Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.


## Electronic Supplementary Information (ESI)

# Drastic Improvement in the Photocatalytic Activity of $Ga_2O_3$ Modified with Mg−Al Layered Double Hydroxide for the Conversion of $CO_2$ in Water

**Corresponding authors**

Prof. Kentaro Teramura and Prof. Tsunehiro Tanaka

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615−8510, Japan

Tel: +81−75−383−2559 Fax: +81−75−383−2561

E–mail address: teramura@moleng.kyoto-u.ac.jp

**List of the authors**

Shoji Iguchi,[a] Yudai Hasegawa,[a] Kentaro Teramura,[a,b] Shotaro Kidera,[a] Soichi Kikkawa,[a] Saburo Hosokawa,[a,b] Hiroyuki Asakura[a,b] and Tsunehiro Tanaka[a,b]

**Affiliation and full postal address**

a. Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615−8510, Japan.

b. Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615−8245, Japan.

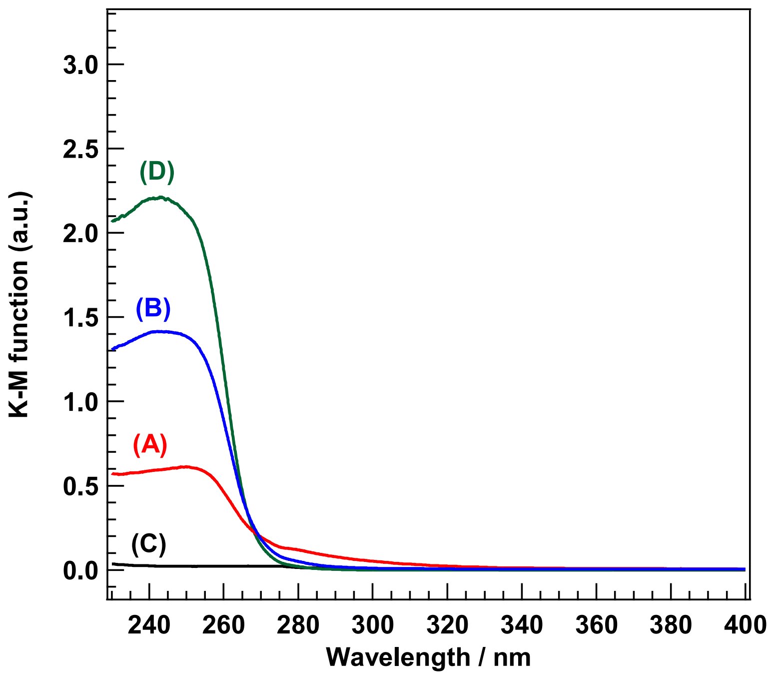


Figure S1 UV/Vis spectra of (A) *0.25*Ag/*95*-MgAl/$Ga_2O_3$, (B) *95*-MgAl/$Ga_2O_3$, (C) Mg−Al LDH, and (D) $Ga_2O_3$. UV/Vis diffuse reflectance spectra of the photocatalysts were measured using a UV-VIS Spectrophotometer (V-650, JASCO) equipped with an integrated sphere. $BaSO_4$ plate was used as a standard baseline for these spectra.

