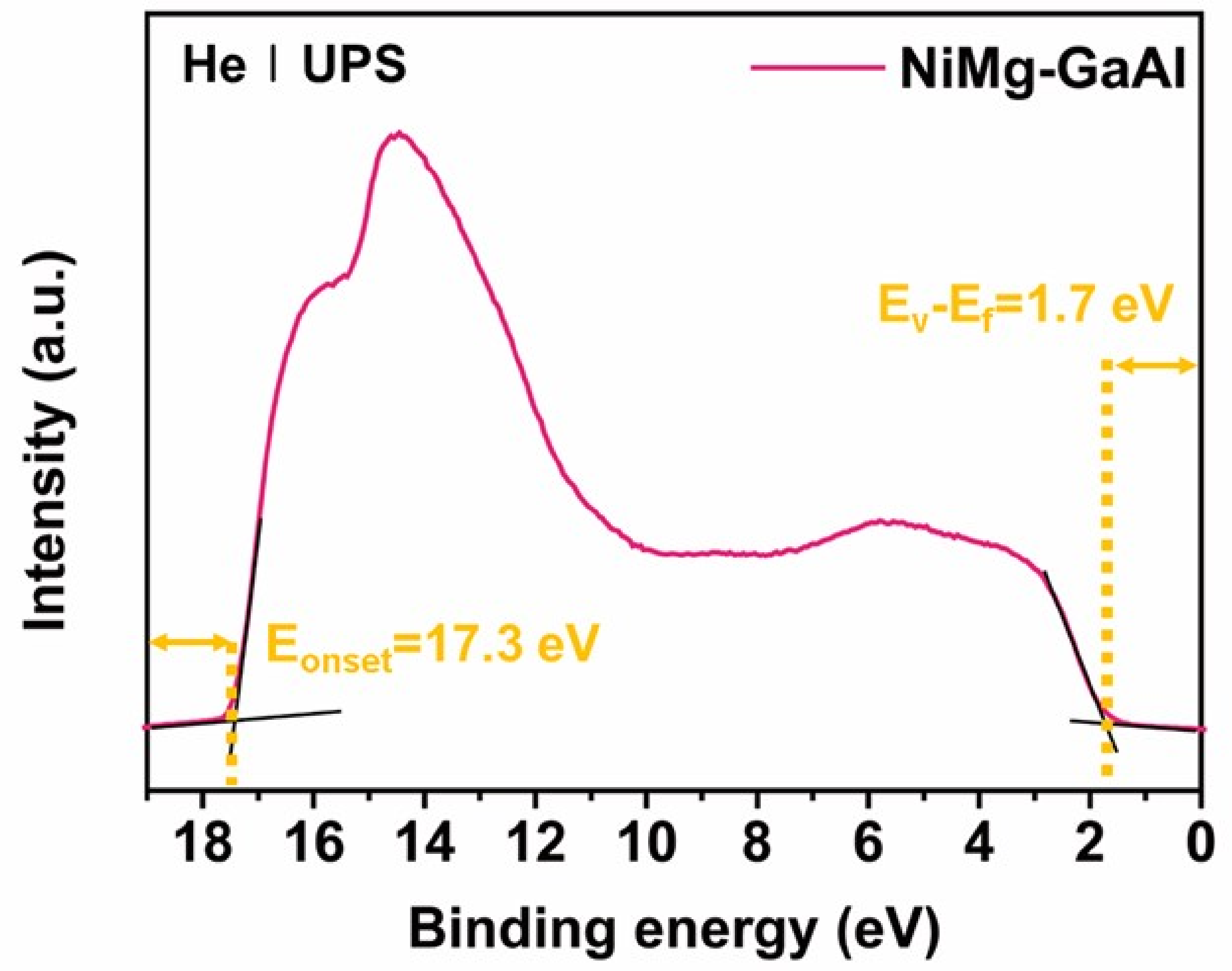

Figure S12. Ultraviolet photoelectron spectroscopy (UPS) data for NMGA.

