Electronic Supplementary Information

Surface Activation of Cobalt Oxide Nanoparticles for Photocatalytic Carbon Dioxide Reduction to Methane

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Experimental Procedures

Chemicals. Cobalt(III) acetylacetonate (Co(acac)$_3$, 99.99%), oleylamine (70%), 1-dodecanethiol (98%), N-bromosuccinimide (NBS, 99%), (diacetoxyiodo)benzene (DIB, 98%) were purchased from Aldrich. Toluene, ethanol, and hexane were purchased from Junsei. All chemicals were used without further purification.

Synthesis of CoO nanoparticles. For the synthesis of CoO nanoparticles, Co(acac)$_3$ (0.10 g, 0.28 mmol) and oleylamine (18 mL) were put into a three-neck round bottom flask and stirred for 4 h at 130 ^{o}C under a nitrogen atmosphere. Then, the temperature increased to 180 ^{o}C, and maintained for 45 min. After cooling down to room temperature, the product was precipitated by centrifugation at 10,000 rpm for 30 min with the addition of ethanol as an anti-solvent. The product was then re-dispersed in toluene (10 mL) without the addition of any surfactants.

Sulfur treatment of CoO nanoparticles. During the synthesis of CoO nanoparticles, 1-dodecanethiol (0.072 mL, 0.30 mmol) was added after the 15 min reaction at 180 ^{o}C, and the resulting mixture was additionally stirred for 30 min at the same temperature. After cooling down to room temperature, the product was precipitated by centrifuged at 10,000 rpm for 30 min with ethanol. The final product was re-dispersed in toluene (10 mL).

Surface activation of CoO nanoparticles. For the oxidation of surface of CoO nanoparticles, one-fifth (2.0 mL) of the particle dispersion and the oxidant (1 equiv with respect to the amount of CoO nanoparticles) were mixed in a sealed vial with a stirring bar. Then, the mixture was heated to 125 ^{o}C, and stirred for 8 min. After cooling down to room temperature, the product was precipitated by centrifugation at 10,000 rpm for 30 min with the addition of hexane as an anti-solvent. The product was washed with ethanol several times and re-dispersed in deionized water for photocatalytic reaction.

Synthesis of Co_3O_4 nanoparticles. Co_3O_4 nanoparticles were synthesized by full oxidation of CoO. The process was the same as the surface activation, but the reaction mixture was stirred for 30 min at 125 °C. The product was cooled down, and was precipitated by centrifugation at 10,000 rpm for 30 min with the addition of hexane as an anti-solvent. The product was washed with ethanol several times and re-dispersed in deionized water or ethanol for afterward use.

Photocatalytic CO_2 reduction. For photocatalytic CO_2 reduction experiments, an appropriate amount (2.7 mg) of the catalyst was dispersed in deionized water (20 mL). The resulting aqueous dispersion was transferred to a quartz reactor, and was purged with supercritical-fluid grade CO_2 gas for 15 min to generate a CO_2-saturated solution. Photocatalytic CO_2 reduction was performed by irradiation using Xe lamp (300 W, Oriel) with a 10 cm IR water filter. The power of Xe lamp was 0.5 W/cm^2 measured by Newport Power Meter (Model 843-R). During the reaction, the gas product was collected by using a needle type probe. The gas samples were analyzed by gas chromatography (YL6100, GC) consisting of thermal conductivity detector (TCD) and flame ionization detector (FID). For the isotope experiment, the gas samples were analyzed by GC-MS (Agilent 5977B GC/MSD) equipped with a HP-molesieve (Agilent, 0.32 mm) capillary column. The possible liquid products were quantified by ^1H NMR (Bruker 400Mhz NMR, BBFO probe) using a solvent presaturation technique to suppress the water peak, in which 700 μL of sample was mixed with 35 μL D_2O, and 0.52 μL dimethyl sulfoxide (DMSO) as an internal standard.

Calculation of quantum yield for photocatalytic CO_2 reduction. A quantum yield was calculated by the following equation:

$$QY\,(\%) = \frac{n_e}{n_p} \times 100 = \frac{8n_{CH_4}}{n_p} \times 100$$

where n_p is the number of photons irradiated on the samples, n_e is the number of electrons participated in the photocatalytic CO_2 reduction, and n_{CH4} is the number of generated CH_4 molecules. The light source is Thorlabs M405LP1 Mounted light emitting diode (LED, 405 nm, 100 mW).

To calculate the number of photons, the energy of each photons was given by:

$$E\,(photon) = \frac{h \times c}{\lambda} = \frac{6.626 \times 10^{-34}\,[j \cdot sec] \times 3 \times 10^{8}\,[m/sec]}{405 \times 10^{-9}\,[m]} = 4.9 \times 10^{-19}\,[\frac{j}{[photon]}]$$

Where h is Planck's constant and c is the speed of light.

