Supplementary information

Barium titanate photocatalysts with silver-manganese dual cocatalyst for carbon dioxide reduction with water

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Experimental Section

Preparation of samples

A phase diagram of barium titanates (a BaO-TiO_2 system) was proposed in literature.[1] $BaTi_nO_{2n+1}$ (n=1, 5) and $Ba_{2(n-1)}Ti_{4n+1}O_{10n}$ (n=2,3,4) were prepared by a solid state reaction method.[2-4] Briefly, the precursors, $BaCO_3$ (Rare Metallic Co., Ltd.) and TiO_2 (rutile, Kojundo Chemical Lab. Co., Ltd) with stoichiometric molar ratio were mixed for about 20 minutes in an alumina mortar and calcined at 1273 K, 4 h for $BaTiO_3$ (BT), at 1523 K, 10 h for $Ba_6Ti_{17}O_{40}$ (B6T17), at 1423 K, 10 h for $Ba_4Ti_{13}O_{30}$ (B4T13), at 1523 K, 10 h for $Ba_2Ti_9O_{20}$ (B2T9), and at 1373 K, 4 h for $BaTi_5O_{11}$ (BT5), respectively.

A flux method was used in the preparation of $BaTi_2O_5$ (BT2) with NaCl (Kishida Chemical Co., Ltd.) and KCl (Nacalai Tesque, Inc.) as a binary flux according to the literature.[5] In short, $BaCO_3$, TiO_2 and the binary flux (NaCl-KCl, 1:1) were mixed with in an overall stoichiometric ratio of 1:2:20, the obtained powder was heated at 1148 K for 9 h. The powder after heating was collected and washed 3 times with hot water of 353 K to remove the flux. The powder after filtration was collected and then dried at 373 K for 24 h.

Although Ag cocatalyst was mainly loaded by using photodeposition method, an impregnation (IMP) method was also used to load Ag cocatalyst on the prepared barium titanate samples for the photocatalytic CO_2 reduction as follows. 2 g of the prepared barium titanates and 372 μl of 0.5 M $AgNO_3$ was dispersed into 100 mL distilled water. The obtained suspension was stirred magnetically and dried up at 353 K, followed by calcined in a muffle furnace at 723 K for 2 h.

Photocatalytic reaction test

The reactor for the photocatalytic reaction test was shown in Figure S1.

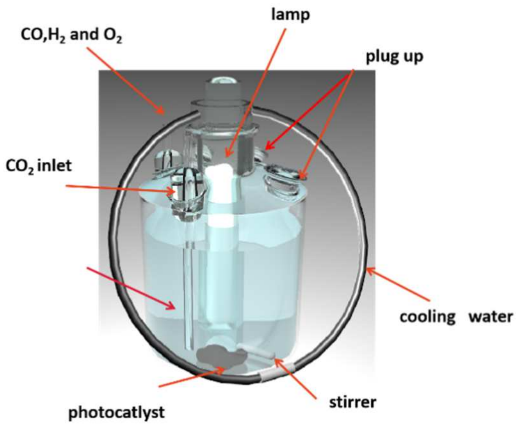

Fig. S1 Image of the inner-irradiation reactor used in the present study.

Analysis of hydrogen peroxide

To confirm hydrogen peroxide (H_2O_2) formation, permanganate titration in neutral conditions were conducted.[6, 7] After the photocatalytic reaction test, 10 mL of 0.2 mM $KMnO_4$ solution was used as reference, 300 μL solution from reactions after filtration or 0.3 mM H_2O_2 solution were added into $KMnO_4$ solution. The remaining concentration of $KMnO_4$ was determined by the absorbance of solution at λ_{max} at 525 nm measured by UV-vis spectroscopy in a transmission mode, from which the amount of H_2O_2 produced was calculated.