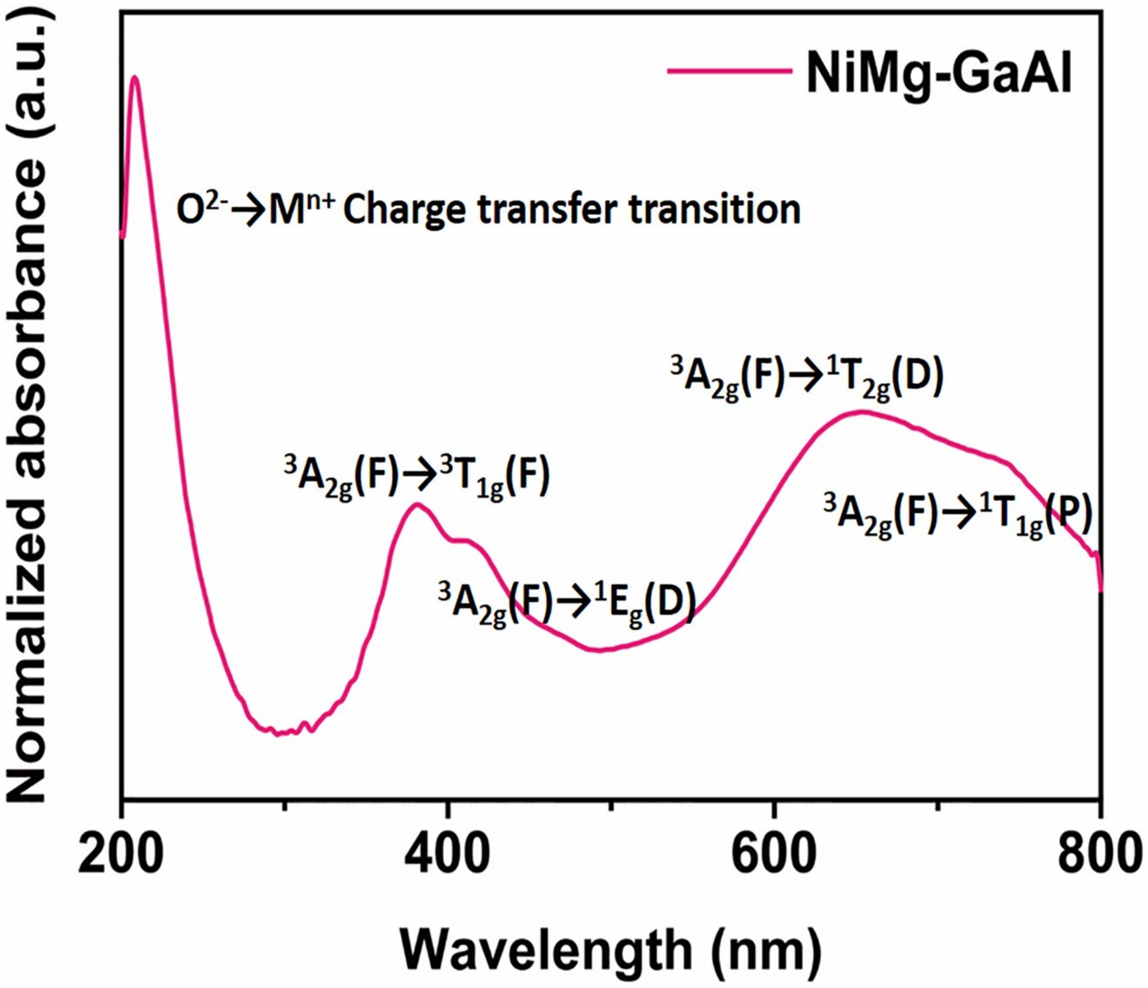

Figure S13. Ultra violet-Visible (UV-Vis) absorption spectra of NMGA.