The LED power was varied at the range of 35-70 mW, the radius of irradiated area was 8 mm, and the radius of sensor was 5 mm, therefore the amount of photons per 60 min was calculated by the following equation:

$$Power = 35\,[mW] \rightarrow \frac{35 \times 10^{-3} \times 60\,[min] \times 60[sec] \times {}^{\pi 8mm^2}\!/_{\pi 5mm^2}}{4.9 \times 10^{-19}\,[\frac{j}{[photon]}]} = 6.6 \times 10^{20}\,[photons]$$

$$Power = 70\,[mW] \rightarrow \frac{70 \times 10^{-3} \times 60\,[min] \times 60[sec] \times {}^{\pi 8mm^2}\!/_{\pi 5mm^2}}{4.9 \times 10^{-19}\,[\frac{j}{[photon]}]} = 1.3 \times 10^{21}\,[photons]$$

XANES analysis. X-ray absorption near edge structure (XANES) of cobalt oxide catalysts over Co K-edge, 7709 eV in cobalt foil was analyzed at Pohang Accelerator Laboratory (7D-XAFS beamline in PLS-II) using Si(111) crystal as a monochromator where the beam energy and ring current were 2.5 GeV and 300 mA, respectively. The step and duration time for XANES were 0.40 eV and 2.0 s. For data processing, Athena implemented in Demeter program package (0.9.25) was used for normalization.

Mott-Schottky plot Measurement. The flat-band edge positions of CoO and Co_3O_4 were measured by electrochemical impedance measurement. The working electrode was made by coating of CoO and Co_3O_4 (0.30 mg) on fluorine-doped tin oxide (FTO) conducting glasses with an area of 0.50 cm^2. The 0.4 M Na_2SO_4 solution (pH 6.8) was used as an electrolyte, a platinum wire was used as a counter electrode, and Ag/AgCl (in 3.0 M NaCl solution) was used as a reference electrode. Electrochemical impedance spectroscopy measurement was carried out by using a CH Instruments Electrochemical Workstation and the potential was scanned with the step of 0.05 V with 5 Hz frequency. Potential conversion between Ag/AgCl and NHE is given by E(NHE) = E(Ag/AgCl) + 0.212 V.

Characterization. The nanoparticles were characterized by transmission electron microscopy (TEM, Philips F20 Tecnai operated at 200 kV, KAIST). The elemental mapping images were analyzed by using Talos F200X operated at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer. The samples for XRD were prepared by drop casting the nanoparticles on glass substrates. The UV-visible absorption and emission spectra were collected using a Shimadzu UV-

3600 spectrophotometer with a 1-cm quartz cuvette at ambient temperature. X-ray photoelectron spectroscopy (XPS) was conducted by using a K-alpha spectrometer with an Al Kα X-ray source.

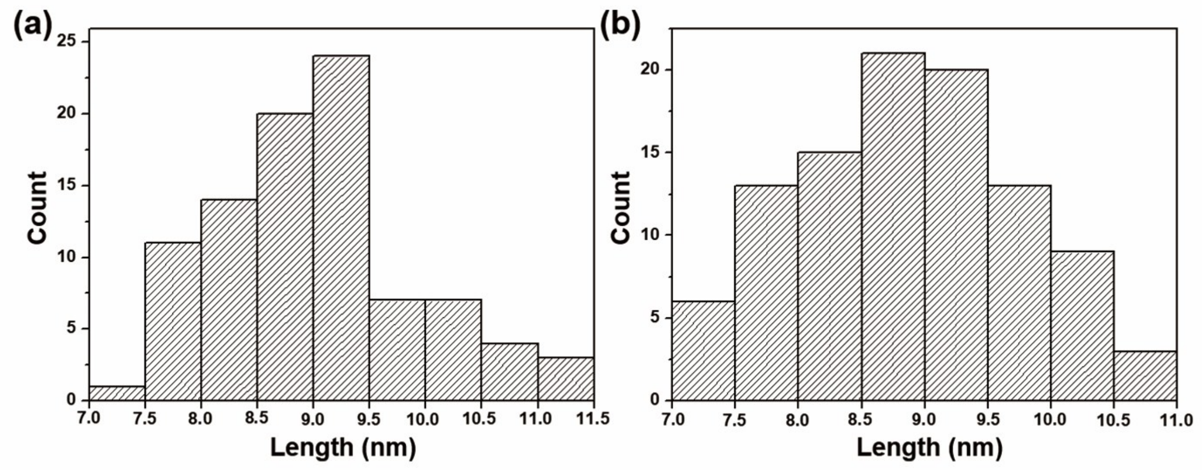

Fig. S1 Size distribution of (a) bare CoO, and (b) NBS treated CoO.

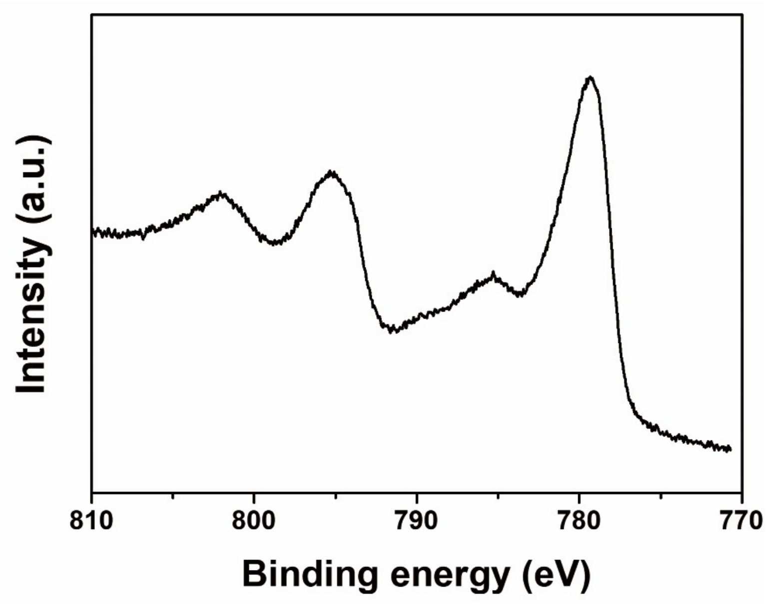

Fig. S2 XPS spectrum of CoO nanoparticles in the Co 2p region.

