Supplementary Information

Plastics-to-Syngas Photocatalyzed by Co-Ga$_2$O$_3$ Nanosheets

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EXPERIMENTAL SECTION

Characterization

Transmission electron microscopy (TEM) images were obtained from a JEOL-2010 TEM. High-resolution TEM (HRTEM) images and the corresponding elemental mapping images were measured on a JEOL JEM-ARM200F TEM/STEM. The field-emission scanning electron microscopy (FE-SEM) images were performed by using a FEI Sirion-200 SEM. X-ray diffraction (XRD) patterns were recorded by a Philips X’Pert Pro Super diffractometer with Cu Kα radiation (λ = 1.54178 Å), in which the voltage was 40 kV, the electric current was 100 mA and the scan speed was 35°/min. Atomic force microscopy (AFM) was carried out on a Veeco DI Nano-scope multimode V system with a scan speed of 1.00 Hz. X-ray photoelectron spectra (XPS) were measured on an ESCALAB MKII with Al Kα (hυ = 1486.6 eV) as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected by referencing C 1s to 284.8 eV. UV–vis diffuse reflectance spectra were performed on a Perkin Elmer Lambda 950 UV–vis–NIR spectrophotometer and the UV–vis absorption spectrum was recorded on UV-2501PC/2550 (Shimadzu Corporation, Japan). Room temperature photoluminescence (PL) spectra were evaluated by a LabRAM HR Evolution Micro-Raman system, the excitation wavelength was 325 nm, and the PL spectra were accumulated for 30 s with an output power of ca. 1.7 mW. The CO₂ temperature programmed desorption (TPD) measurements were carried out on AutoChem II 2920 with a temperature ramp rate of 10 °C/min. In situ FT-IR spectra were executed by a Thermo Scientific Nicolet iS50. In situ ESR spectra were obtained using a JEOL JESFA200 ESR spectrometer. Synchrotron radiation photoemission spectroscopy (SRPES) was performed at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The work function (Φ) is determined by the difference between the photon energy and the binding energy of the secondary cutoff edge, according to the formula of Φ = hυ – E_{cutoff} (hυ refers to the utilized photon energy of 40.00 eV and a sample bias of −5 V was applied to observe the secondary electron cutoff).

Photoconversion of Commercial Plastic Products and Reagent-Grade PE Powders

Commercial plastic products of PE plastic bags, PP plastic boxes and PET plastic bottles were initially crushed into fine powders (<5 mm) by a pulverizer (Benchen Science and Technology, Figures S10-S12). Reagent-grade PE powders with the size of ca. 5 mm were purchased from Alfa Aesar (China) without any further purification. It should be mentioned that small plastics (≤5 mm) were commonly defined as the microplastics, which were particularly difficult to be recycled and may cause some unpredictable damages to the ecosystem. Then, a closed glass gas-circulation system (Labsolar-IIIAG, Beijing
Perfectlight Technology Co., Ltd) was used to conduct the photoconversion tests. In detail, 50 mg photocatalysts and 100 mg plastic products powders were initially dispersed in 100 mL deionized water under stirring. The dispersion was put into the reaction vessel, which was soaked in an outer vessel so that cooling water could circulate to keep the temperature of the reaction solution at 298 ± 0.2 K. The reaction system was vacuum-treated and then filled with high-purity air to reach an atmospheric pressure. The light source for the photocatalysis was a 300 W Xe lamp (CEL-HXFUV300, Beijing Ceaulight Technology Co., Ltd., China) with a standard AM 1.5 filter to simulate one-sun irradiation, in which the outputting light density was about 100 mW/cm². During the light irradiation, the evolved gas products were qualitatively and quantificationally analyzed by Agilent GC-7890B gas chromatograph. The liquid products were quantified by NMR (Bruker AVANCE AV III 400) spectroscopy, in which 0.4 mL supernate was mixed with 0.1 mL D₂O (deuterated water) and 0.02 mL dimethyl sulfoxide (DMSO, Sigma, 99.99%) was added as an internal standard. The one-dimensional ¹H spectrum was measured with water suppression using a pre-saturation method. To analyze the content of CO₂ dissolved in the solution, 2.0 mL supernate was taken immediately after the photocatalysis. Upon adding excess Ba(OH)₂ powders to the solution, the white precipitate could be obtained. Taking the Co-Ga₂O₃ nanosheets as examples, after the following centrifugation and the gravimetric analysis for the white precipitate, the produced CO₂ and CO dissolved in the solution after the photoconversion of pure PE or PP or PET could be calculated to be ca. 2.88, 2.53 and 1.65 mmol, respectively. And meanwhile, the amount of gas CO₂ and CO after the photoconversion of pure PE or PP or PET detected by gas chromatograph was roughly 0.69, 0.64 and 0.43 mmol, respectively. That is to say, the total carbon content for the photoconversion of all these three plastics over both the two catalysts can exceed 90% (Table S5-6). In addition, a handful of microplastics with smaller size were also detected by the SEM images (Fig. S14), which might be produced during the photoconversion processes, conforming to the principle of carbon balance.