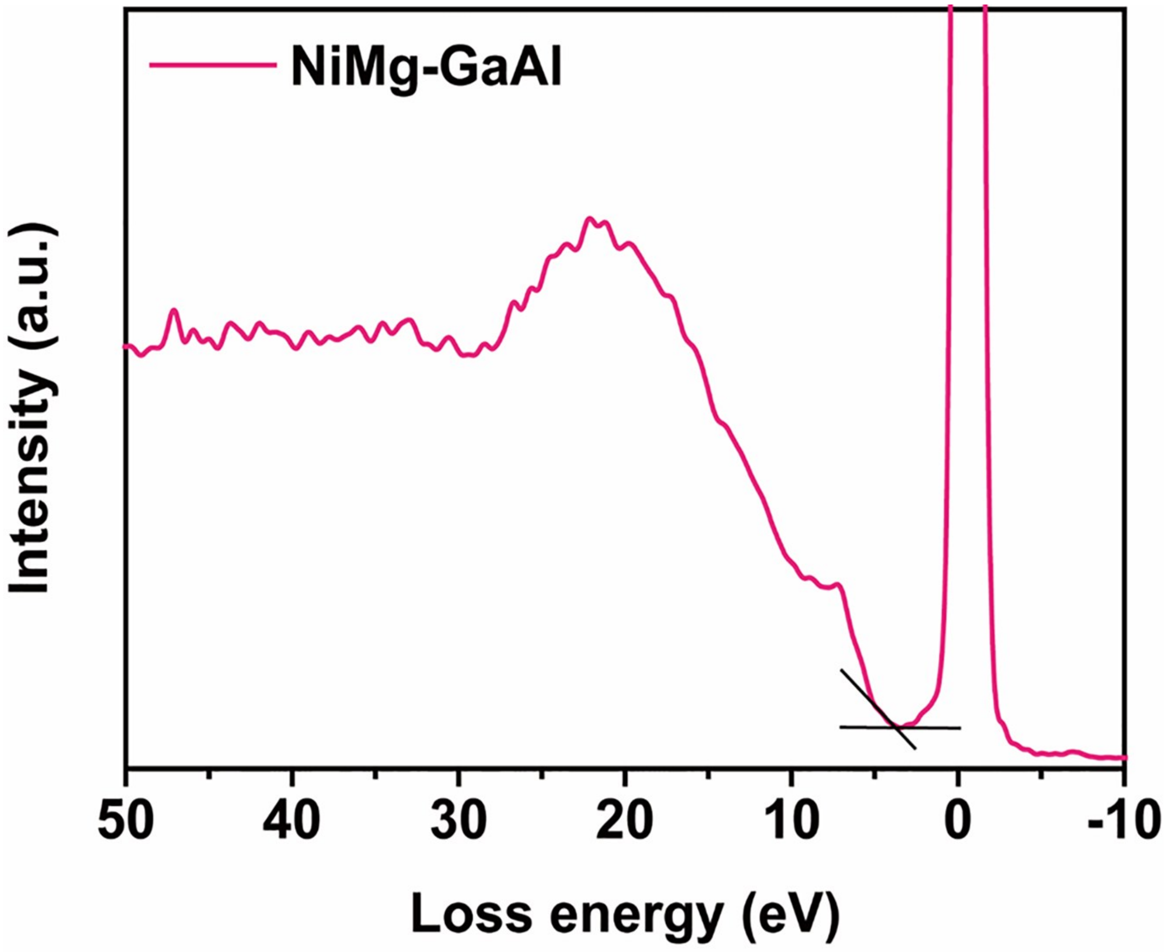

Figure S14. REELS spectra for NMGA obtained using the primary electron energy of 1 keV.

