Supplementary Material (ESI) for Chemical Communications
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Modification of Ga_2O_3 by Ag−Cr Core−shell Cocatalyst Enhances Photocatalytic CO Evolution for the Conversion of CO_2 by H_2O

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Experimental Section

Preparation of Ag−Cr/Ga_2O_3

Ag−Cr/Ga_2O_3 was prepared by a facile simultaneously photodeposition method.[1, 2] Generally, 1.0 g of Ga_2O_3 (Kojundo, 99.99%) powder was dispersed in 1.0 L of ultra−pure water containing a required amount of $AgNO_3$ and $Cr(NO_3)_3$, and the dissolved air in the solution was completely degassed by a flow of Ar gas. The suspension was irradiated under a 400 W high−pressure Hg lamp with Ar gas flowing for 1.0 h, followed by filtration and drying at room temperature. The amount of Ag and Cr was the molar ratio of Ag/Ga and Cr/Ga.

1. K. Maeda, D. Lu, K. Teramura and K. Domen, *J. Mater. Chem.*, 2008, **18**, 3539−3542.
2. K. Maeda, D. Lu, K. Teramura and K. Domen, *Energ. Environ. Sci.*, 2010, **3**, 470−477.

Characterization

The as−prepared Ag−Cr/Ga_2O_3 was studied by X−ray diffractometry (XRD, Rigaku Multiflex) with Cu Kα radiation ($\lambda = 0.154$ nm), field−emission scanning electron microscopy (FE−SEM, SU−8220, Hitachi High Technologies), transmission electron microscopy (TEM, JEM−2100F), X−ray photoelectron spectroscopy (XPS, Shimadzu, ESCA 3400, Mg Kα), and X−ray absorption fine structure (XAFS) at the Ag K−edge and Cr K−edge (beam line BL01B1 of SPring−8).

Photocatalytic reaction

The photocatalytic reduction of CO_2 was carried out using a flow system with an inner−irradiation−type reaction vessel at ambient pressure. First, the synthesized photocatalyst (0.5 g) was dispersed in ultrapure water (1.0 L) containing 0.1 M $NaHCO_3$. Second, CO_2 was bubbled into the solution at a flow rate of 30 mL min^{-1}. Third, the suspension was illuminated using a 400 W high−pressure mercury lamp with a quartz filter connected to a water cooling system. The amounts of evolved H_2 and O_2 were detected using a thermal conductivity detector–gas chromatography system (TCD−GC, Shimadzu Corp; MS−5A column, Ar carrier). The amount of evolved CO was analyzed by a flame ionization detector–GC with a methanizer (FID−GC, ShinCarbon ST column, N_2 carrier), the reactor set−up is shown in Figure S1.

In the backward reaction, the processes were almost the same as those of the photocatalytic reduction of CO_2, except that the CO, O_2 and diluent gas Ar were bubbled into the ultrapure water solution with a total flow rate of 30 mL min^{-1}, and the amount of evolved CO_2 was analyzed by a FID−GC.

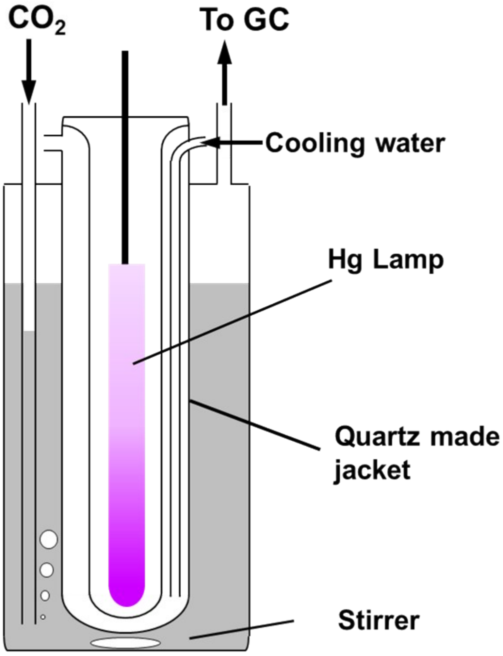

Fig. S1 Reactor set−up for the photocatalytic reduction of CO_2 under UV light irradiation