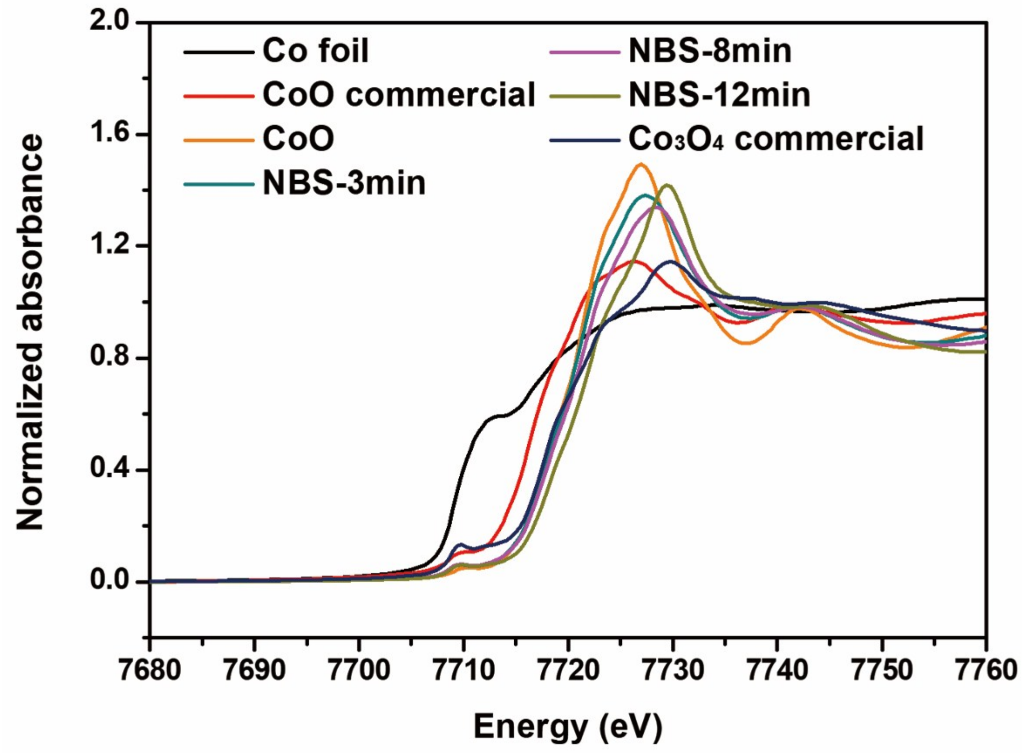

Fig. S3 Co K-edge XANES spectra of Co foil, commercial CoO, CoO nanoparticles, NBS-treated CoO nanoparticles for 3, 8, 30 min, and commercial Co_3O_4.

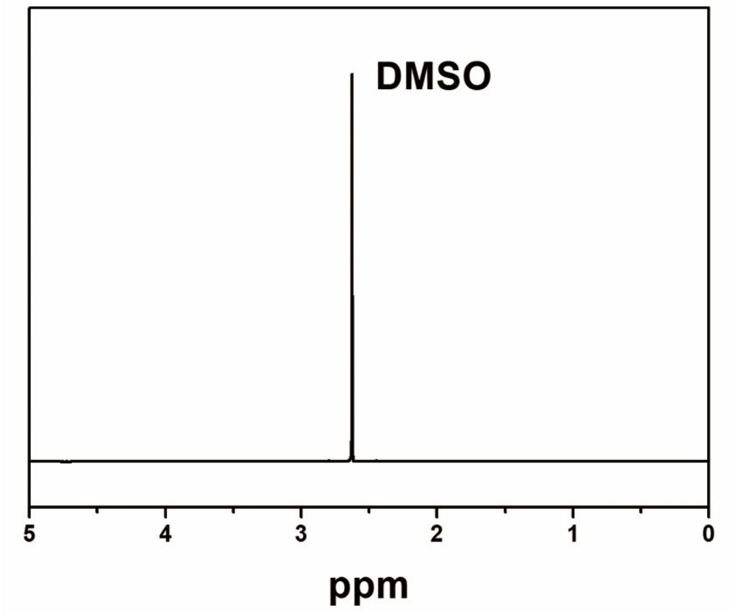

Fig. S4 ^{1}H-NMR spectra of the solvent after the photocatalytic CO_2 reduction for 2 h. The peak presented was DMSO as an internal standard.