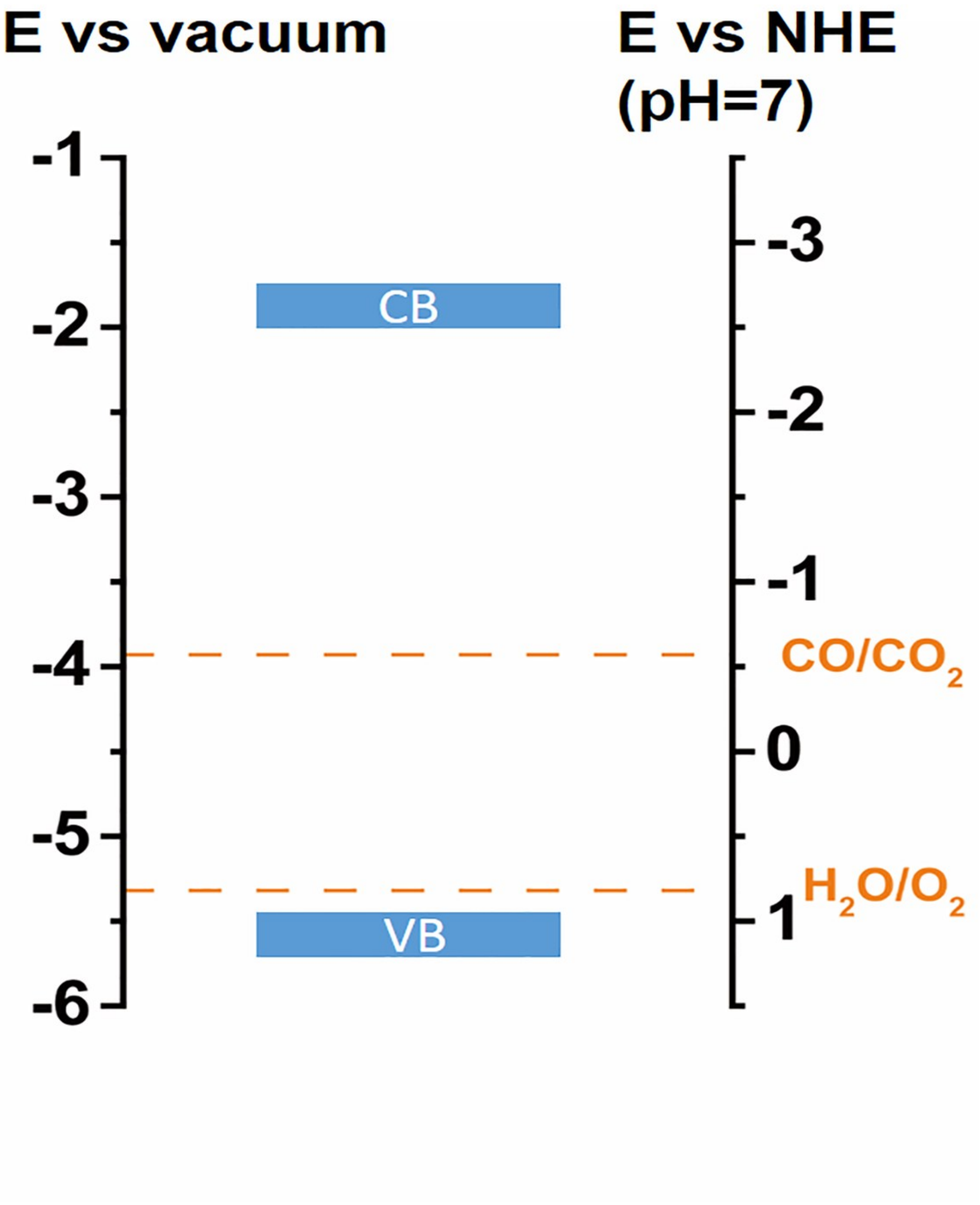

Figure S15. The band structure for NMGA.

