

Electronic Supplementary Information

One-step aerosol synthesis of a double perovskite oxide (KBaTeBiO_6) as potential catalysts for CO_2 photoreduction

Hao Zhou,^a Mojgan Kouhnavard,^a Sungyoon Jung,^a Rohan Mishra,^b Pratim Biswas^{a*}

^aAerosol and Air Quality Research Laboratory

^aDepartment of Energy, Environmental and Chemical Engineering

^bInstitute of Materials Science & Engineering

Washington University in St. Louis

St. Louis, Missouri 63130, USA

* Corresponding author, pbiswas@wustl.edu

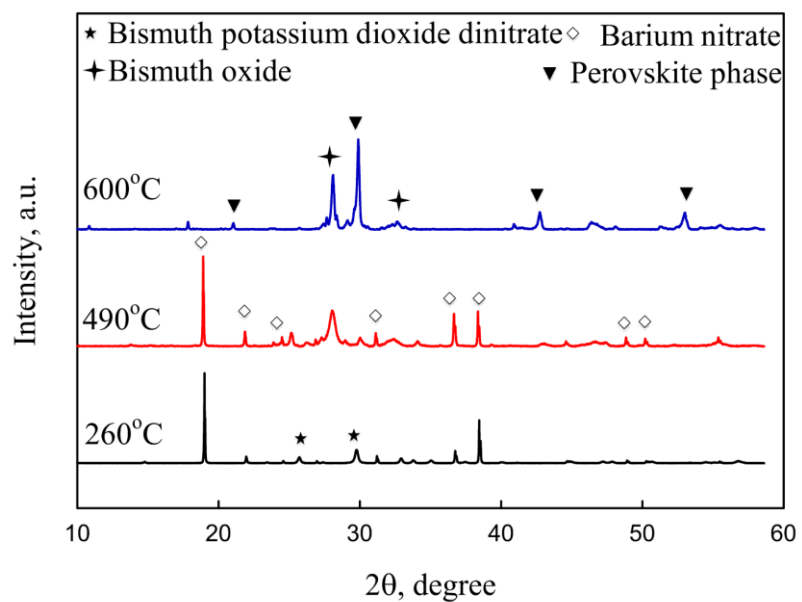


Figure S1. XRD patterns of KBaTeBiO_6 for 0.025M equimolar precursor heated at a rate of 10 °C/min