Supplementary Figures and Table

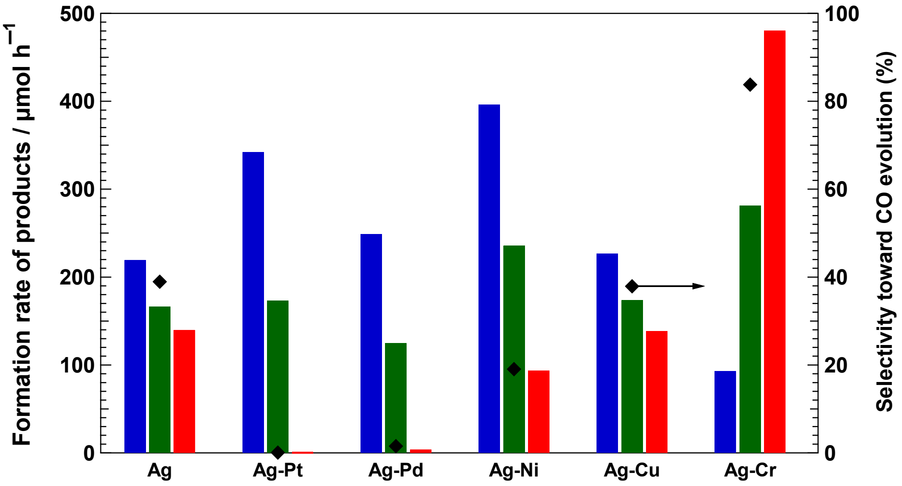

Fig. S2 Formation rate of H_2 (blue), O_2 (green), CO (red), and selectivity toward CO (black diamond) evolution for the photocatalytic conversion of CO_2 in water over Ag/Ga_2O_3 and Ag−metals/Ga_2O_3 photocatalysts. Photocatalyst powder: 0.5 g, reaction solution volume: 1.0 L, additive: 0.1 M $NaHCO_3$, Ag loading amount: 1.0 mol% (Ag/Ga), metals loading amount: 1.0 mol% (metals/Ga), modification method: simultaneously photodeposition (SPD) method, CO_2 flow rate: 30 mL min^{-1}, light source: 400 W high−pressure Hg lamp.

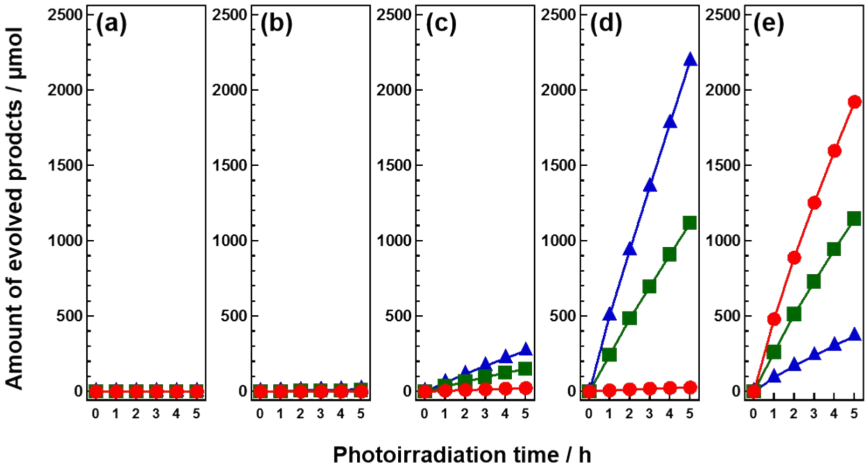

Fig. S3 Amounts of H_2 (blue triangle), O_2 (green square), and CO (red circle) from controlled experiments for the photocatalytic conversion of CO_2 in water using the Ag−Cr/Ga_2O_3 photocatalyst. (a) dark condition; (b) no photocatalyst; (c) no additive; (d) with Ar gas flow; (e) typical condition. Photocatalyst powder: 0.5 g, reaction solution volume: 1.0 L, additive: 0.1 M $NaHCO_3$, Ag loading amount: 1.0 mol%, Cr loading amount: 1.0 mol%, CO_2 flow rate: 30 mL min^{-1}, light source: 400 W high−pressure Hg lamp.