**Detection of the Isotope Tracing Gas Products**

Synchrotron-based vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) was carried out at the combustion endstation at the BL03U beamline at the National Synchrotron Radiation Laboratory at Hefei, China. In detail, 50 mg Co-Ga₂O₃ nanosheets and 100 mg reagent-grade PE powders were initially dispersed in 100 mL deionized water under stirring. The reaction system was vacuum-treated three times to remove air completely, which was then pumped by high-purity N₂ to reach an atmospheric pressure. For the ¹⁸O or H₂¹⁸O labelling experiments, a small amount of ¹⁸O₂ or 1 mL H₂¹⁸O were added to the reaction system, and a certain amount of gas was taken immediately after 24 h irradiation and was analyzed at the photon energy of 14.5 eV. For the D₂ labelling experiments, D₂O were
utilized to replace $\text{H}_2\text{O}$.

**In situ FTIR experiments**

All FTIR spectra were recorded on Thermo Scientific Nicolet iS50. The spectra were displayed in absorbance units and acquired with a MCT detector and a resolution of 8 cm$^{-1}$, using 64 scans. The dome of the reaction cell had two KBr windows allowing IR transmission and a third window allowing transmission of irradiation introduced through a liquid light guide that connects to a 300 W Xe lamp. The Co-Ga$_2$O$_3$ nanosheets and Ga$_2$O$_3$ nanosheets powders were added to the reaction cell. After spraying some water on the powders, the reaction cell was sealed. Then, the reaction system was vacuum-treated three times to remove air completely, which was then pumped by high-purity CO$_2$ to reach an atmospheric pressure. Next, the FTIR spectra were recorded as a function of time to investigate the dynamics of the reactant adsorption in the dark and desorption/conversion under irradiation.

**In situ ESR Experiments**

(1) Detection of superoxide radical anion ($\text{O}_2^-$): 5 mg Co-Ga$_2$O$_3$ nanosheets and 15 mg reagent-grade PE powders were dispersed in 1 mL of methanol followed by addition of 20 μL DMPO methanol solution (100 mM). After 10 s irradiation, the mixed reaction solution was analyzed by in situ ESR spectra.

(2) Detection of hydroxyl radical (·OH): 5 mg Co-Ga$_2$O$_3$ nanosheets and 15 mg reagent-grade PE powders were dispersed in 1 mL of H$_2$O followed by addition of 1 mL DMPO solution (2 mM in water). After 10 s irradiation, the mixed reaction solution was analyzed by in situ ESR spectra.

**Detection of H$_2$O$_2$**

2.0 mL reaction solution was taken immediately after 24 h photoconversion of reagent-grade PE powders. Then, 2 mL 1% o-tolidine in 0.1 M HCl was added to the above reaction solution. Subsequently, the solution was acidified with 1 M HCl (2 mL). The absorption spectrum of the solution was immediately recorded with a UV–vis spectrophotometer and the H$_2$O$_2$ has a characteristic absorption peak at ca. 436 nm.