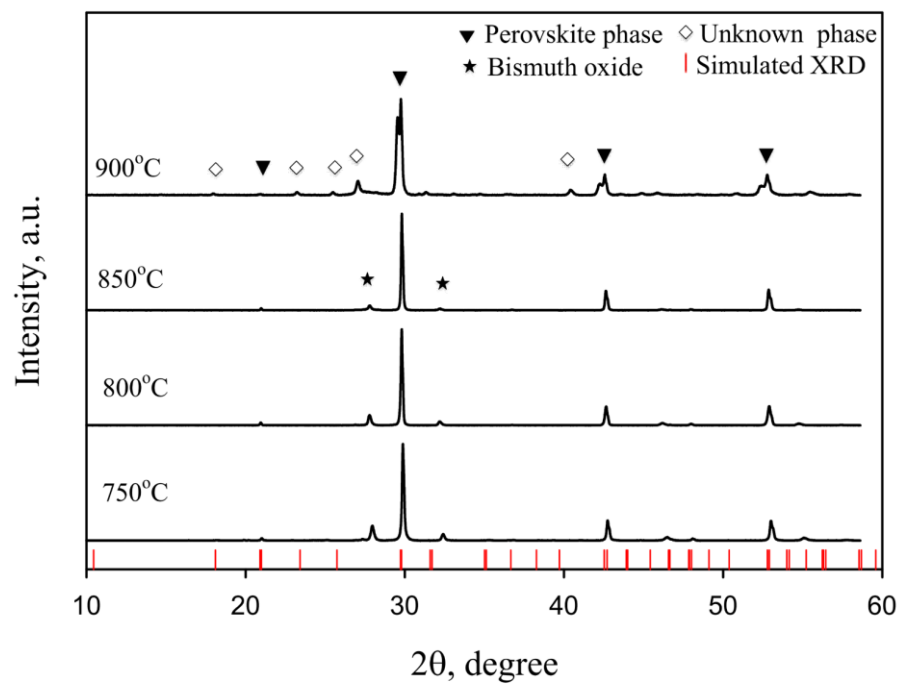


Figure S2. XRD patterns of KBaTeBiO₆ under different temperatures for 0.01M equimolar precursor

Table S1. The actual cation ratio under different conditions

No.	K:Ba:Te:Bi	Flow rate /L min ⁻¹	T/°C	C _{Ba} / M	The residence time τ_{res} /s	The reaction time τ_r /s
1	1:1:1:1	1.8	650	0.025	4.8	175.0
2	1:1:1:1	1.8	750	0.025	4.4	30.1
3	1:1:1:1	1.8	850	0.025	4.0	7.1
4	1:1:1:1	1.8	900	0.025	3.8	3.8
5	1:1:1:1	1.8	950	0.025	3.6	2.1
6	1:1:1:1	1.8	1000	0.025	3.5	1.2
7	1:1:1:1	0.9	900	0.025	7.6	3.8
8	1:1:1:1	3.6	900	0.025	1.9	3.8
9	1:1:1:1	4.5	900	0.025	1.5	3.8
10	1:1:1:1	1.8	900	0.050	3.8	3.8
11	1:1:1:1	1.8	900	0.010	3.8	3.8

Table S2. The actual cation ratio under different conditions

No.	K:Ba:Te:Bi	Flow rate/ L min ⁻¹	T/°C	C _{Ba} /M	C _{HNO₃} /M	K	Ba	Te	Bi	A/B
1	1:1:1:1	1.8	650	0.025	0.625	0.35	1.00	0.99	0.99	0.68
2	1:1:1:1	1.8	750	0.025	0.625	0.24	1.00	0.86	0.90	0.70
3	1:1:1:1	1.8	850	0.025	0.625	0.27	1.00	0.78	0.72	0.85
4	1:1:1:1	1.8	900	0.025	0.625	0.29	1.00	0.66	0.59	1.03
5	1:1:1:1	1.8	950	0.025	0.625	0.23	1.00	0.75	0.61	0.9
6	1:1:1:1	1.8	1000	0.025	0.625	0.19	1.00	0.77	0.62	0.86
7	1:1:1:1	0.9	900	0.025	0.625	0.09	1.00	0.83	0.51	0.95
8	1:1:1:1	3.6	900	0.025	0.625	0.32	1.00	0.77	0.77	0.84
9	1:1:1:1	4.5	900	0.025	0.625	0.39	1.00	0.85	0.83	0.83
10	1:1:1:1	1.8	900	0.050	1.25	0.33	1.00	0.83	0.76	0.84
11	1:1:1:1	1.8	900	0.010	0.625	0.13	1.00	0.68	0.57	0.90
12	1:1:1:1	1.8	850	0.010	0.625	0.14	1.00	0.74	0.64	0.83
13	1:1:1:1	1.8	800	0.010	0.625	0.20	1.00	0.73	0.79	0.79
14	1:1:1:1	1.8	750	0.010	0.625	0.15	1.00	0.86	0.87	0.66
15	1:1:1:0.8	1.8	850	0.010	0.625	0.18	1.00	0.72	0.50	0.97
16	1:1:1:0.8	1.8	900	0.025	0.625	0.25	1.00	0.67	0.51	1.06