Results and discussion

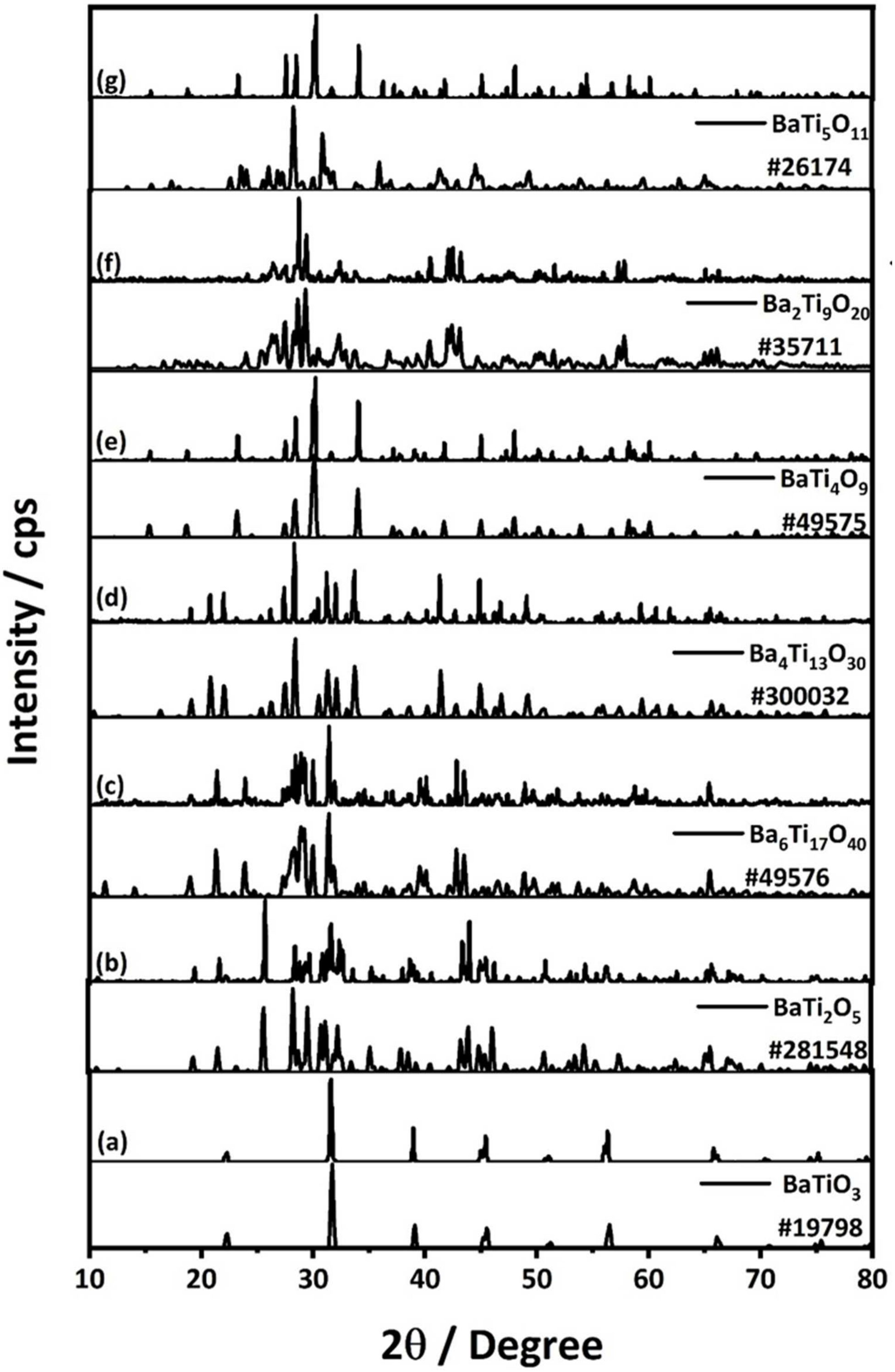

Fig. S2 XRD patterns of the samples, (a) BT, (b) BT2, (c) B6T17, (d) B4T13, (e) BT4, (f) B2T9, and (g) B5T11 with corresponding references from ICSD database.