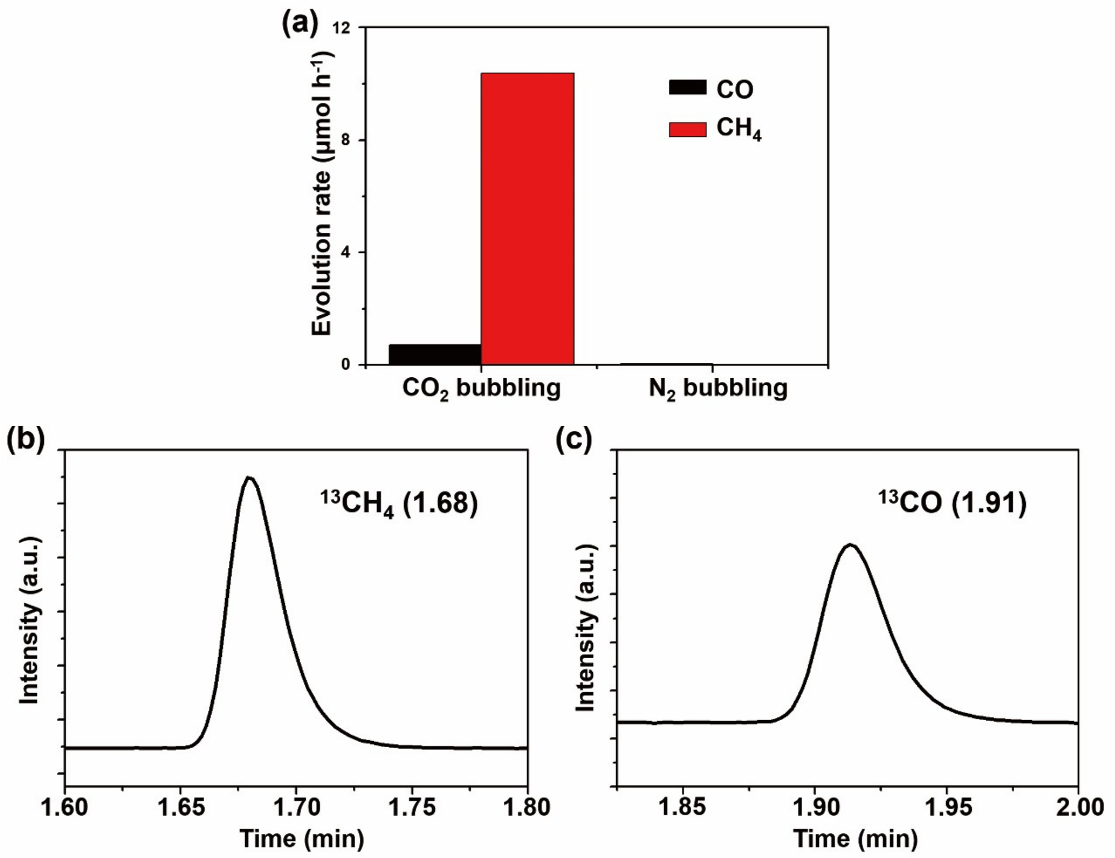

Fig. S5 (a) Photocatalytic evolution rates with CO_2 and N_2 bubbling using CoO/Co_3O_4 nanoparticles. GC-MS analysis of (b) $^{13}CH_4$ and (c) ^{13}CO generated in the photocatalytic reduction of $^{13}CO_2$ using CoO/Co_3O_4 nanoparticles.

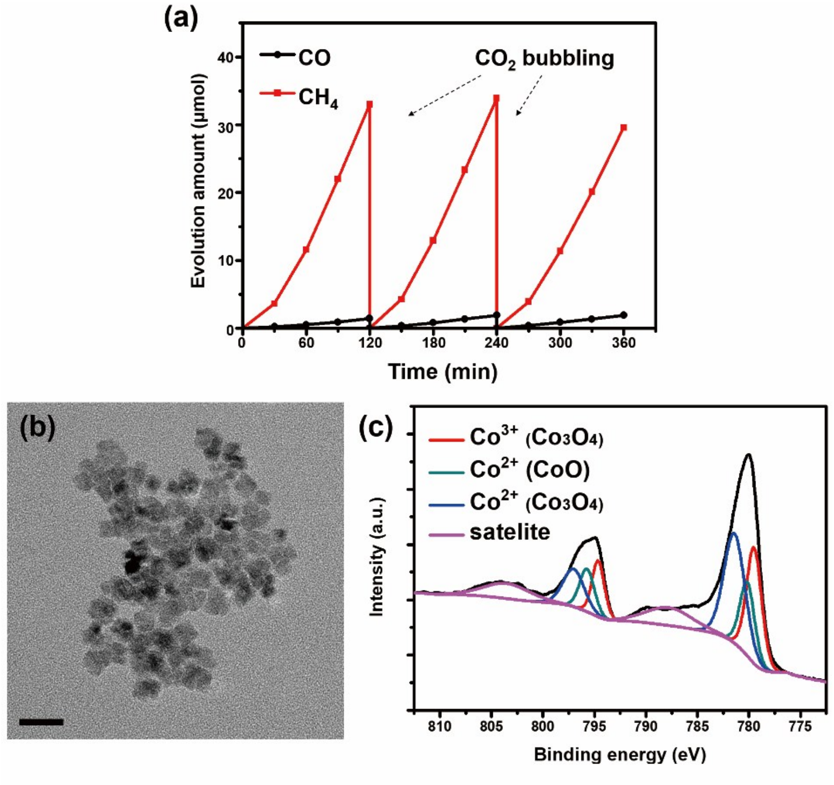

Fig. S6 (a) Stability test of photocatalytic CO_2RR using CoO/Co_3O_4 nanoparticles. (b) TEM image, and (c) Co 2p XPS spectra of CoO/Co_3O_4 nanoparticles after three repetitive photocatalytic reactions. The bar represents (b) 20 nm.