**Detection of H$_2$O$_2$ with o-tolidine**

Hydrogen peroxide (H$_2$O$_2$) measurements were performed on an UV–vis–NIR spectrophotometer. 2.0 mL reaction solution was taken immediately after 5 h irradiation of pure PE over the Co-Ga$_2$O$_3$ nanosheets under simulated natural environments. Then, 2 mL 1% o-tolidine in 0.1 M HCl was added to the above reaction solution. Subsequently, the solution was acidified with 1 M HCl (2 mL). The absorption spectrum
of the solution was immediately recorded with a UV–vis spectrophotometer. The H$_2$O$_2$ has a characteristic absorption peak at 436 nm.

**CO$_2$ Photoreduction Tests**

A closed glass gas-circulation system (Labsolar-IIIAG, Beijing Perfectlight Technology Co., Ltd) was used to conduct the photocatalytic CO$_2$ tests. In detail, 50 mg Co-Ga$_2$O$_3$ nanosheets or Ga$_2$O$_3$ nanosheets were initially dispersed in 100 mL deionized water under stirring. The dispersion was put into the reaction vessel, which was soaked in an outer vessel so that cooling water could circulate to keep the temperature of the reaction solution at room temperature. Then, the reaction system was vacuum-treated three times to remove air completely, which was then pumped by high-purity CO$_2$ ($^{13}$CO$_2$ was used for the $^{13}$C labelling experiments) to reach an atmospheric pressure. The light source for the photocatalysis was a 300 W Xe lamp (CEL-HXFUV300, Beijing Ceaulight Technology Co., Ltd., China) with a standard AM 1.5 filter, in which the outputting light density was about 100 mW/cm$^2$.

**Calculation Details**

The first-principles calculations were performed with the Vienna ab initio simulation package.$^{1,2}$ The interaction between ions and valence electrons was described using projector augmented wave (PAW) potentials, and the exchange–correlation between electrons was treated through using the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form.$^3$ To achieve the accurate density of the electronic states, the plane wave cutoff energy was 480 eV, a gamma-centre $3 \times 9 \times 1$ for sheet k-point mesh were used. Ionic relaxations were carried out under the conventional energy ($10^{-5}$ eV) and force (0.01 eV/Å) convergence criteria. All periodic slabs have a vacuum spacing of 15 Å to avoid the interaction between adjacent layers. The structure model of Co-Ga$_2$O$_3$ nanosheets and Ga$_2$O$_3$ nanosheets contain a supercell size of a = 17.37 Å, b = 5.96 Å, c = 25.66 Å, α = β = γ = 90°.

Gibbs free energies for each gaseous and adsorbed species were calculated at 298.15 K, according to the expression:

$$G = E_{DFT} + E_{ZPE} - TS$$  \hspace{1cm} (Eq. S1)

$$E_{ZPE} = \sum_i 1/2 \nu_i$$  \hspace{1cm} (Eq. S2)

$$\Theta_i = \nu_i / k$$  \hspace{1cm} (Eq. S3)

$$S = \sum_i R[\ln(1 - e^{-\Theta_i/T})^{-1} + \frac{\Theta_i}{T}(e^{\Theta_i/T} - 1)^{-1}]$$  \hspace{1cm} (Eq. S4)