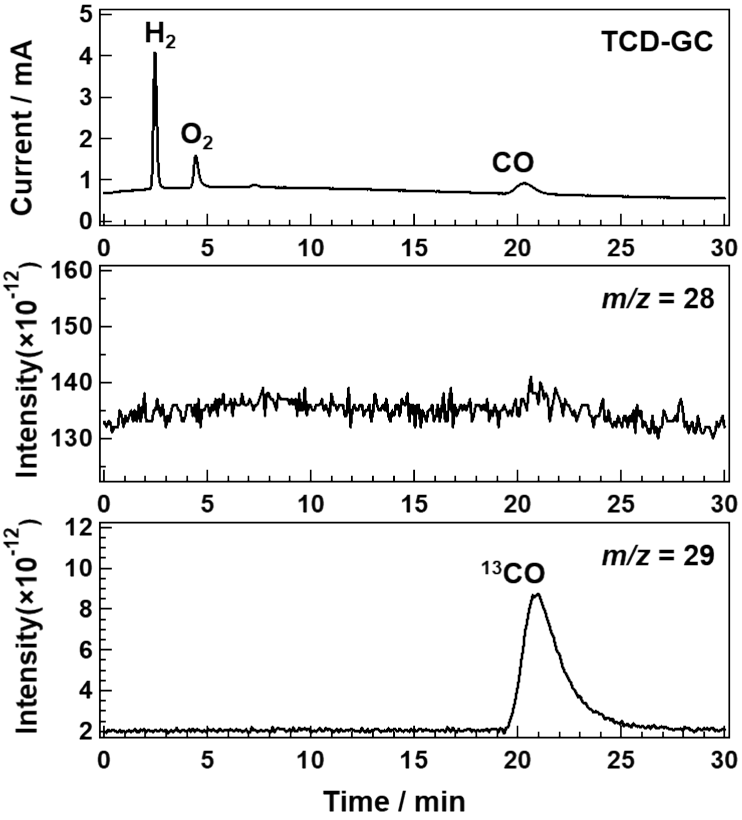

Fig S4. Gas chromatograms and mass spectra (*m/z* 28, 29) for the photocatalytic conversion of $^{13}CO_2$ by H_2O over Ag−Cr/Ga_2O_3. Photocatalyst powder: 0.5 g, reaction solution volume: 1.0 L, additive: 0.1 M $NaHCO_3$, Ag loading amount: 1.0 mol%, Cr loading amount: 1.0 mol%, CO_2 flow rate: 30 mL min^{-1}, light source: 400 W high−pressure Hg lamp.

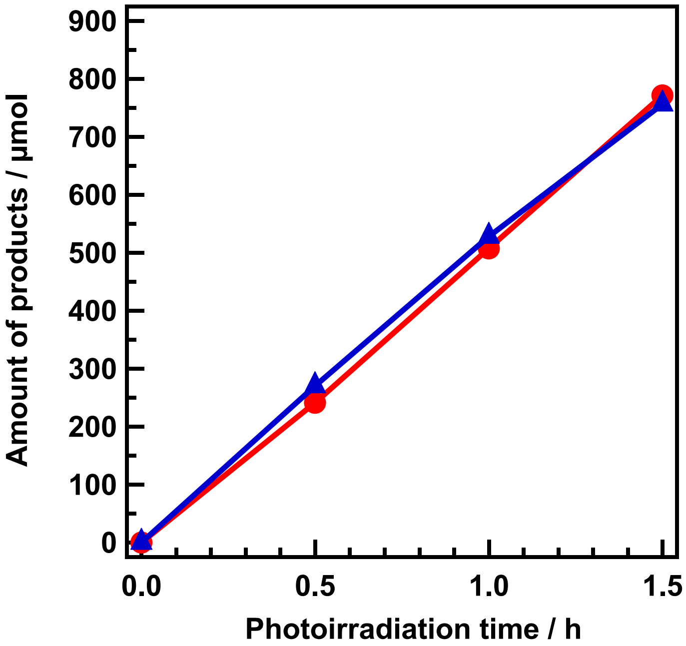

Fig S5. Time course of CO (triangle) and ^{13}CO (circle) determined by FID−GC and mass, respectively, for the photocatalytic conversion of CO_2 over Ag−Cr/Ga_2O_3. Photocatalyst powder: 0.5 g, reaction solution volume: 1.0 L, additive: 0.1 M $NaHCO_3$, Ag loading amount: 1.0 mol%, Cr loading amount: 1.0 mol%, CO_2 flow rate: 30 mL min^{-1}, light source: 400 W high−pressure Hg lamp.