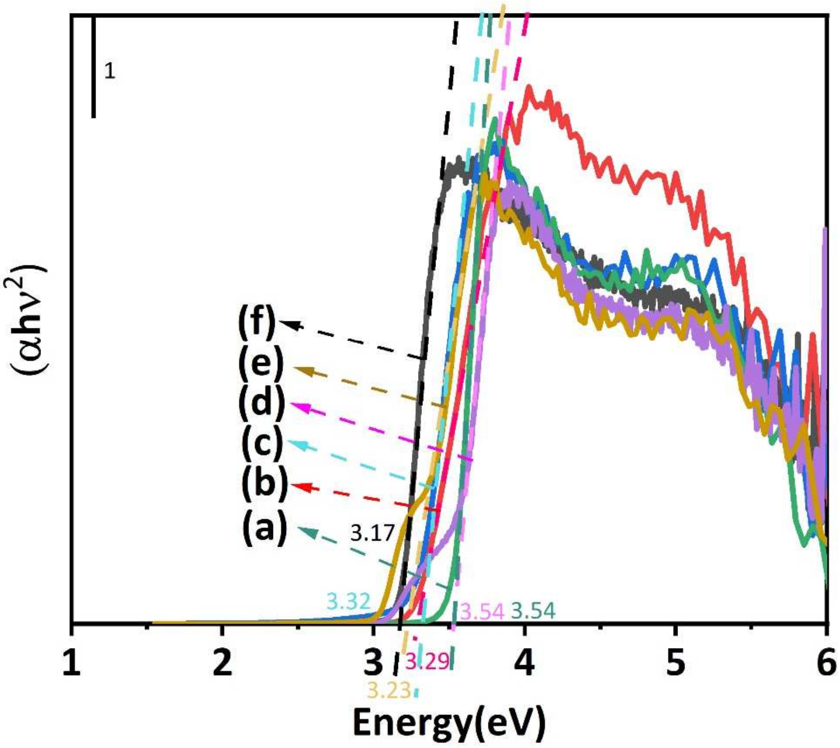

Fig. S3 Tauc plots of prepared B4T13 (a), BT2 (b), B6T17 (c), BT4 (d), B2T9 (e), and BT (f) samples.

Table S1 Estimated bandgap and bottom of conduction band of the samples.

Entry	Samples	Bandgap (eV) [a]	Estimated bottom of conduction Band (eV)[b]
1	BT	3.17	-0.43
2	BT2	3.29	-0.55
3	B6T17	3.32	-0.58
4	B4T13	3.54	-0.80
5	BT4	3.54	-0.80
6	B2T9	3.23	-0.49

[a] The bandgap was estimated from each DR UV-vis spectrum (Fig. S3).

[b] The conduction band was estimated from the bandgap and the assumption that the top of their valence band are very close to each other.[8]

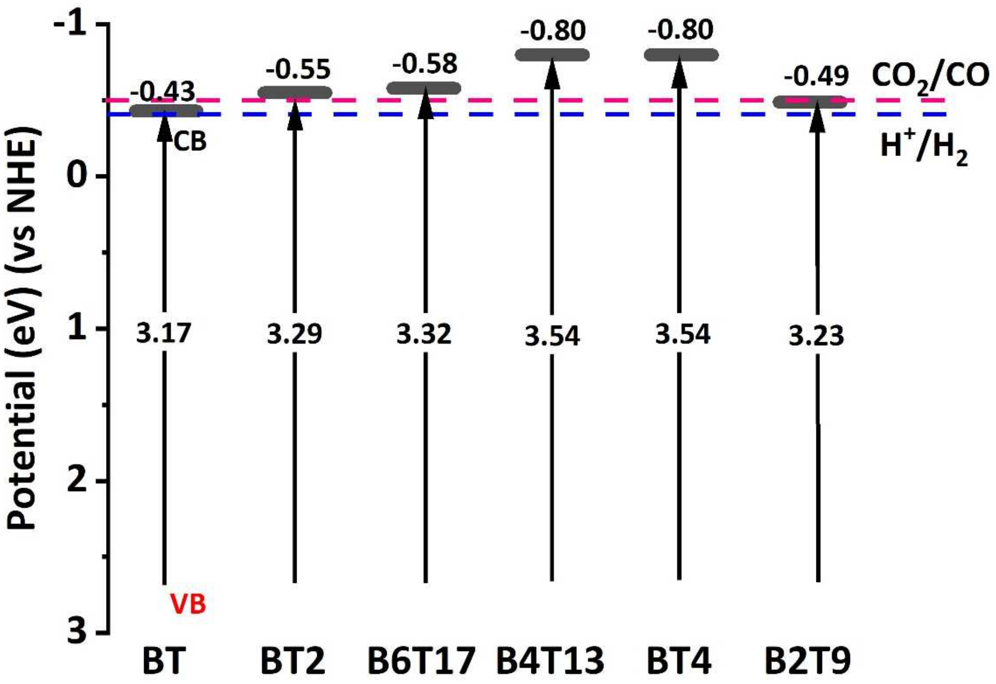

Fig. S4 The potential of the conduction band bottom of the barium titanate samples. The values are from Table S3.

Table S2 Crystal structure parameters of barium titanates.