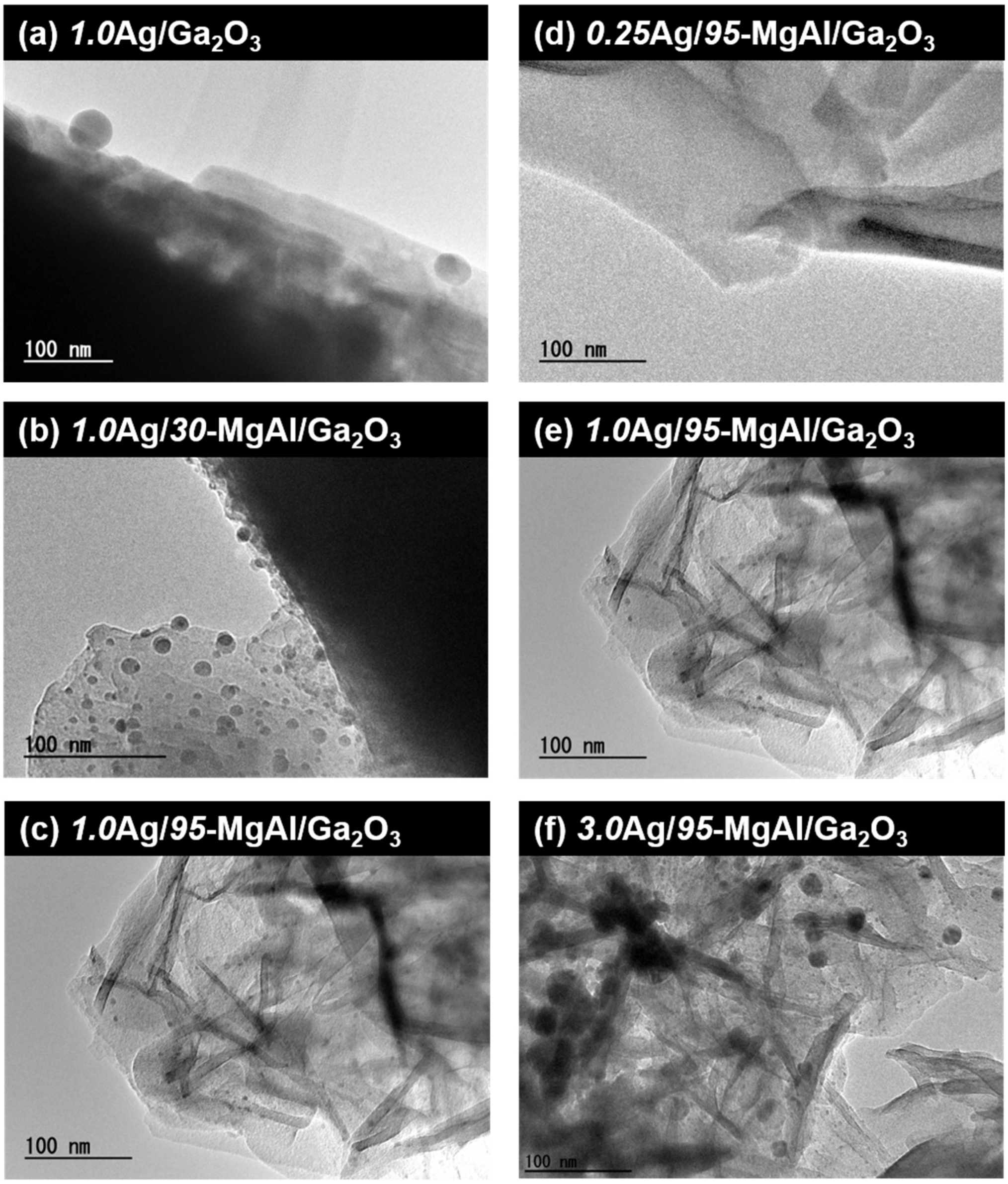


Figure S2 TEM images of (a) *1.0*Ag/$Ga_2O_3$, (b) *1.0*Ag/*30*-MgAl/$Ga_2O_3$, (c) *1.0*Ag/*95*-MgAl/$Ga_2O_3$, (d) *0.25*Ag/*95*-MgAl/$Ga_2O_3$, (e) *1.0*Ag/*95*-MgAl/$Ga_2O_3$, and (f) *3.0*Ag/*95*-MgAl/$Ga_2O_3$, captured on JEM-2100F TEM system (Japan Electron Optics Laboratory).