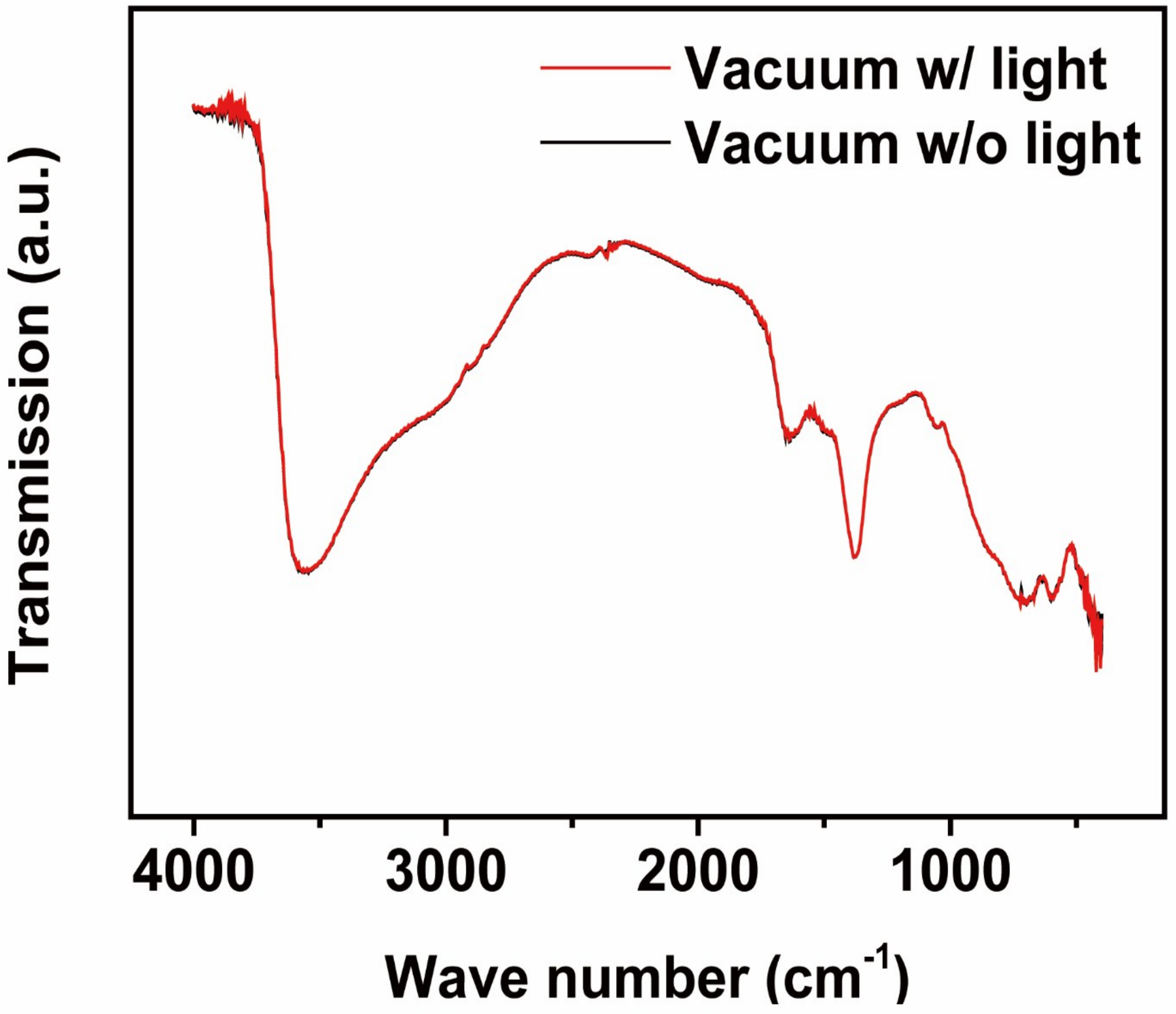

Figure S16. *In-situ* FT-IR spectra of NMGA between 4000 cm^{-1} and 400 cm^{-1} under vacuum with and without UV and visible irradiations.