Entry	Crystal	a, b, c (Å)	α, β, ɣ (°)	Crystal system	Cell volume (Å^3)	PF (%)^a
1	BT	3.789, 5.675, 5.693	90.0, 90.0, 90.0	Orthorhombic	128.85	71.56
2	BT2	9.409, 3.932, 16.907	90.0, 103.0, 90.0	Monoclinic	608.21	68.56
3	B6T17	9.887, 17.097, 18.918	90.0, 98.7, 90.0	Monoclinic	3160.90	70.62
4	B4T13	170.62, 9.862, 14.051	90.0, 90.0, 90.0	Orthorhombic	2364.3	66.12
5	BT4	14.530, 3.790, 6.290	90.0, 90.0, 90.0	Orthorhombic	346.38	61.03
6	B2T9	14.358, 14.095, 7.477	95.5, 100.6, 89.9	Triclinic	1480.45	67.18

[a] Crystal packing factor (PF) was calculated as the ratio of volume of atoms to the unit cell volume.

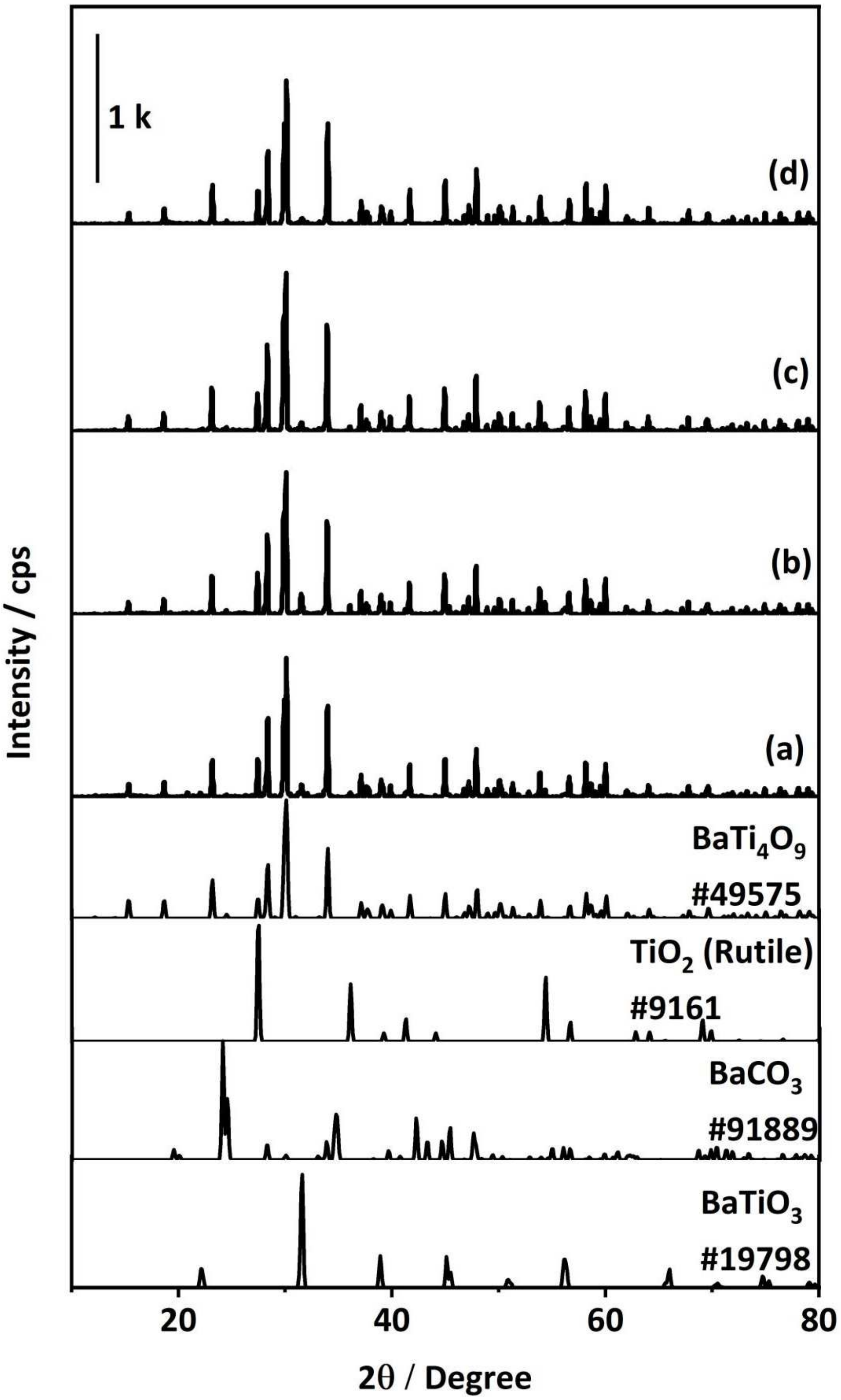

Fig. S5 XRD patterns of the BT4(*x*,1273) samples prepared by different holding time (*x*) of 5 (a), 10 (b), 20 (c), and 50 h (d) and references. Calcination was carried out at 1273 K. The intensity of the diffraction patterns from the database as references are normalized.