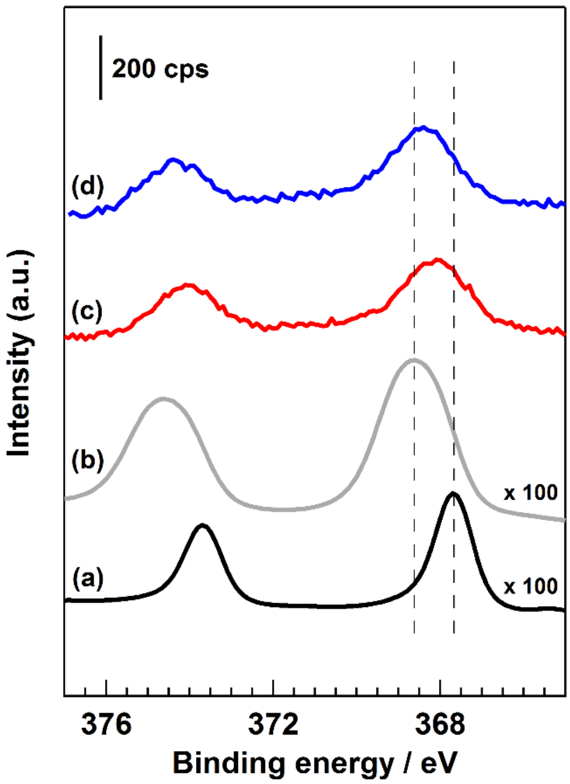


Figure S3 Ag 3d X-ray photoelectron spectra of (a) Ag powder, (b) $Ag_2O$, (c) *0.25*Ag/*95*-MgAl/$Ga_2O_3$, and (d) *0.25*Ag/*95*-MgAl/$Ga_2O_3$ after photoirradiation for 5 h. X-ray photoelectron spectra of composite photocatalysts were measured by ESCA-3400 (Shimadzu) using Mg $K_\alpha$ characteristic X-ray radiation. Peak positions were corrected by using C 1s peaks.

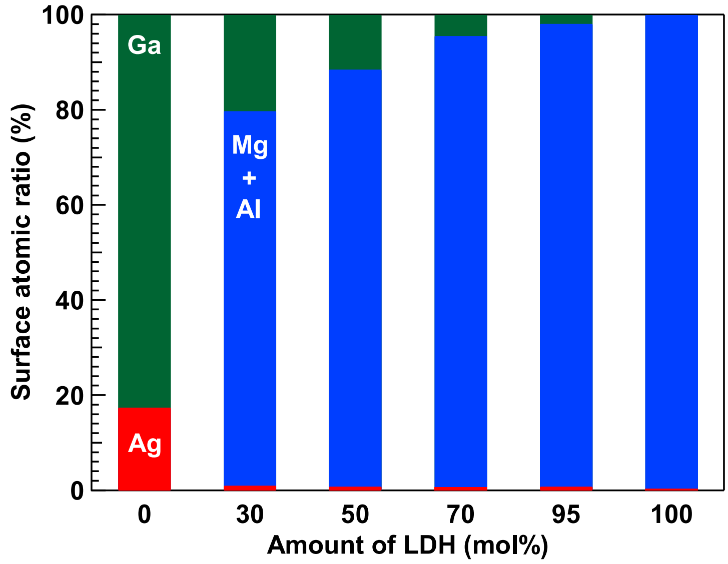


Figure S4 Surface atomic ratio of Ag cocatalyst loaded $x$-MgAl/$Ga_2O_3$ composite photocatalysts ($x$ = 0, 30, 50, 70, 95) and bare Mg−Al LDH. X-ray photoelectron spectra of composite photocatalysts were measured by ESCA-3400 (Shimadzu) using Mg $K_\alpha$ characteristic X-ray radiation. Surface atomic ratios of elements were calculated using the following equations.

$\boldsymbol{A}_{\mathbf{total}} = \boldsymbol{A}_{\mathbf{Ag}} + \boldsymbol{A}_{\mathbf{Ga}} + \boldsymbol{A}_{\mathbf{Mg}} + \boldsymbol{A}_{\mathbf{Al}}$

Ag (%) = $100 \times \boldsymbol{A}_{\mathbf{Ag}} / \boldsymbol{A}_{\mathbf{total}}$

Ga (%) = $100 \times \boldsymbol{A}_{\mathbf{Ga}} / \boldsymbol{A}_{\mathbf{total}}$

Mg + Al (%) = $100 \times (\boldsymbol{A}_{\mathbf{Mg}} + \boldsymbol{A}_{\mathbf{Al}}) / \boldsymbol{A}_{\mathbf{total}}$

, where $\boldsymbol{A}_{\mathbf{Ag}}$, $\boldsymbol{A}_{\mathbf{Ga}}$, $\boldsymbol{A}_{\mathbf{Mg}}$, and $\boldsymbol{A}_{\mathbf{Al}}$ are peak areas in the spectra attributed to Ag 3d, Ga 2p, Mg 2p, and Al 2p, respectively.