Where $E_{DFT}$ is the electronic energy calculated for specified geometrical structures, $E_{ZPE}$ is the zero-point energy, $S$ is the entropy, $h$ is the Planck constant, $\nu$ is the computed vibrational frequencies, $\Theta$ is the
characteristic temperature of vibration, $k$ is the Boltzmann constant, and $R$ is the molar gas constant. For adsorbates, all $3N$ degrees of freedom were treated as frustrated harmonic vibrations with negligible contributions from the catalysts’ surfaces. No bias was applied ($U = 0 \text{ V}$), the free energy of the $(H^+ + e^-)$ pair is related to that of $1/2 \text{ H}_2$ in the gas-phase. Free energy changes with respect to an initial state of gaseous $\text{CO}_2$ and $\text{H}_2$ freely above an empty surface can be represented by the following:

\[
\begin{align*}
\Delta G[\text{COOH*}] &= G[\text{COOH*}] + G[H^+ + e^-] - (G[*] + G[\text{CO}_2] + 2 \times G[H^+ + e^-]) \\
\Delta G[\text{CO*}] &= G[\text{CO*}] + G[\text{H}_2\text{O}] - (G[*] + G[\text{CO}_2] + 2 \times G[H^+ + e^-]) \\
\Delta G[\text{H*}] &= G[\text{H*}] - (G[*] + G[H^+ + e^-]) \\
G[H^+ + e^-] &= 1/2G[\text{H}_2]
\end{align*}
\] (Eq. S5, S6, S7, S8)
Scheme S1. Schematic representations for the photoconversion of non-recyclable plastics into syngas. In the photoconversion process, various commercial plastics and H$_2$O were sustainably and efficiently converting into renewable syngas under mild conditions (25 °C, 1 atm). That is to say, commercial plastics are photodegraded to CO, while H$_2$O is photoreduced to H$_2$ over the same photocatalyst.

Figure S1 XRD patterns of the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets.
Figure S2 TEM image of the Co-Ga$_2$O$_3$ nanosheets.

Figure S3 (A) High-resolution TEM image, (B) AFM image and (C) the corresponding height profiles of the Co-Ga$_2$O$_3$ nanosheets. The number 1, 2 and 3 in (B) correspond to the numbers 1 to 3 in (C), respectively.
Figure S4 Annular dark-field TEM image and the corresponding elemental mapping images of the Co-Ga$_2$O$_3$ nanosheets, in which the scale bar is 200 nm.

Figure S5 XPS spectra of Co 2p core level for the Co-Ga$_2$O$_3$ nanosheets.
Figure S6 TEM image of the Ga$_2$O$_3$ nanosheets, in which the scale bar is 200 nm.

Figure S7 (A) AFM image and (B) the corresponding height profiles of the Ga$_2$O$_3$ nanosheets. The number 1, 2 and 3 in (B) correspond to the numbers 1 to 3 in (A), respectively.
Figure S8 UV–vis diffuse reflectance spectra for the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets, in which the violet circled area indicated the obviously enhancement of photoabsorption due to the Co-doping. Inset denotes the corresponding Kubelka-Munk plots.

Figure S9 (A) Secondary electron cutoff and (B) valence-band spectra for Co-Ga$_2$O$_3$ nanosheets (red) and Ga$_2$O$_3$ nanosheets (blue) measured by synchrotron-radiation photoemission spectroscopy spectra.
As displayed in Figures S10-S12, commercial plastics including PE plastic bags, PP plastic boxes and PET plastic bottles were initially crushed into fine powders by a pulverizer to ensure their good contact with H₂O. The corresponding SEM images showed that the sizes of most powders are smaller than 5 mm.
Figure S13 $^1$H NMR spectra for the products for the photoconversion of (A) PE plastic bags, (B) PP plastic boxes and (C) PET plastic bottles after 24 h irradiation over the Co-Ga$_2$O$_3$ nanosheets and Ga$_2$O$_3$ nanosheets under mild conditions.

As displayed in Figures S13, there was no detectable liquid product for all these three plastics after 24 h irradiation over the Co-Ga$_2$O$_3$ nanosheets and Ga$_2$O$_3$ nanosheets under mild conditions.

Figure S14 The SEM images of microplastics in the solution after the photoconversion of (A, B) PE plastic bags, (C, D) PP plastic boxes and (E, F) PET plastic bottles after 24 h irradiation over the Co-Ga$_2$O$_3$ atomic layers and Ga$_2$O$_3$ atomic layers under mild conditions, respectively.