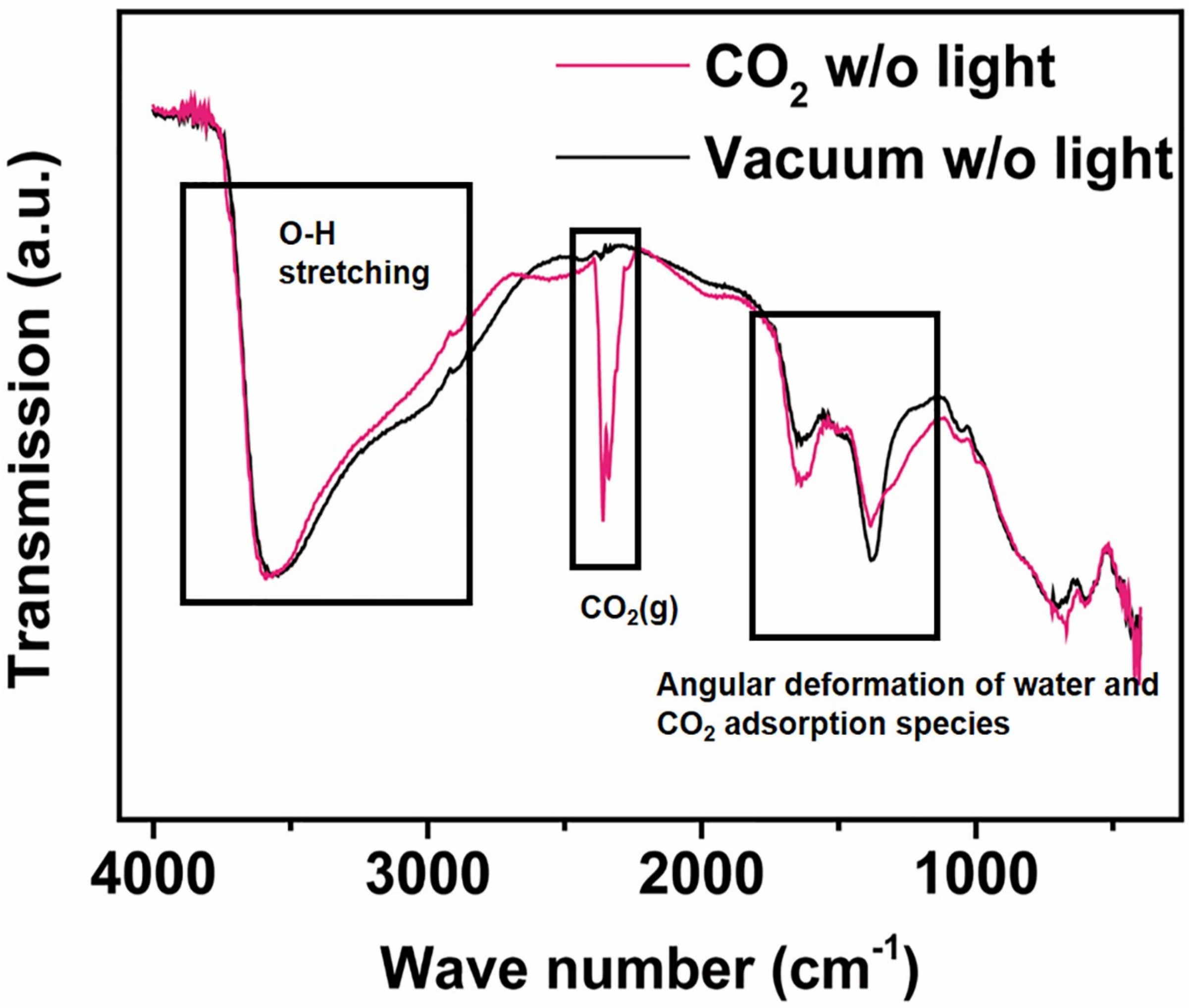

Figure S17. *In-situ* FT-IR spectra of NMGA between 4000 cm^{-1} and 400 cm^{-1} under vacuum and CO$_2$ purged state without UV and visible irradiations.