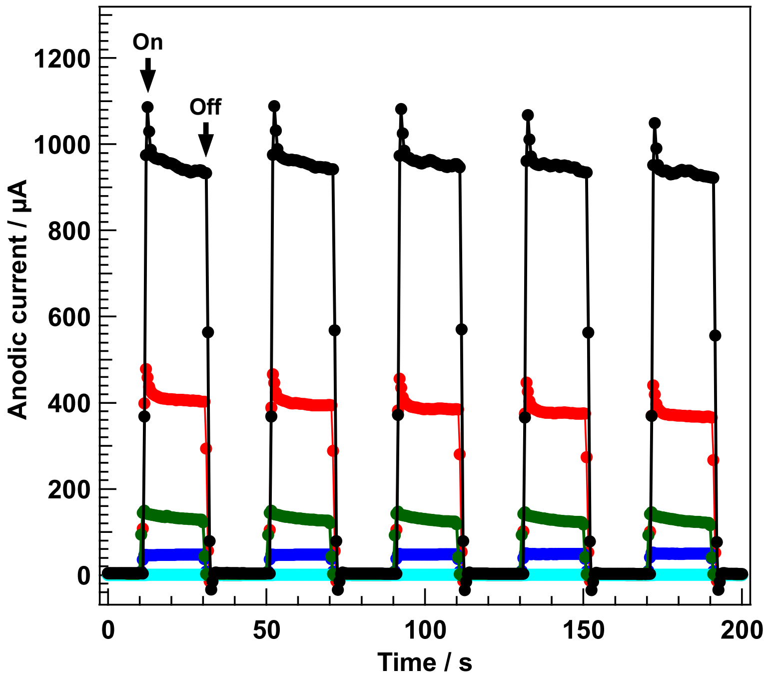


Figure S5 Anodic photocurrent value of Ag cocatalyst loaded *x*-MgAl/$Ga_2O_3$ composite photocatalysts (*x* = —: 0, —: 30, —: 50, —: 70, —: 95) with on/off UV light irradiation in the presence of methanol in the electrolyte solution. The composite photocatalysts were coated on a fluorine doped tin oxide (FTO) conductive glass by the electrophoresis deposition. The powder sample of the composite photocatalyst was dispersed thoroughly in an acetone solution containing iodine ($I_2$), and then direct current (DC) was applied to the FTO glasses, which comprised two-electrode electrochemical cell, at 10.0 V stable bias. Photocurrent value was measured by using three-electrode electrochemical cell under the photoirradiation by 200 W Hg-Xe lamp through quartz glass window. The obtained anodic photocurrent values were normalized by the weight of $Ga_2O_3$ contained in the composite photocatalysts.

Table S1

The result of photocatalytic conversion of $CO_2$ in water for *0.25*Ag/*95*-MgAl/$Ga_2O_3$ composite photocatalyst and a series of reference photocatalysts. The content of $Ga_2O_3$ in photocatalyst powder was fixed at 0.19 g. Reaction solution: 1.0 L of aqueous $NaHCO_3$ solution (0.1 M), $CO_2$ supply: 30 mL $min^{-1}$, light source: 400 W high-pressure Hg lamp (through quartz glass jacket), photoirradiation time: 1 h.

| Sample | Type | Weight / g | | Formation rate / μmol $h^{-1}$ | | | Selectivity to CO (%) |
|---|---|---|---|---|---|---|---|
| | | Total | $Ga_2O_3$ | $H_2$ | $O_2$ | CO | |
| *95*-MgAl/$Ga_2O_3$ | composite | 1.0 | 0.19 | 534.9 | 252.0 | 1.4 | 0.2 |
| *0.25*Ag/*95*-MgAl/$Ga_2O_3$ | composite | 1.0 | 0.19 | 131.2 | 166.9 | 211.7 | 61.7 |
| *95*-MgAl/*0.25*Ag/$Ga_2O_3$ | composite | 1.6 | 0.19 | 148.0 | 76.2 | 31.5 | 17.5 |
| *95*-MgAl + *0.25*Ag/$Ga_2O_3$ | mixture | 1.0 | 0.19 | 348.2 | 191.4 | 56.8 | 14.0 |
| *0.25*Ag/$Ga_2O_3$ | bare | 0.19 | 0.19 | 130.7 | 85.0 | 43.6 | 25.0 |
| *1.0*Ag/Mg−Al LDH | bare | 0.50 | 0.00 | trace | trace | trace | − |