As displayed in Figures S14, a handful of microplastics with smaller size were also detected, which might be produced during the photoconversion processes, conforming to the principle of carbon balance.
Figure S15 The weight losses of commercial PE plastic bags, PP plastic boxes and PET plastic bottles for the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets in a simulated sunlight (AM 1.5G, 100 mW/cm$^2$) at ambient temperature and pressure after 24 h irradiation, respectively. The error bars represent the standard deviations of three independent measurements.

After the photodegradation processes, the residual plastic powders were collected to calculated their weight losses. To be specific, the plastic powders and photocatalysts were collected by centrifugation after the photoconversion (total residual weight, $W_1$). To lower the deviation, the residual weight of the photocatalysts ($W_2$) were estimated first (when 50 mg photocatalysts were dispersed into 100 mL H$_2$O, around 46 mg samples could be collected by centrifugation). Then the weight losses of plastics were calculated by the following formula:

\[
\text{Plastics weight losses (\%)} = 1 - \frac{W_1 - W_2}{\text{initial mass of plastics}} \quad \text{(Eq. S9)}
\]

Considering the losses of the plastics during the centrifugation, the calculated plastics weight losses may still be little high. The weight losses of PE plastic bags powders were 53%, 49% and 42% for the Co-Ga$_2$O$_3$ nanosheets, while those were 30%, 29% and 26% for the Ga$_2$O$_3$ nanosheets after 24 h irradiation. More importantly, the weight losses of the PE plastic bags, PP plastic boxes and PET plastic bottles were up to ca. 81%, 78% and 72% after 48 h irradiation over the Co-Ga$_2$O$_3$ nanosheets.
Figure S16 Cycling stability tests: another 100 mg commercial PE plastic bags were added to the system after 24 h irradiation, then the reaction system was vacuum-treated and refilled with high-purity air to reach an atmospheric pressure.

As shown in Figure S16, the formation rates of H\textsubscript{2}, CO and CO\textsubscript{2} for the Co-Ga\textsubscript{2}O\textsubscript{3} nanosheets did not show any obvious drop upon adding another 100 mg commercial PE plastic bags to the system after 24 h irradiation for the cycling measurements, suggesting their superb photocatalytic stability.

Figure S17 Photoconversion of reagent-grade PE powders over the Co-Ga\textsubscript{2}O\textsubscript{3} nanosheets and the Ga\textsubscript{2}O\textsubscript{3} nanosheets in a simulated sunlight (AM 1.5G, 100 mW/cm\textsuperscript{2}) at ambient temperature and pressure: the formation rates of H\textsubscript{2}, CO and CO\textsubscript{2}. The error bars represent the standard deviations of three independent measurements.

Taking commercial PE powders as example, the Co-Ga\textsubscript{2}O\textsubscript{3} nanosheets displayed H\textsubscript{2}, CO and CO\textsubscript{2} formation rates of 692.0, 177.8 and 476.4 μmol g\textsuperscript{-1} h\textsuperscript{-1}, while those of the Ga\textsubscript{2}O\textsubscript{3} nanosheets were 441.1, 97.6 and 297.7 μmol g\textsuperscript{-1} h\textsuperscript{-1}, respectively.
Figure S18 Photocatalytic water-splitting tests for the Co-doped Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets in N$_2$ atmosphere (no PE powders were added): the formation rates of H$_2$ and O$_2$ in 5 h. The error bars represent the standard deviations of three independent measurements.

As shown in Figure S18, H$_2$O could be directly split into O$_2$ and H$_2$ over the Co-doped Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets when no PE powders were added. The formation rates of H$_2$ and O$_2$ of the Co-doped Ga$_2$O$_3$ nanosheets were 352.0 and 164.9 µmol g$^{-1}$ h$^{-1}$, while those for the Ga$_2$O$_3$ nanosheets were 191.4 and 86.1 µmol g$^{-1}$ h$^{-1}$ respectively.