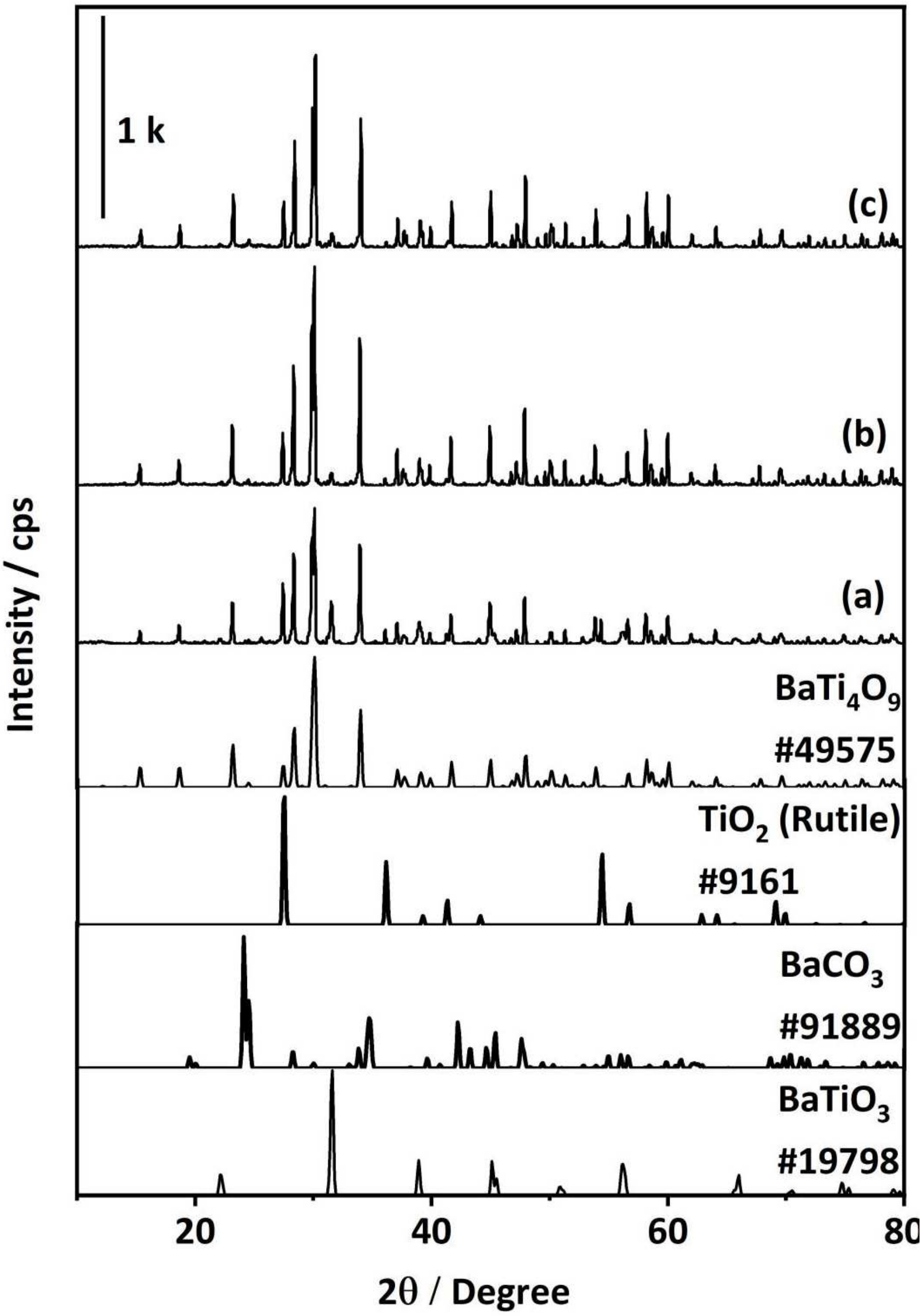

Fig. S6 XRD patterns of BT4(20,*y*) prepared by different calcination temperature (*y*) of 1173 (a), 1273 (b), and 1373 K (c) and references. Calcination was carried out at each temperature for 20 h. The intensity of the diffraction patterns from the database as references are normalized.