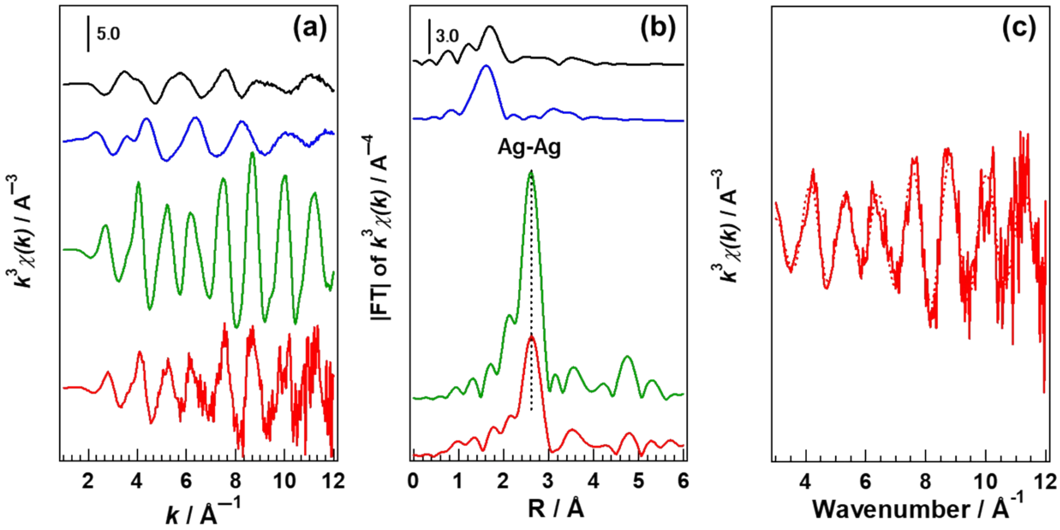

Fig. S6 Ag K−edge (a) EXAFS and (b) Fourier transforms (FT) of the EXAFS spectra of Ag_2CO_3 (black), Ag_2O (blue), Ag foil (green), and Ag−Cr/Ga_2O_3 (red), (c) Fourier−filtered EXAFS function (solid line) and resulting curve fit (dotted line) for the main peak appearing at 2.0–3.0 Å in FT of k^3−weighted EXAFS (Ag−Cr/Ga_2O_3 spectrum in Fig. S6b).

Table S1 Curve−fitting analysis of Fourier−transformed EXAFS of Ag−Cr/Ga_2O_3.

Samples	Scatter atom	N[a]	R[b] (Å)	$\Delta(\sigma^2)$[c] (Å^2)	R_f[d]
Ag−Cr/Ga_2O_3	Ag	4.80	2.87	1.08×10^{-2}	5.77×10^{-3}
Ag foil[e]	Ag	(12)	2.89		

[a] Coordination number, [b] Bond distance, [c] Debye–Waller factor, [d] Residual factor, [e] Data from X−ray crystallography

As shown in Fig. S6b, the peak at 2.6 Å is assigned to the Ag–Ag shell. Inverse Fourier transform of the Ag−Cr/Ga_2O_3 (red) spectrum at 2.6 Å (R = 2.0–3.0 Å) in Fig. S6b gives the EXAFS oscillation of Ag–Ag shell, as shown in Fig. S6c. The dotted line in Fig. S6c shows the result of a curve−fitting analysis using Ag–Ag shell parameters in the k region of 3.0–14.0 Å^{-1}. A simulated spectrum fitted well with the experimental one. As shown in Table 1, the curve−fitting analysis of the peak at 2.6 Å showed that this peak can be assigned to Ag–Ag shell with a coordination number of 4.8 and bond distance 2.87 Å, which is smaller with Ag foil.[3] The height of Ag−Ag shell peak of Ag−Cr/Ga_2O_3 was lower than that of Ag foil, which indicates that the particle size of Ag in Ag−Cr/Ga_2O_3 is smaller than Ag foil.