Figure S19 UV–vis absorption spectrum of the reaction solution after the photocatalytic water-splitting tests for 5 h over the Co-Ga$_2$O$_3$ nanosheets.

As shown in Figure S19, some amount of H$_2$O$_2$ was formed during the water splitting process over the Co-Ga$_2$O$_3$ nanosheets.
Figure S20  Synchrotron-based vacuum UV photoionization mass spectrometry (SVUV-PIMS) of the gas products after $^{13}$CO$_2$ photoreduction over the Co-Ga$_2$O$_3$ nanosheets at $h\nu$ = 14.5 eV.

As revealed in Figure S20, $^{13}$CO was detected after the CO$_2$ photoreduction experiments, which clearly showed that CO came from the reduction of CO$_2$.

Figure S21  The synchrotron-based vacuum UV photoionization mass spectrometry (SVUV-PIMS) of the gas products after 24 h irradiation: blank controlled experiments for the photoconversion of reagent-grade PE powders over the Co-Ga$_2$O$_3$ nanosheets at $h\nu$ = 14.5 eV. The reaction system was vacuum-treated three times to remove air completely, which was then pumped by high-purity N$_2$ to reach an atmospheric pressure.

As displayed in Figure S21, upon removing H$_2^{18}$O and $^{18}$O$_2$ from the reaction system, no C$^{16}$O$^{18}$O was detected in blank controlled experiments, further confirming that H$_2$O and O$_2$ participated in the oxidation of PE powders into CO$_2$. 
Figure S22 In situ ESR spectra during the photoconversion of reagent-grade PE powders over the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets with H$_2$O as solvent and DMPO as spin-trapping agent.

As shown in Figure S22, the ESR signals exhibited 1:2:2:1 quartet pattern in water solution, which could be assigned to the ·OH radicals captured by DMPO.

Figure S23 In situ ESR spectra during the photoconversion of reagent-grade PE powders over the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets with methanol as solvent and DMPO as spin-trapping agent.

As displayed in Figure S23, the ESR signals showed quartet pattern with the intensity of nearly 1:1:1:1 in methanol solution, which could be assigned to the superoxide radicals (O$_2^-$) captured by DMPO.
**Figure S24** UV–vis absorption spectrum for the reaction solution after 24 h irradiation of the reagent-grade PE photoconversion over the Co-Ga$_2$O$_3$ nanosheets.

**Figure S25** Density of states of (A) the Co-Ga$_2$O$_3$ nanosheets and (B) the Ga$_2$O$_3$ nanosheets. The yellow bars in A and B represent the valence band edge.
Figure S26 PL spectra for the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets.

Figure S27 CO$_2$ temperature programmed desorption (CO$_2$-TPD) measurements of the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets.
Figure S28 (A) Optimized crystal structure of the Ga$_2$O$_3$ nanosheets and (B) the corresponding differential charge density map. The value of isosurfaces is 0.007 eÅ$^{-3}$, while the yellow and blue contours manifest electron accumulation and depletion, respectively.

Figure S29 The differential charge density maps of *COOH for the Ga$_2$O$_3$ nanosheets, in which the yellow and blue contours manifest electron accumulation and depletion, respectively. The value of isosurfaces is 0.002 eÅ$^{-3}$.

As shown in Figure S28, the charge of Ga on the Ga$_2$O$_3$ nanosheets mainly localize on Ga atoms. The introduction of Co atoms causes the charge redistribution of the neighboring Ga atoms, and the charge of Ga atoms would shift to the Co side (Figure 3D), which helps to stabilize the *COOH and lower its formation energy (Figure S29, Figure 3B, Figure 3E).
Figure S30 The differential charge density maps of *H for Ga$_2$O$_3$ nanosheets, in which the yellow and blue contours manifest electron accumulation and depletion, respectively. The value of isosurfaces is 0.002 eÅ$^{-3}$.