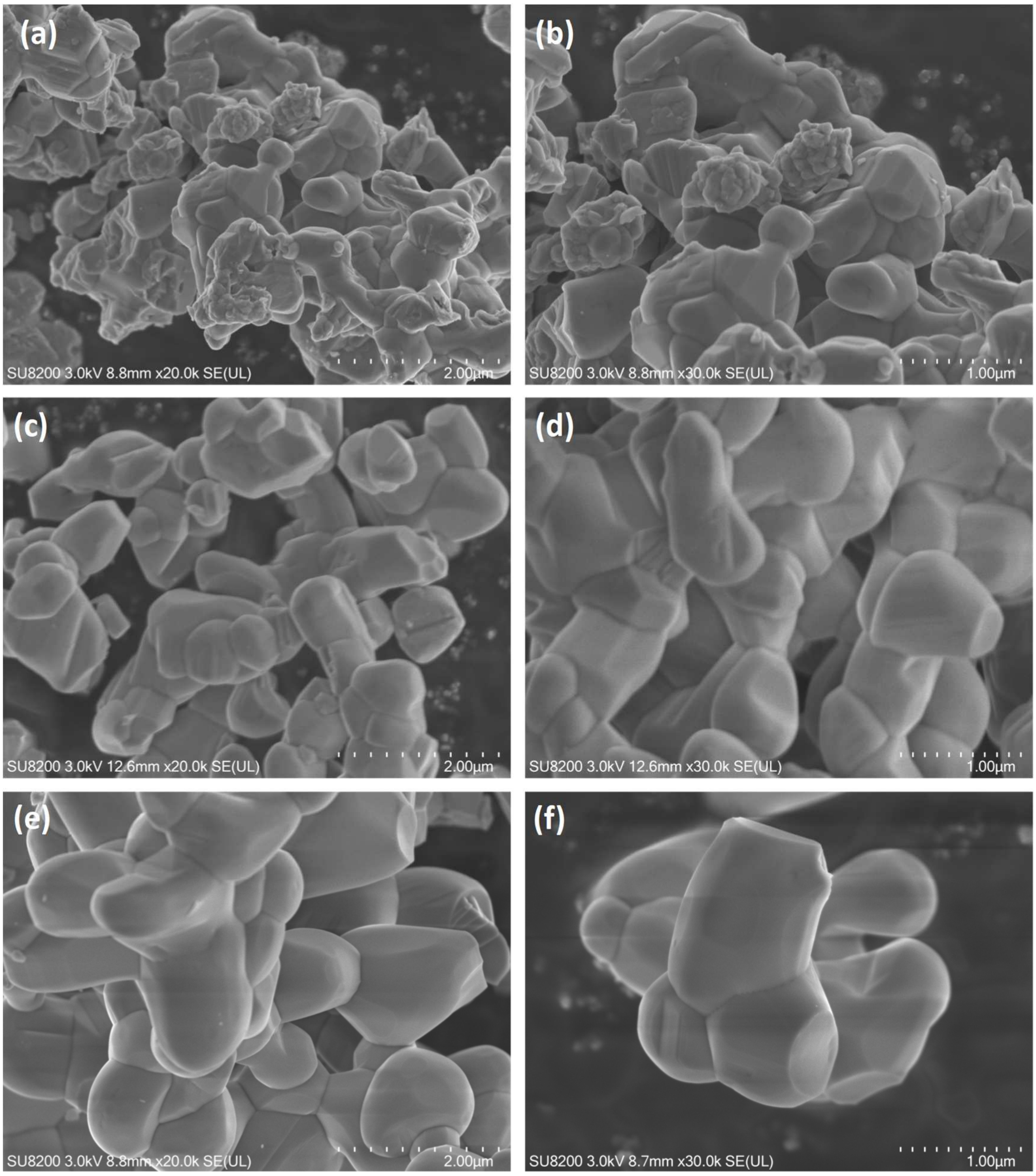

Fig. S7 SEM images of the BT4(20,*y*) samples prepared by different calcination temperature (*y*) of 1173 (a), 1273 (c), and 1373 K (e) and amplified SEM image of BT4 under 1173 (b), 1273 (d), and 1373 K (f). Calcination was carried out at each temperature for 20 h.

Table S3 SSA of bare BT4(*x*,*y*) samples prepared by different holding time and calcination temperature.