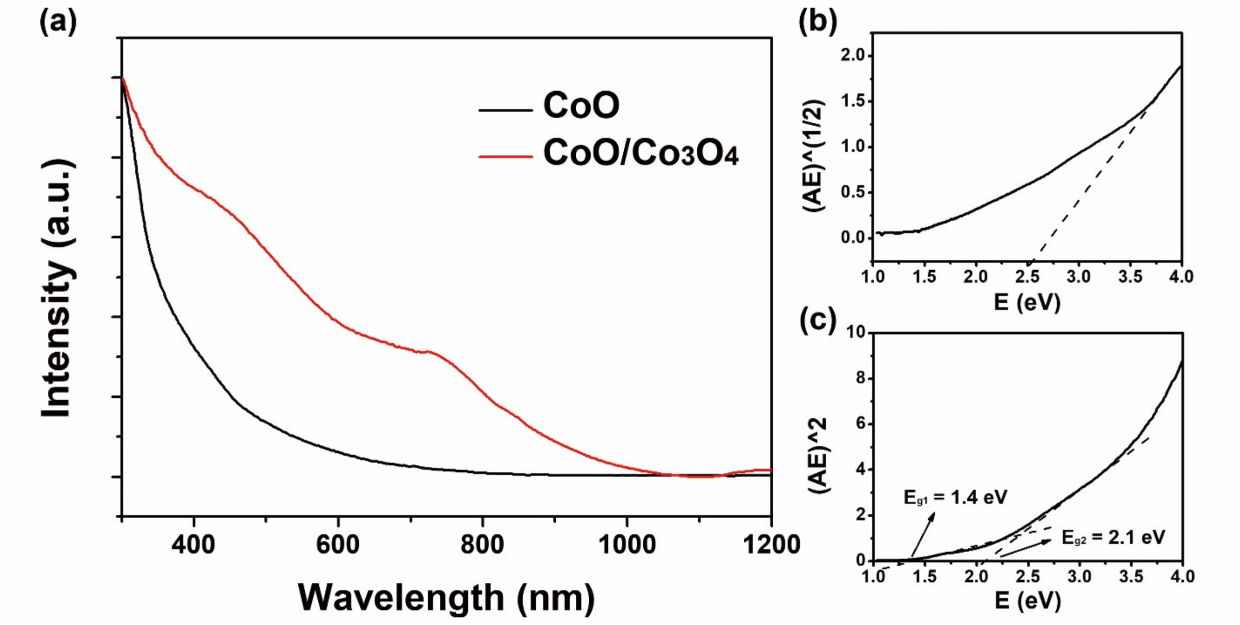

Fig. S7 (a) UV-visible absorption spectra of (black) CoO and (red) CoO/Co_3O_4 nanoparticles. Tauc plots for (b) CoO and (c) CoO/Co_3O_4 nanoparticles.

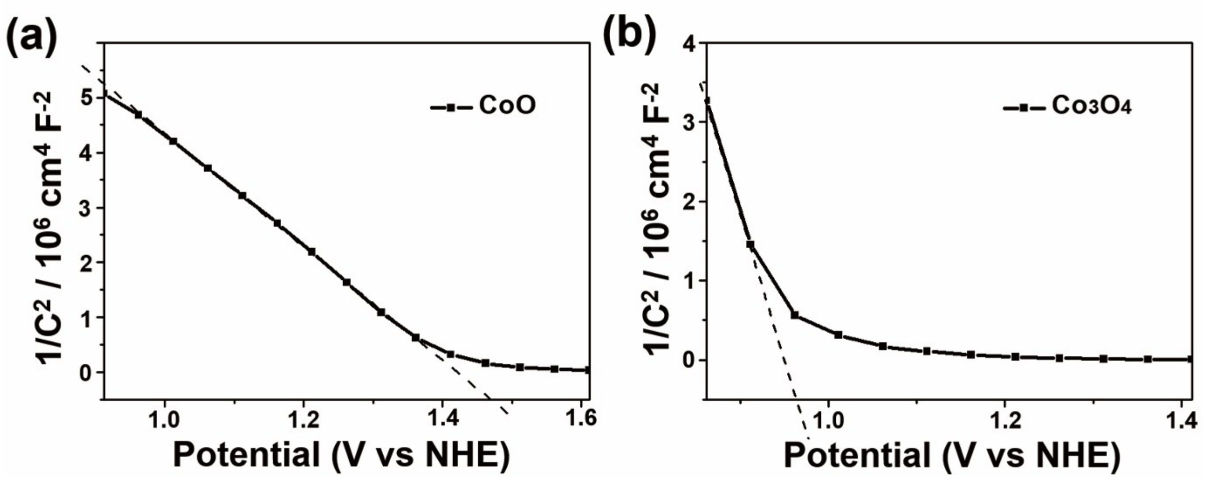

Fig. S8 Mott-Schottky plots for (a) CoO and (b) Co_3O_4 nanoparticles according to the impedance measurements.