As shown in Figure S30 and Figure 3C, 3F, the introduction of Co atoms results in the increased charge density around Co atoms that would tend to bond with the *H intermediates and hence lowers their formation energies.

Table S1
The formation rates of H$_2$, CO and CO$_2$ during the photoconversion of various commercial plastic products on the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets with a simulated sunlight (AM 1.5G, 100 mW/cm$^2$) at ambient temperature and pressure.

| Photocatalysts       | Products (μmol g$^{-1}$ h$^{-1}$) | PE plastic bags | PP plastic boxes | PET plastic bottles |
|----------------------|------------------------------------|-----------------|-----------------|--------------------|
| Co-Ga$_2$O$_3$       | H$_2$                              | 647.8           | 603.5           | 384.2              |
|                      | CO                                 | 158.3           | 147.2           | 100.6              |
|                      | CO$_2$                             | 419.3           | 389.1           | 258.9              |
| Ga$_2$O$_3$          | H$_2$                              | 408.0           | 392.7           | 218.3              |
|                      | CO                                 | 84.2            | 75.6            | 61.8               |
|                      | CO$_2$                             | 263.9           | 252.4           | 163.4              |
**Table S2**
The weight losses of commercial PE plastic bags, PP plastic boxes and PET plastic bottles for the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets with a simulated sunlight (AM 1.5G, 100 mW/cm$^2$) at ambient temperature and pressure after 24 h irradiation.

| Photocatalysts       | PE plastic bags | PP plastic boxes | PET plastic bottles |
|----------------------|-----------------|------------------|---------------------|
| Co-Ga$_2$O$_3$       | 53%             | 49%              | 42%                 |
| nanosheets           |                 |                  |                     |
| Ga$_2$O$_3$          | 30%             | 29%              | 26%                 |
| nanosheets           |                 |                  |                     |

**Table S3**
Control experiments: the formation rates of H$_2$, CO and CO$_2$ during the photoconversion of reagent-grade PE powders on the Co-Ga$_2$O$_3$ nanosheets and the Ga$_2$O$_3$ nanosheets with a simulated sunlight (AM 1.5G, 100 mW/cm$^2$) at ambient temperature and pressure when light, photocatalysts or PE powders was removed. The “n.d.” refers to “not detected”.

| Photocatalysts       | Products (μmol g$^{-1}$ h$^{-1}$) | No light | No photocatalysts | No PE powders |
|----------------------|-----------------------------------|----------|-------------------|---------------|
| Co-Ga$_2$O$_3$       | H$_2$                             | n.d.     | n.d.              | 329.3         |
| nanosheets           | CO                                | n.d.     | n.d.              | n.d.          |
|                      | CO$_2$                            | n.d.     | n.d.              | n.d.          |
| Ga$_2$O$_3$          | H$_2$                             | n.d.     | n.d.              | 175.5         |
| nanosheets           | CO                                | n.d.     | n.d.              | n.d.          |
|                      | CO$_2$                            | n.d.     | n.d.              | n.d.          |

Control experiments showed that only H$_2$ was detected when no PE powders was added in the photocatalytic system, suggesting that H$_2$ may be came from the reduction of water. No CO and CO$_2$ were detected upon light, photocatalysts or PE powders was removed, which firmly confirmed CO and CO$_2$ came from the photodegradation of reagent-grade PE powders by the photocatalysts.
Table S4
Control experiments: the formation rates of H\textsubscript{2}, CO and CO\textsubscript{2} during the photoconversion of reagent-grade PE powders on the Co-Ga\textsubscript{2}O\textsubscript{3} nanosheets and the Ga\textsubscript{2}O\textsubscript{3} nanosheets with a simulated sunlight (AM 1.5G, 100 mW/cm\textsuperscript{2}) at ambient temperature and pressure when 2 mmol/L AgNO\textsubscript{3} solution, or high-purity O\textsubscript{2}, or N\textsubscript{2} was used. The “n.d.” refers to “not detected”.