3. H. A. Gasteiger, S. S. Kocha, B. Sompalli and F. T. Wagner, *Appl. Catal. B: Environ.*, 2005, **56**, 9−35.

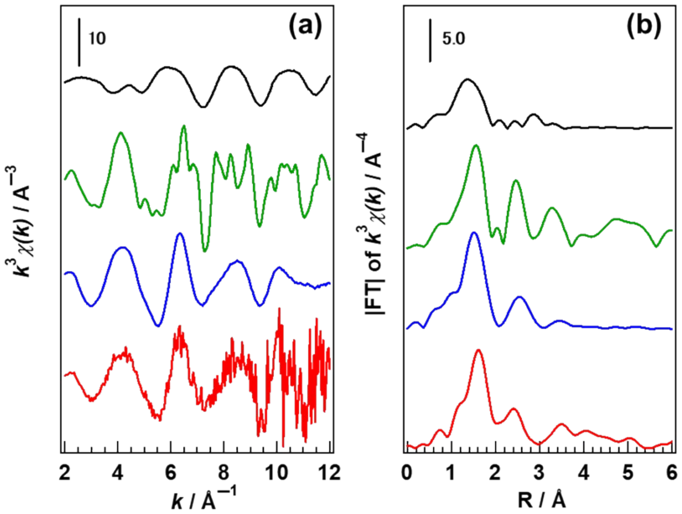

Fig. S7 Cr K−edge (a) EXAFS and (b) Fourier transforms (FT) EXAFS spectra of CrO_3 (black), Cr_2O_3 (blue), $Cr(OH)_3$□xH_2O (green), and Ag−Cr/Ga_2O_3 (red).

As shown in Fig. S7b, the peak with the largest FT moduli at 1.7 Å is assigned to oxygen atoms in the first coordination sphere of Cr (Cr−O). At further radial distance of about 2.6 Å and 3.2 Å with smaller FT moduli are assigned as contributions from distal Cr atoms (Cr−Cr).[4]

4. D. Rai, D. A. Moore, N. J. Hess, K. M. Rosso, L. Rao and S. M. Heald, *J. Solution Chem.*, 2007, **36**, 1261−1285.

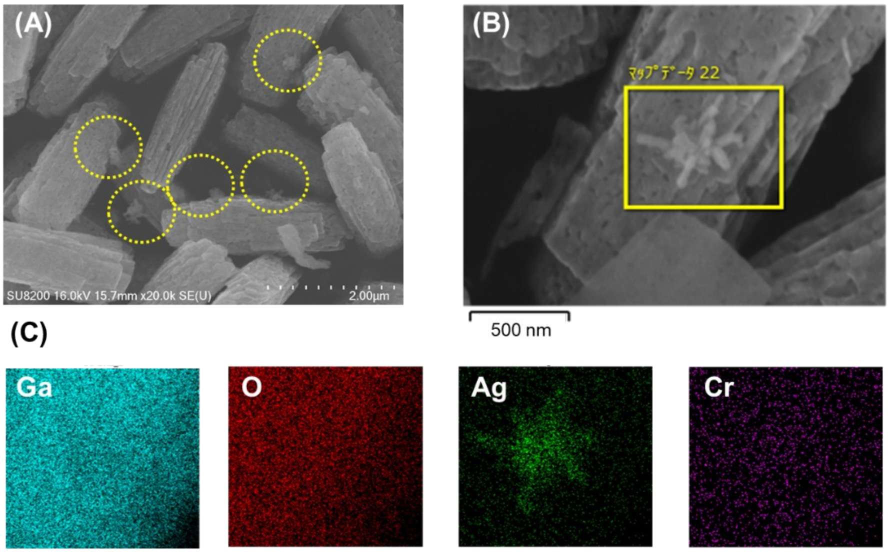

Fig. S8 (A) SEM image of $\mathrm{Ag{-}Cr(OH)_3}$□$\mathrm{xH_2O/Ga_2O_3}$; EDS analysis of $\mathrm{Ag{-}Cr(OH)_3}$□$\mathrm{xH_2O/Ga_2O_3}$: (B) selected SEM images, (C) Ga, O, Ag, and Cr mapping images. Ag loading amount: 1.0 mol%, Cr loading amount: 1.0 mol%.