Entry	Sample	Specific Surface Area (SSA) [a] / m^2·g^{-1}	CO formation rate (R_{CO}) / µmol h^{-1}
1	BT4(5,1273)	2.27	2.54
2	BT4(10,1273)	1.78	2.89
3	BT4(20,1273)	1.54	4.08
4	BT4(50,1273)	1.48	4.16
5	BT4(20,1173)	2.04	1.97
6	BT4(20,1373)	1.43	2.11

[a] Estimated by a BET method from N_2 adsorption at 77 K

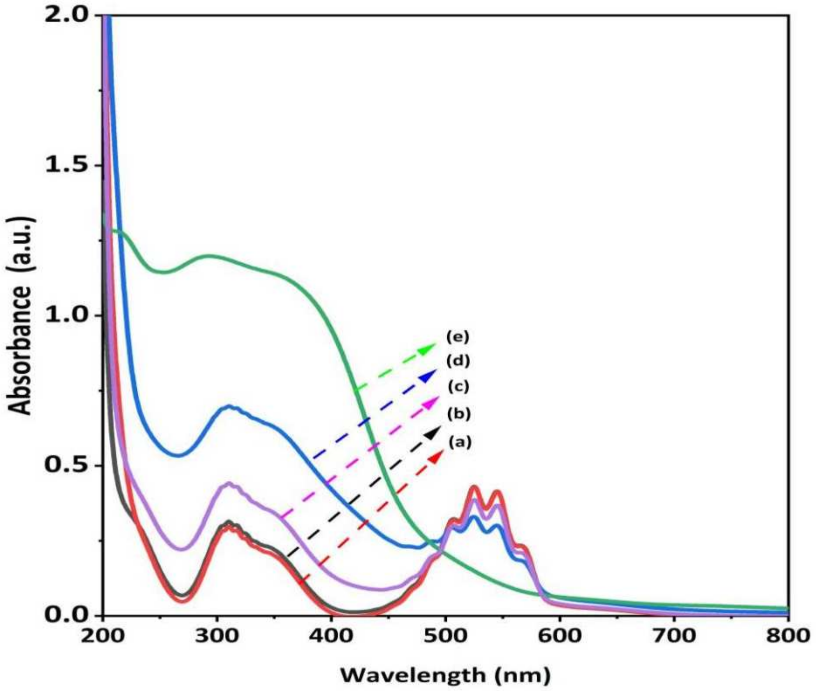

Fig. S8 UV-vis spectra for the measurement of the concentration of H_2O_2 in the resulting aqueous solution after the photocatalytic reaction test for 3 h with the photocatalyst samples, (a) Ag(1)/BT4, (c) MnO_x(0.740)/BT4, and (d) Ag(1)-MnO_x(0.492)/BT4. As reference, (b) the aqueous solution of $KMnO_4$ and (e) the aqueous solution of H_2O_2 after the reaction with $KMnO_4$. The BT4 sample used was the BT4(20,1273) sample.

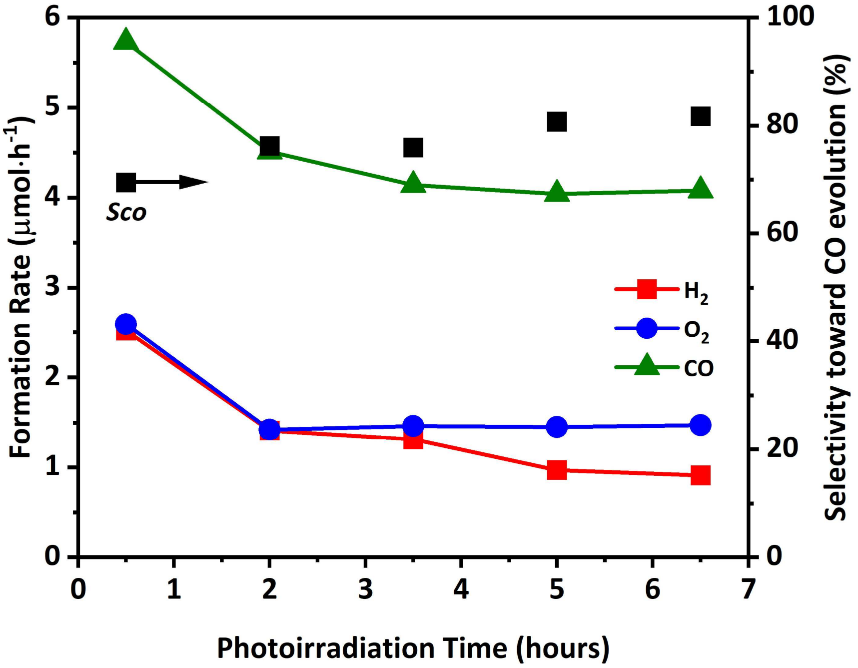

Fig. S9 Time course of formation rates of H_2 (red), O_2 (blue), and CO (green) and selectivity toward CO evolution (S_{CO}, square) in the photocatalytic reaction tests for CO_2 reduction with water as electron donor with the Ag(1)-MnO_x(0.492)/BT4(20,1273) sample. This photocatalytic reaction test was carried out with 0.3 g of catalyst in 360 mL of an aqueous solution of 1.0 M $NaHCO_3$, which conditions were different from those in the main text (Fig. 2, 4, and 5).