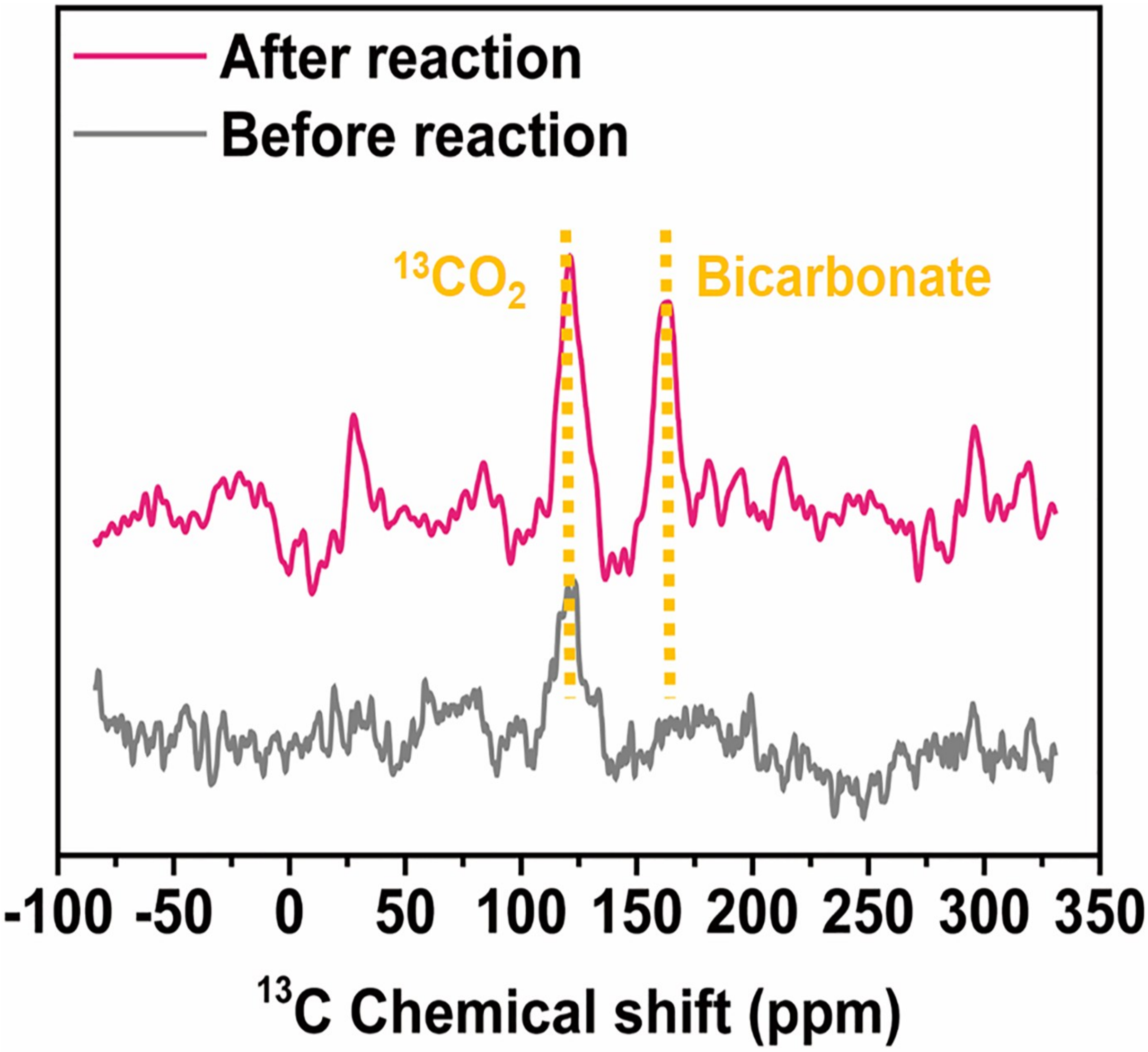

Figure S18. ^{13}C solid state NMR spectra obtained from NMGA.