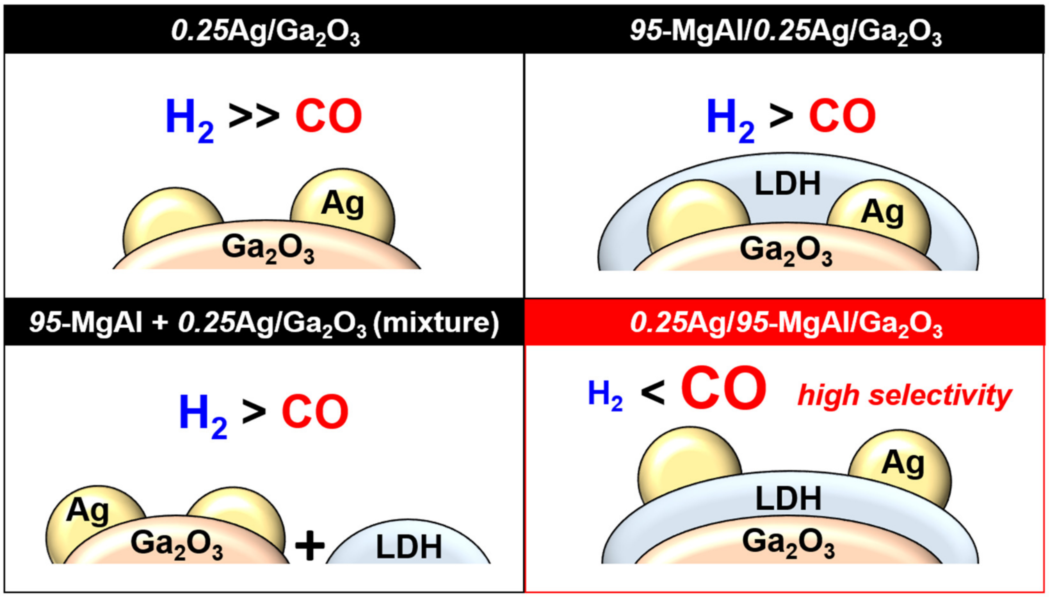


Figure S6 Schematic illustrations of *0.25*Ag/$Ga_2O_3$ (bare photocatalyst), *95*-MgAl/*0.25*Ag/$Ga_2O_3$ (reference composite photocatalyst), *95*-MgAl + *0.25*Ag/$Ga_2O_3$ (mixture photocatalyst), and *0.25*Ag/*95*-MgAl/$Ga_2O_3$ (composite photocatalyst).