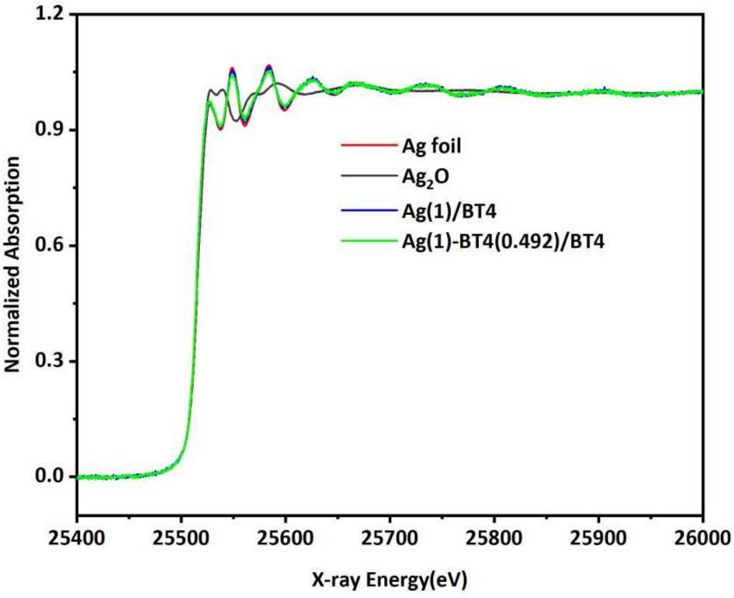

Fig. S10 XANES of the prepared samples and references.

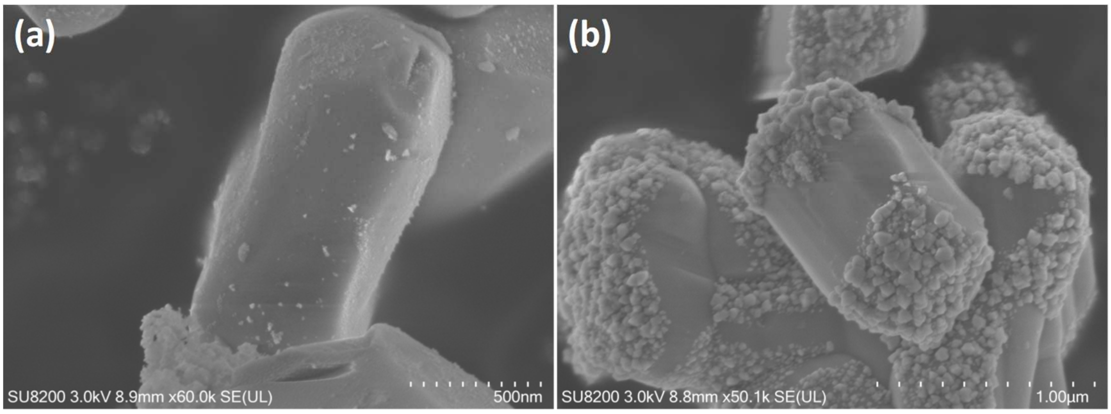

Fig. S11 SEM images of (a) Pt/BT4 and (b) PbO_2/BT4. The BT4 sample used was the BT4(20,1273) sample. The Pt (1 wt%) was loaded by the PD method without any sacrificial reagent while the Pb (3.62 wt%) was loaded by the PD method with $NaIO_3$ as a sacrificial reagent.

Schemes for the photodeposition used to obtain the Pt/BT4 and PbO_2/BT4 samples (Fig. S9) are as follows:

$Pt^{4+}+4e^{-}\rightarrow Pt$ (S1)

$2H_2O+4h^{+}\rightarrow 2O_2+4H^{+}$ (S2)

where eq. S1 shows the reduction of platinum cations and eq. S2 shows the oxidation of water to maintain charge balance in the aqueous solution.

$Pb^{2+}+2h^{+}+2H_2O\rightarrow PbO_2+4H^{+}$ (S3)

$IO_3^{-}+6e^{-}+6H^{+}\rightarrow I^{-}+3H_2O$ (S4)

where eq. S3 shows the oxidation of lead cations to its oxide states and eq. S4 shows the corresponding reduction of iodate to iodide ions.

References

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