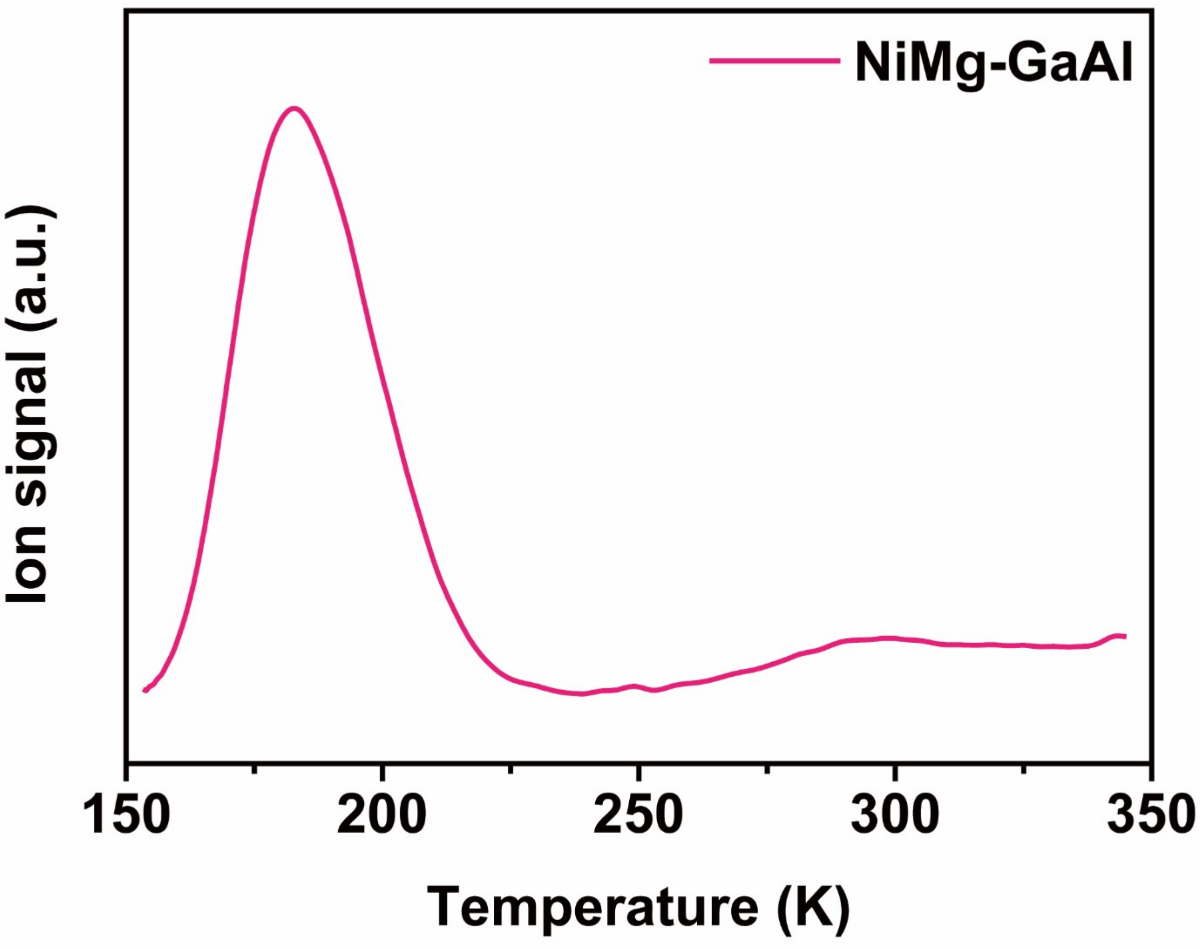

Figure S19. CO-TPD profiles obtained from NMGA.

Section S3. Supporting Tables

Sample	**Molar ratio**			
	Ni	Mg	Ga	Al
NG	4.504	-	1	-
NMG	2.351	2.387	1	-
NGA	8.884	-	1	1.531
NMGA	4.776	3.865	1	1.366

Table S1. Molar ratios for the metal elements being contained in the LDH, which were obtained through the inductively coupled plasma mass spectroscopy (ICP-mass) analysis. It is notable that all the LDHs were treated by mixtures of the nitric acid (70%) and hydrochloric acid (30%) and that the Ga element is fixed with 1 as the standard.