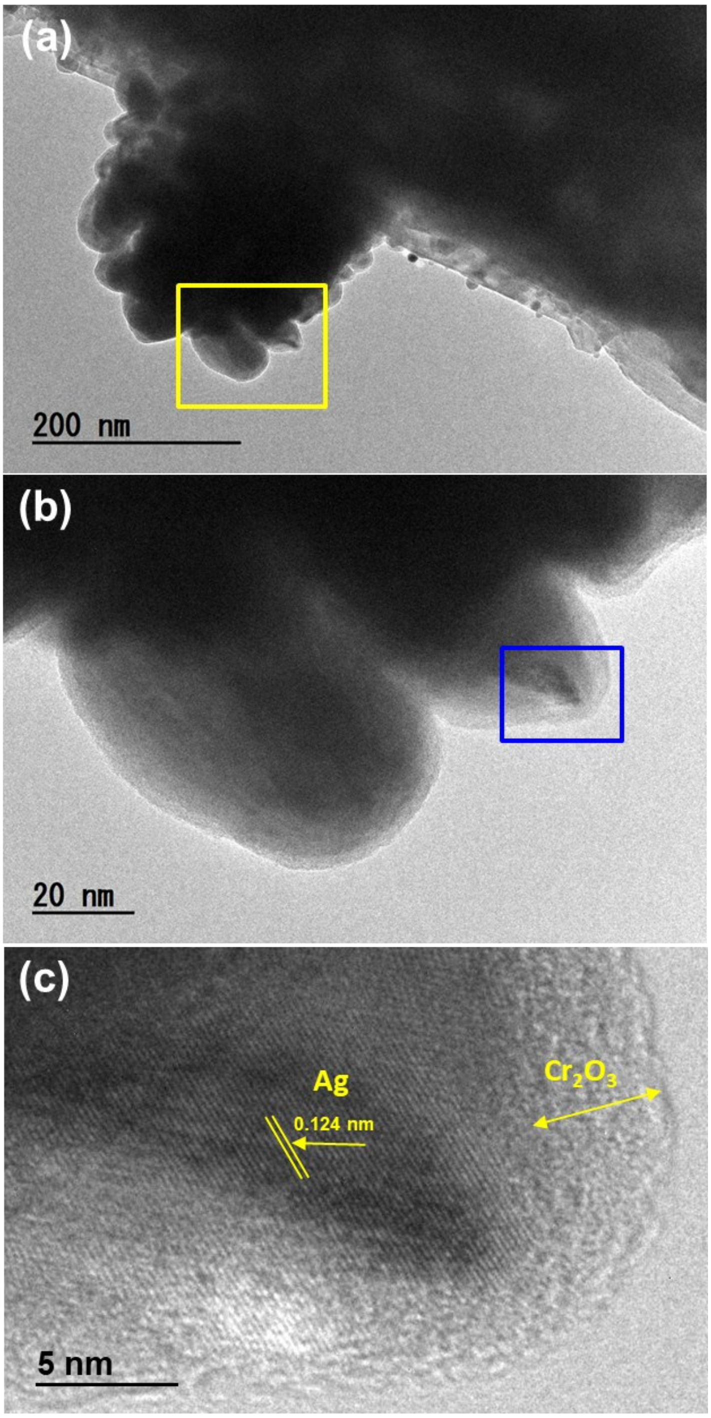

Fig. S9 (a), (b) TEM images, and (c) high−resolution TEM (HRTEM) image of Ag−$Cr(OH)_3$□xH_2O cocatalyst ((b) and (c) are the enlarged TEM images of the yellow rectangular in Figure (a) and blue rectangular in Figure (b), respectively).