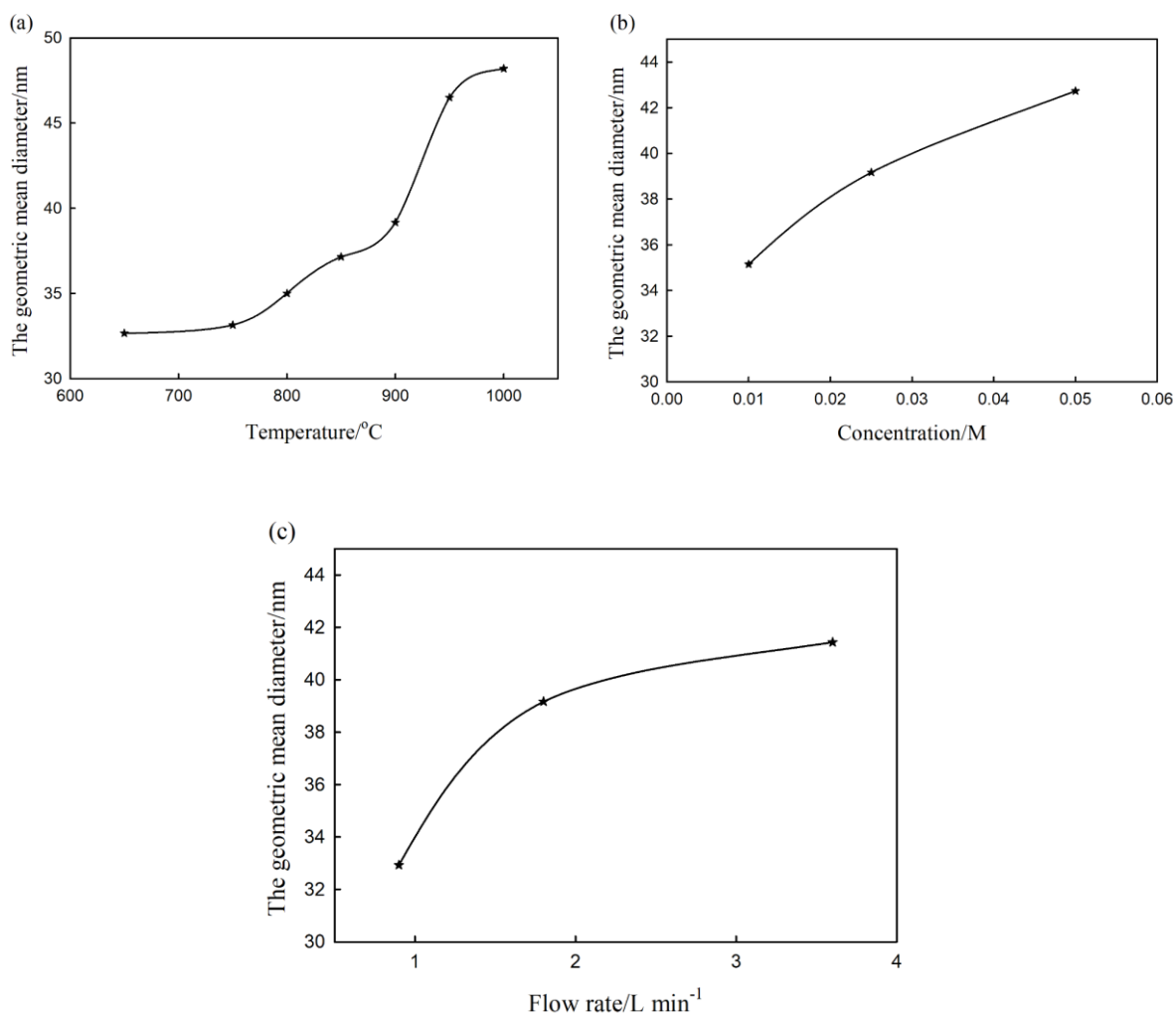
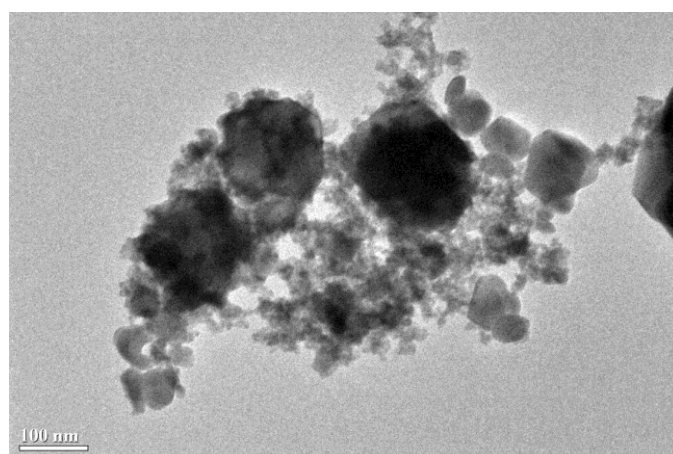
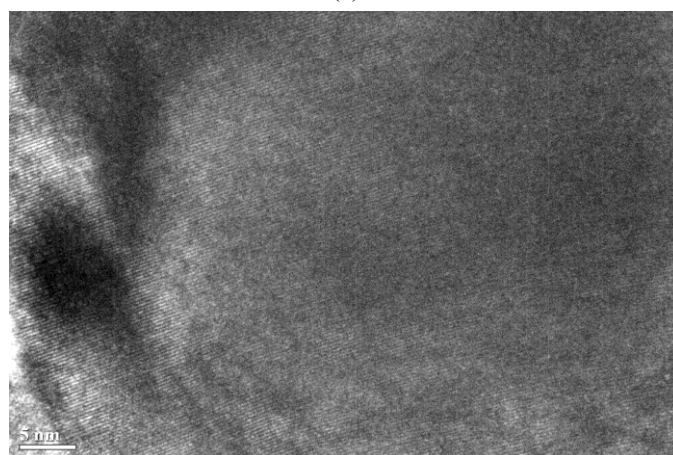