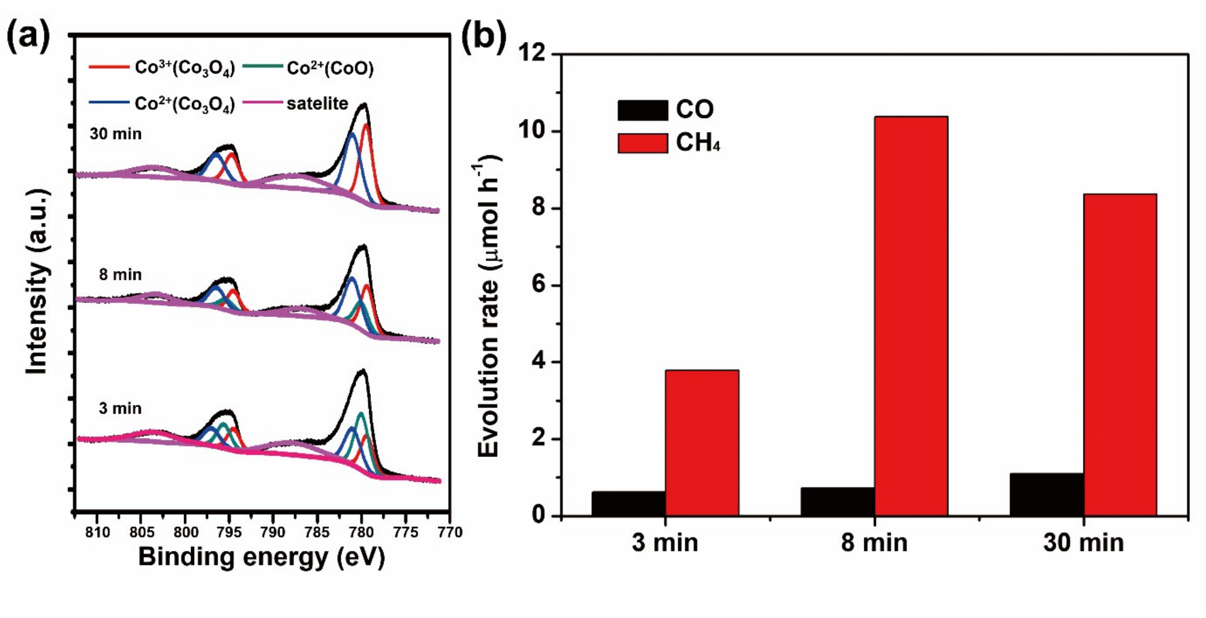

Fig. S9 (a) XPS spectra and (b) photocatalytic CH_4 evolution rates of CoO/Co_3O_4 nanocatalysts treated with NBS for 3, 8, and 30 min.

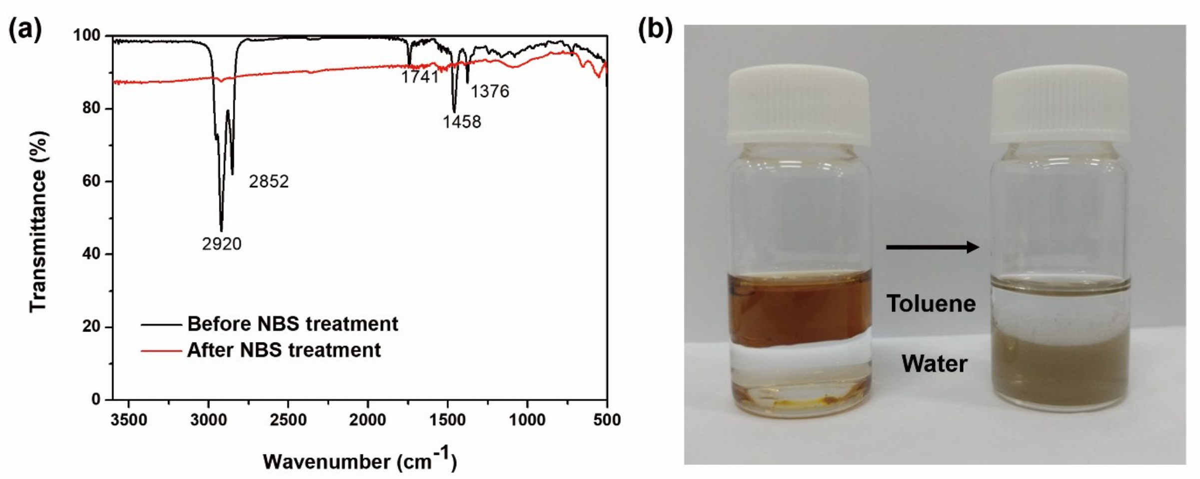

Fig. S10 (a) Fourier transform infrared spectra of (black) before and (red) after the NBS treatment. (b) Photograph showing successful transfer of CoO nanoparticles from toluene to water phase by the NBS treatment.