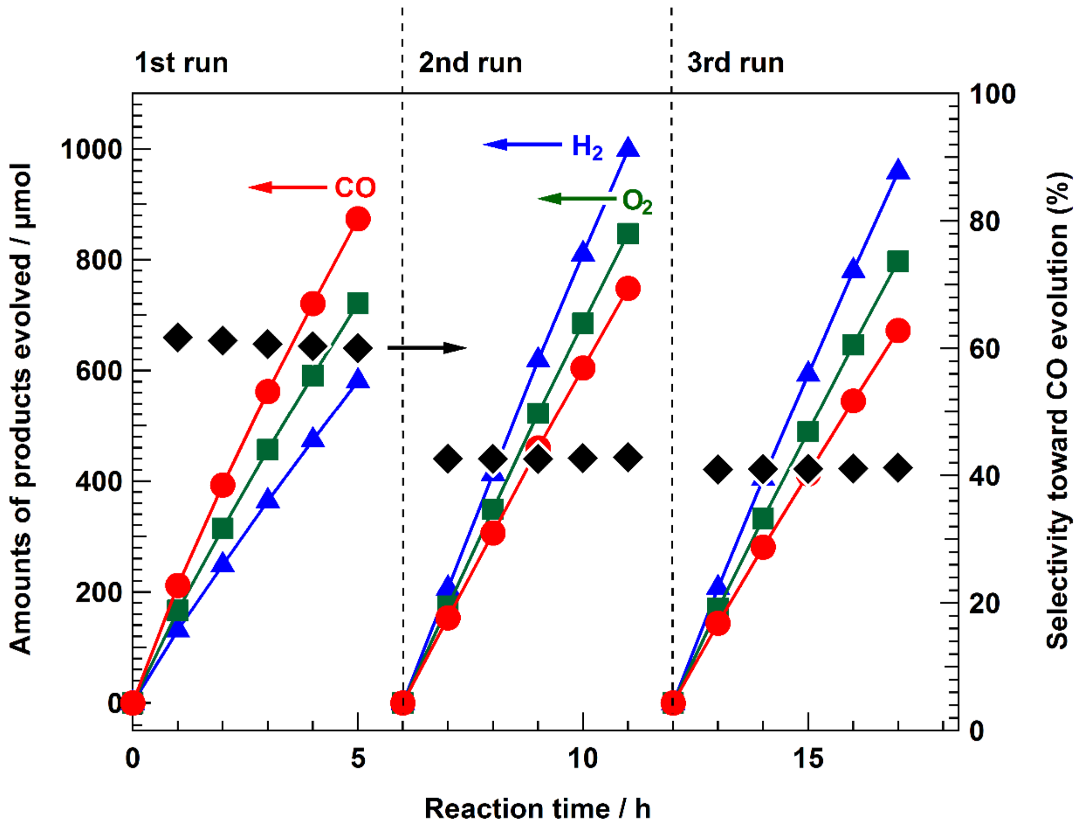


Figure S7 The amounts of products evolved (left axis) and the selectivity toward CO evolution (right axis) in the repeating test for the photocatalytic conversion of $CO_2$ in water using *0.25*Ag/*95*-MgAl/$Ga_2O_3$ photocatalyst. Red circle: CO, green square: $O_2$, blue triangle: $H_2$, black diamond: selectivity toward CO evolution. Photocatalyst weight: 1.0 g, reaction solution: 1.0 L of an aqueous $NaHCO_3$ solution (0.1 M), $CO_2$ supply: 30 mL min$^{-1}$, light source: 400 W high-pressure Hg lamp (through a quartz glass jacket). The reaction solution was thoroughly degassed by a flow of high-purity $CO_2$ gas after 1st and 2nd run.

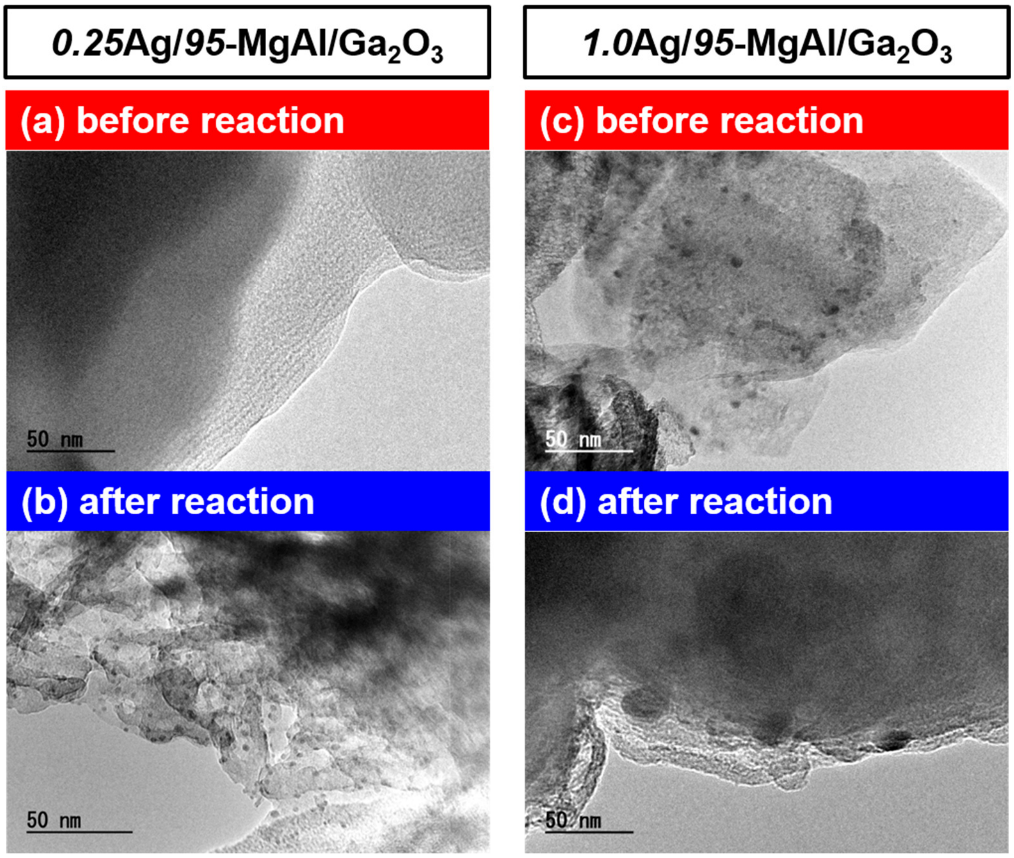


Figure S8 TEM images of (a) before and (b) after reaction for *0.25*Ag/*95*-MgAl/$Ga_2O_3$, and (c) before and (d) after reaction for *1.0*Ag/*95*-MgAl/$Ga_2O_3$, captured on JEM-2100F TEM system (Japan Electron Optics Laboratory).