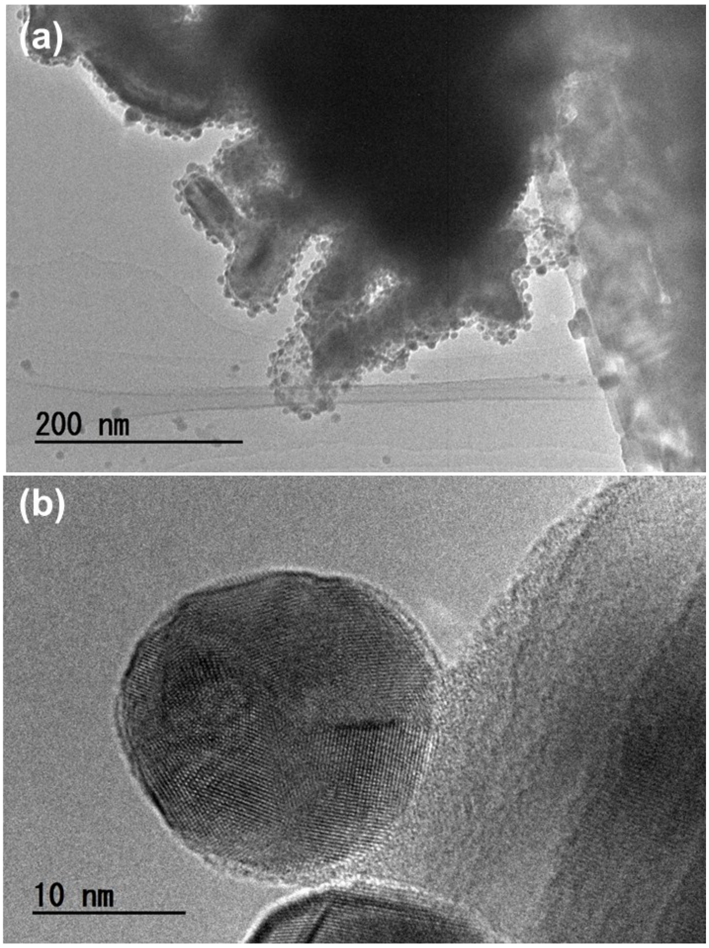

Fig. S10 (a) TEM image and (b) HRTEM image of the as prepared $Ag-Cr(OH)_3$□xH_2O/Ga_2O_3.

Table S2 Backward reactions for the photocatalytic reduction of CO_2 in H_2O over Ag/Ga_2O_3 and Ag−$Cr(OH)_3$□xH_2O/Ga_2O_3.[b]

Catalyst	Flow rates of gases / µmol h^{-1}		Rates of detected gases / µmol h^{-1}				Balance 1 $\boldsymbol{R}_{CO2} / \boldsymbol{R}_{CO}$	Balance 2 $\boldsymbol{R}_{CO2} / 2\boldsymbol{R}_{O2}$
	CO	O_2	H_2	O_2	CO	CO_2		
Ag/Ga_2O_3	487	301	20.8	260	382	103	0.98	1.01
	982	538	56.8	420	670	320	1.03	1.03
	2500	1590	7.45	1200	1750	820	1.09	1.02
Ag−Cr/Ga_2O_3	487	301	226	383	402	84.5	0.99	1.03
	982	538	282	590	782	202	1.01	1.02
	2500	1590	300	1560	2170	320	0.97	0.99

[b] Photocatalyst powder: 0.5 g, reaction solution: 1.0 L H_2O, Ag loading amount: 1.0 mol%, Cr loading amount: 1.0 mol%, light source: 400 W high−pressure Hg lamp.

Backward reaction: $2CO + O_2 \rightarrow 2CO_2$

Balance 1: Produced CO_2 / Consumed CO = $\boldsymbol{R}_{CO2} / \boldsymbol{R}_{CO}$

Balance 2: 0.5 × Produced CO_2 / Consumed O_2 = $\boldsymbol{R}_{CO2} / 2\boldsymbol{R}_{O2}$

where R_x is the formation rate of species x

Calculation of the consumed amount of CO and O_2 for the backward reaction.

Consumed amount of CO = Flowing amount of CO − Detected amount of CO

Because the water splitting and backward reaction for CO_2 reduction happen simultaneously in the reactor under photoirradiation, as a result, the detected O_2 contains two parts: the residual of flowing O_2 after the backward reaction, and the O_2 produced by water splitting. The detected amount of O_2 can be calculated as follows:

Detected amount of O_2 = Flowing amount of O_2 − Consumed amount of O_2 + Produced amount of O_2

Consumed amount of O_2 = Flowing amount of O_2 − Detected amount of O_2 + Produced amount of O_2 = Flowing amount of O_2 − Detected amount of O_2 + 0.5 × Produced amount of H_2