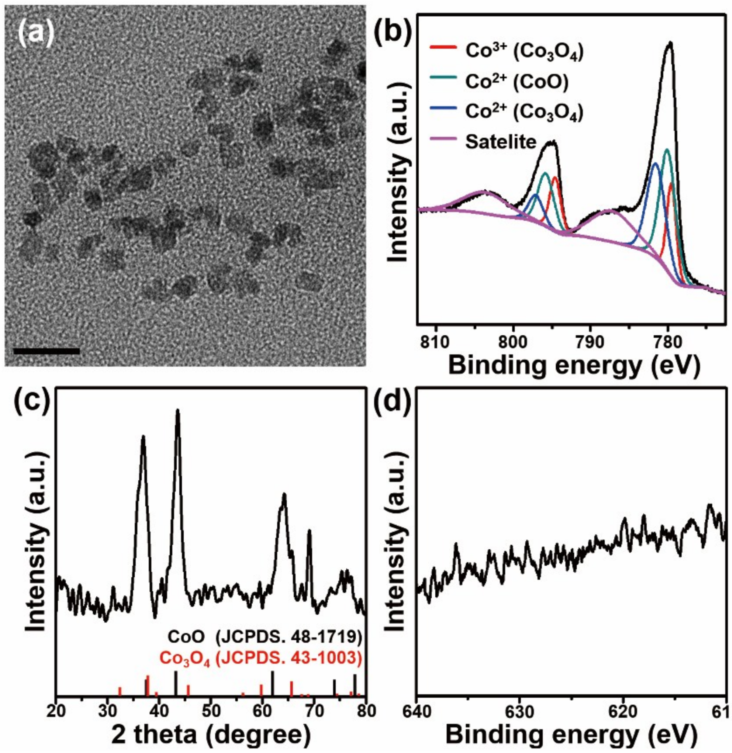

Fig. S11 (a) TEM image, (b) XPS (Co 3p), (c) XRD, and (d) XPS (I 3d) spectra of DIB- treated CoO/Co_3O_4 nanoparticles. The bar represents 20 nm.

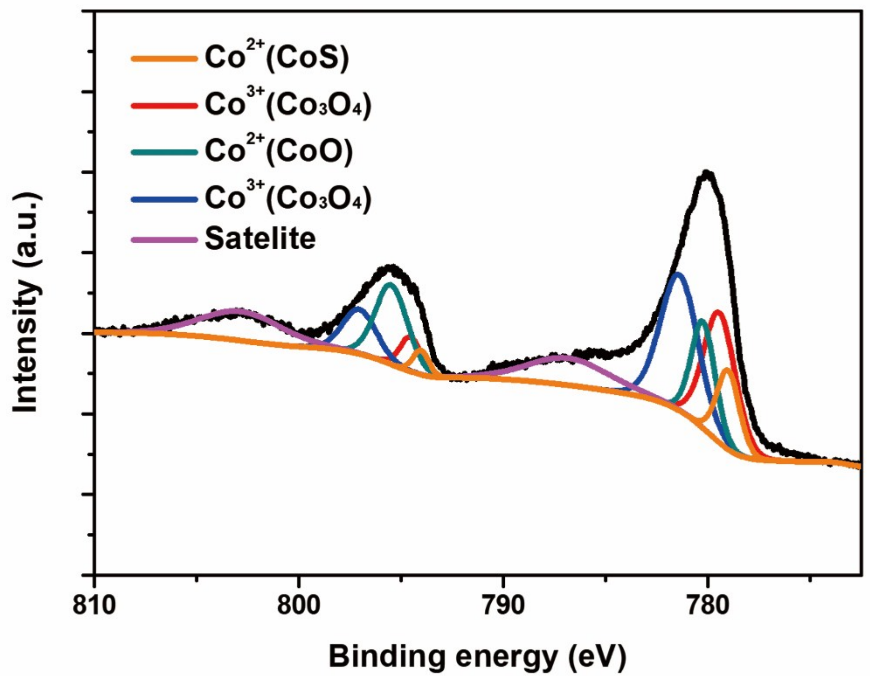

Fig. S12 XPS spectrum in the Co 2p region of S-doped CoO/Co$_3$O$_4$ nanoparticles after the NBS treatment.

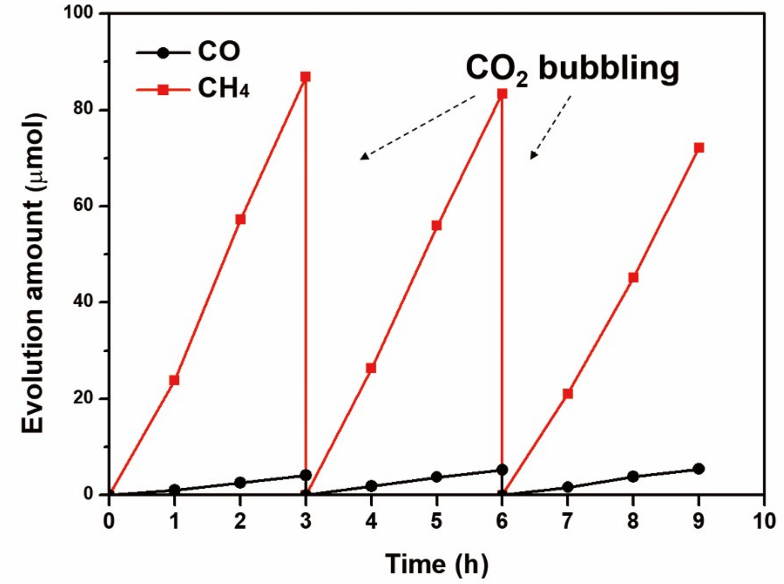

Fig. S13 Stability test of photocatalytic CO$_2$RR using S-doped CoO/Co$_3$O$_4$ nanoparticles.