Figure S3. Geometric mean diameter of nanoparticles for a) different temperatures (0.025M, equimolar, 1.8L min^{-1}); b) different concentrations (equimolar, 900°C , 1.8L min^{-1}); c) different flow rates (0.025M, equimolar, 900°C)



(a)



(b)

Figure S4. a) TEM image and b) HR-TEM of the single-phase perovskite oxide KBaTeBiO_6 synthesized by FuAR

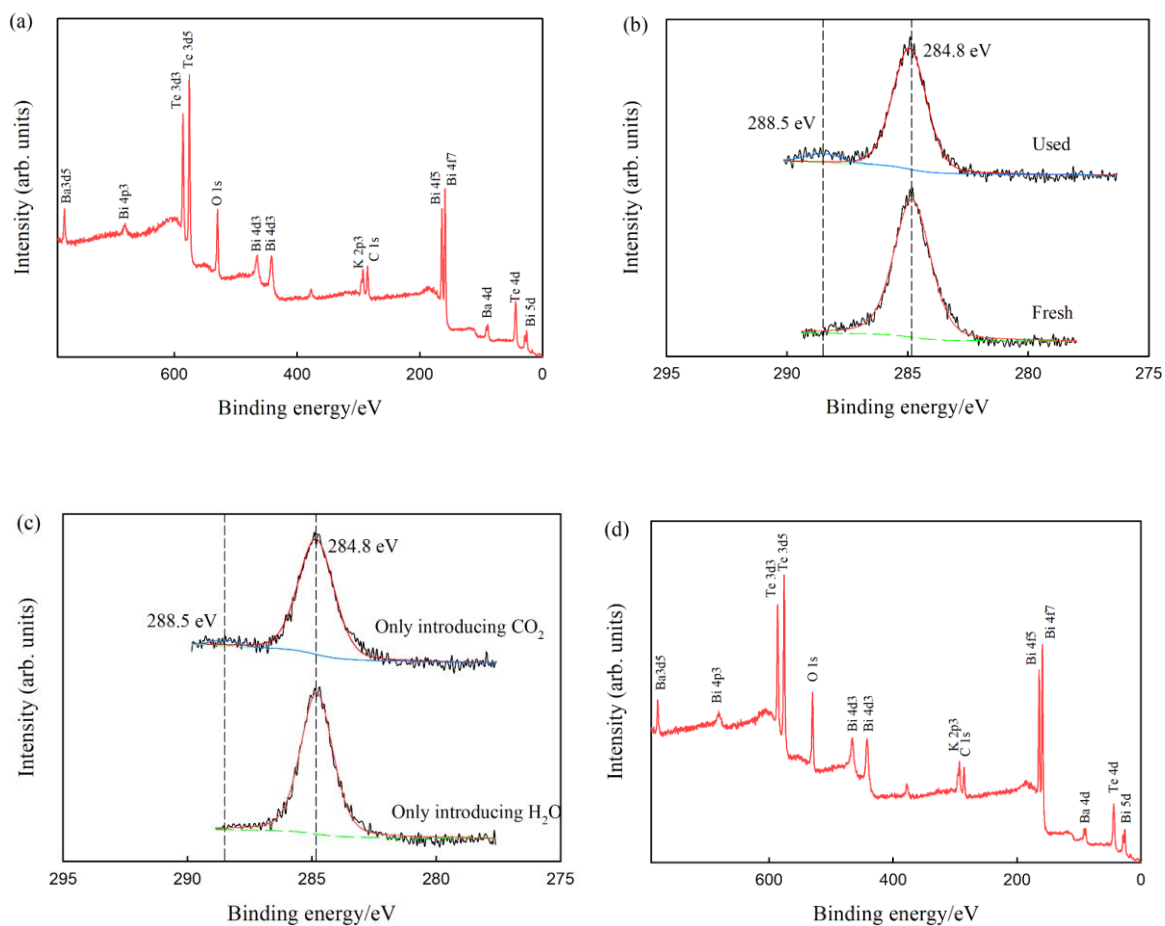


Figure S5. XPS spectra of a) fresh sample; b) high-resolution C 1s for fresh and used sample after photoreduction; c) high-resolution C 1s for used sample after only introducing CO₂ and only introducing H₂O; d) used sample after only introducing H₂O