| Photocatalysts          | Products (μmol g\textsuperscript{-1} h\textsuperscript{-1}) | AgNO\textsubscript{3} | O\textsubscript{2} | N\textsubscript{2} |
|-------------------------|-------------------------------------------------------------|------------------------|---------------------|-------------------|
| Co-Ga\textsubscript{2}O\textsubscript{3} nanosheets | H\textsubscript{2}                                           | n.d.                  | 673.2              | 787.7             |
|                         | CO                                                        | n.d.                  | 175.6              | 76.5              |
|                         | CO\textsubscript{2}                                        | 735.6                 | 508.2              | 214.7             |
| Ga\textsubscript{2}O\textsubscript{3} nanosheets | H\textsubscript{2}                                           | n.d.                  | 430.8              | 505.6             |
|                         | CO                                                        | n.d.                  | 94.5               | 48.3              |
|                         | CO\textsubscript{2}                                        | 500.7                 | 312.9              | 139.8             |

Table S5
The calculation of carbon balance after the photodegradation of commercial plastic products on Co-Ga\textsubscript{2}O\textsubscript{3} nanosheets in simulated sunlight (AM 1.5G, 100 mW/cm\textsuperscript{2}) at ambient temperature and pressure.

| Plastic types | Carbon Losses (mmol) | CO\textsubscript{2}+CO (gas, mmol) | CO\textsubscript{2}+CO (dissolved, mmol) | Carbon Balance (%) |
|---------------|----------------------|-----------------------------------|------------------------------------------|--------------------|
| PE bags       | 3.79                 | 0.69                              | 2.88                                     | 94.2               |
| PP boxes      | 3.50                 | 0.64                              | 2.53                                     | 90.6               |
| PET bottles   | 2.19                 | 0.43                              | 1.65                                     | 95.0               |

Table S6 The calculation of carbon balance after the photodegradation of commercial plastic products on Ga\textsubscript{2}O\textsubscript{3} nanosheets in simulated sunlight (AM 1.5G, 100 mW/cm\textsuperscript{2}) at ambient temperature and pressure.

| Plastic type   | Carbon Losses (mmol) | CO\textsubscript{2}+CO (gas, mmol) | CO\textsubscript{2}+CO (dissolved, mmol) | Carbon Balance (%) |
|----------------|----------------------|-----------------------------------|------------------------------------------|--------------------|
| PE bags        | 2.14                 | 0.42                              | 1.56                                     | 92.5               |
| PP boxes       | 2.07                 | 0.39                              | 1.48                                     | 90.3               |
| PET bottles    | 1.35                 | 0.27                              | 0.99                                     | 93.3               |
**Table S7**
Free energy and free energy corrections (eV) for species.

| Species | \( E_{\text{DFT}} \) | ZPE | TAS | \( G \) |
|---------|-----------------|-----|-----|-----|
| \( \text{H}_2\text{O} \) | -14.21 | 0.56 | 0.67 | -14.32 |
| \( \text{H}_2 \) | -6.76 | 0.27 | 0.40 | -6.89 |
| \( \text{CO}_2 \) | -22.98 | 0.31 | 0.66 | -23.33 |
| \( \text{CO} \) | -14.79 | 0.13 | 0.60 | -15.26 |
| *\( \text{CO} \) | 0.22 | | 0.08 |
| *\( \text{COOH} \) | 0.64 | | 0.15 |
| *\( \text{H} \) | 0.176 | 0.02 |

**Table S8**
Free energy (eV) of the Co-Ga\(_2\)O\(_3\) nanosheets and the Ga\(_2\)O\(_3\) nanosheets with and without intermediates.

| Samples | G(*) | G(*COOH) | G(*CO) | G(*H) |
|---------|------|----------|--------|-------|
| Ga\(_2\)O\(_3\) nanosheets | -604.62 | -629.65 | -619.27 | -607.19 |
| Co-Ga\(_2\)O\(_3\) nanosheets | -606.95 | -632.92 | -622.62 | -609.71 |

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