Table S1. Summary of catalytic systems for photocatalytic CO_2 reduction

Catalyst	Light source	Reaction medium	Major Product	Activity	Reference
S-doped CoO/Co_3O_4	**300 W Xe lamp (0.5 W/cm^2)**	**CO_2 in water**	**CH_4**	**10 mmol/g·h (28 μmol/h)**	**This work**
Co_3O_4	200 W Xe lamp with an AM 1.5G filter	CO_2 vapor with adding H_2O	CO	46.3 μmol/g·h	Wang et al. (ref. 1)
ZnO-Cu_2O	300 W Xe lamp	CO_2 in water, 0.2 M Na_2CO_3	CH_4	1.1 mmol/g·h	Song et al. (ref. 2)
Nafion/Pd-TiO_2	300 W Xe lamp	CO_2 in water, 0.2 M Na_2CO_3	CH_4	45 μmol/g·h	Choi et al. (ref. 3)
TiO_2-F (Anatase or Rutile)	300 W Xe lamp with an AM 1.5 filter	CO_2 and H_2O vapor	CH_4, CO	5.6 μmol/g·h, 5.1 μmol/g·h	Yin et al. (ref. 4)
C_3N_4-Pt+$NaNbO_3$	300 W Xe lamp with a UV cutoff filter ($\lambda > 420$ nm).	CO_2 and H_2O vapor	CH_4	6.4 μmol/g·h	Zou et al. (ref. 5)
SiC@MoS_2	300 W Xe lamp with a UV cutoff filter ($\lambda > 420$ nm)	CO_2 vapor with adding H_2O	CH_4, O_2	323 μL/g·h, (13.0 μmol/g·h) 621 μL/g·h (25.0 μmol/g·h)	Li et al. (ref. 6)
Pt/C-In_2O_3	300 W Xe lamp	CO_2 in water, TEOA	CO, CH_4	126.6 μmol/h (633 μmol/g·h), 27.9 μmol/h (139.5 μmol/g·h)	Goodenough et al. (ref. 7)
$ZnIn_2S_4$-In_2O_3	300 W Xe lamp with a 400 nm long pass cutoff filter	CO_2 in water, TEOA	CO	3075 μmol/g·h	Lou et al. (ref. 8)

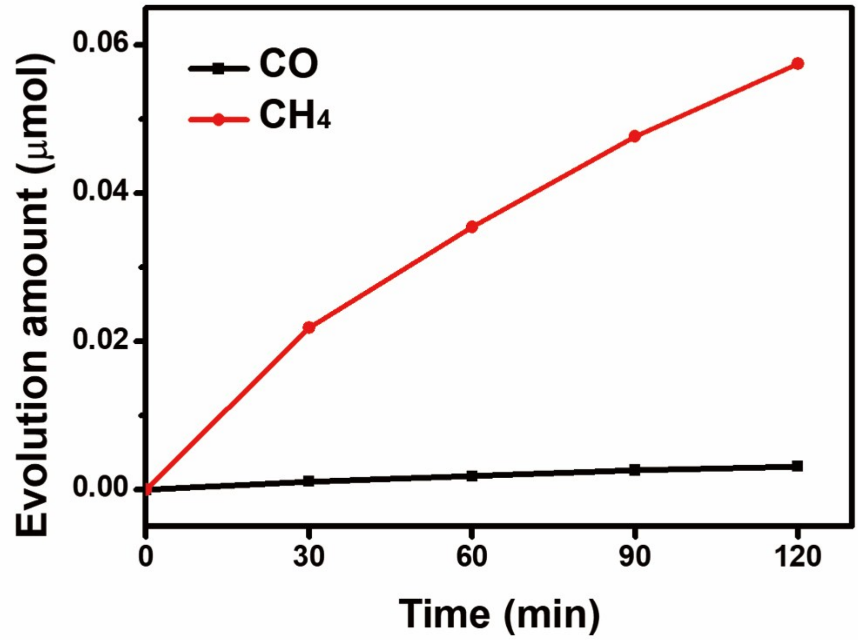

Fig. S14 Photocatalytic evolution amount along the reaction progress using S-doped CoO/Co_3O_4 nanoparticles by irradiation of simulated solar light with a AM 1.5G filter. The same amount (2.7 mg) of catalyst was used.

Table S2. Summary of catalytic systems for aqueous photocatalytic CO_2 reduction by irradiation with a AM 1.5 G filter.

Catalyst	Light source	Reaction medium	Major Product	Activity	Reference
S-doped CoO/Co_3O_4	**300 W Xe lamp with AM 1.5G filter (0.2 W/cm^2)**	**CO_2 in water**	**CH_4**	**10.6 μmol/g·h (QY = 2.3% with 405 nm LED)**	**This work**
CdS with Co-porphyrin Nickel terpyridine complexes	0.1 W/cm^2 with UV cutoff filter (λ > 420 nm) and AM 1.5G filter	CO_2 in water, 0.1 M TEOA	CO	QY = 0.28%	Reisner et al. (ref. 9)
$CsPbBr_3$ QD/graphene oxide	100 W Xe lamp with AM 1.5G filter	CO_2 in ethyl acetate	CO, CH_4	4.9 μmol/g·h, 2.5 μmol/g·h	Su et al. (ref. 10)
MnO_x@TiO_2@CuPt	0.1 W/cm^2 with AM 1.5G filter	CO_2 in water, 0.1 M Na_2CO_3, 0.1 M $KHCO_3$	CO	84.2 μmol/g·h	Gong et al. (ref. 11)

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