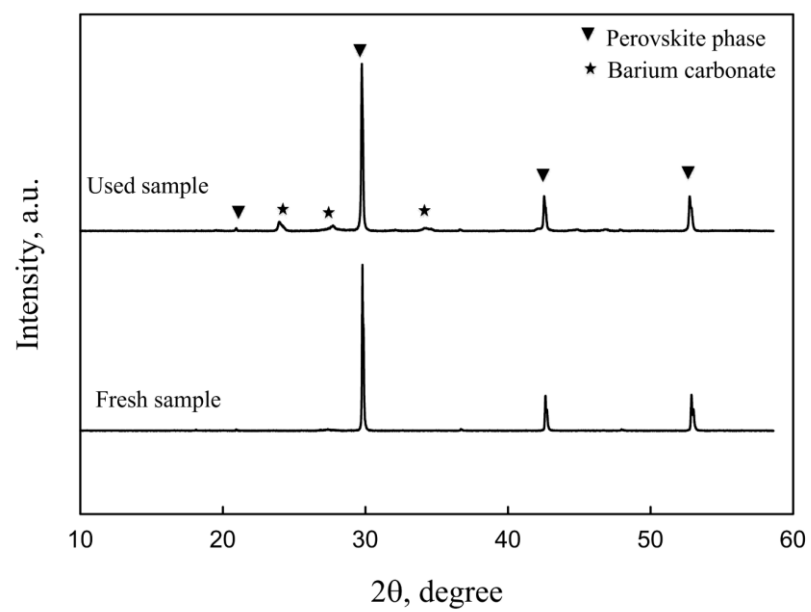


Figure S6. Comparison of XRD pattern between fresh samples and used samples

Table S3. Comparison with other perovskite oxides

Catalyst	Light source	Reaction gas	Products	Ref.
KBaTeBiO ₆ (This work)	400W Xe lamp	CO ₂ +H ₂ O	CO (180μmol g ⁻¹ h ⁻¹ in the first half hour)	-
Au-SrTiO ₃	300W Xe lamp	CO ₂ +H ₂ O	CO (0.35μmol g ⁻¹ h ⁻¹) CH ₄ (0.275μmol g ⁻¹ h ⁻¹)	[1]
Au-NaTaO ₃	200W Hg-Xe arc lamp	CO ₂ +H ₂ O	CO (0.173μmol g ⁻¹ h ⁻¹) CH ₄ (0.036μmol g ⁻¹ h ⁻¹)	[2]
Pt-NaNbO ₃	300W Xe lamp	CO ₂ +H ₂ O	CH ₄ (5.25μmol g ⁻¹ h ⁻¹)	[3]
C-LaCoO ₃	125W Hg lamp	CO ₂ +H ₂ O	HCOOH (95μmol g ⁻¹ h ⁻¹)	[4]
Bi ₂ WO ₆	300W Xe lamp	CO ₂ +H ₂ O	CH ₃ OH (75μmol g ⁻¹ h ⁻¹)	[5]
Bi ₂ WO ₆	300W Xe lamp	CO ₂ +H ₂ O	CO (0.5μmol g ⁻¹ h ⁻¹)	[6]

Coast and Redfern approximation method

The general kinetic equation can be expressed as:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1 - \alpha)^n \quad (\text{S1})$$

where α is the conversion degree, t is time, A is pre-exponential factor, R is the universal gas constant, T is the temperature, n is the reaction order.

Eq. (1) is integrated by using Coast–Redfern method⁷:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (\text{S2})$$

where

$$g(\alpha) = \begin{cases} -\ln(1 - \alpha), & n = 1 \\ \frac{1 - (1 - \alpha)^{1-n}}{1-n}, & n \neq 1 \end{cases}$$

β is the heating rate; the term of $2RT/E$ can be neglected since it is much less than one. A plot of $\ln \left[\frac{g(\alpha)}{T^2} \right]$ against $\frac{1}{T}$ should result in a straight line of slope $-\frac{E}{R}$ for the correct reaction order n . The pre-exponential factor A can be determined by the intercept of the line.

Photoconversion (Quantum) efficiency calculation

The quantum efficiency (quantum yield) based on CO yield, ϕ , is calculated using the following equation:

$$\phi = \frac{2 \times \text{CO yield (mol)}}{\text{photon absorbed by catalyst (mol)}} \times 100\% \quad (\text{S3})$$

The average CO production rate $180 \mu\text{mol g}^{-1} \text{h}^{-1}$ in the first half hour was chosen to calculate the quantum efficiency. The photon absorbed by catalyst was calculated by equation 2:

$$\text{photon absorbed by catalyst (mol)} = \frac{\text{total energy absorbed by catalyst}}{\text{average photon energy} \times N_A} \quad (\text{S4})$$

where N_A is the Avogadro's constant.

The photon energy at a certain wavelength can be calculated by equation 3:

$$E = \frac{hc}{\lambda} \quad (\text{S5})$$

Where h , c and λ are Planck constant, speed of light and wavelength, respectively. The photon energy is estimated from 250nm to 354nm due to the wide band gap 3.5eV. The effective accumulated light intensity in this experiment is 3.6 mW/cm^2 . Parameters for calculation are summarized in the following:

Light intensity in the effective UV range:	3.6 mW/cm^2
Deposited film area:	13.85 cm^2
Average photon energy:	$6.58 \times 10^{-19} \text{ J}$
Yield of CO:	$180 \mu\text{mol g}^{-1} \text{h}^{-1}$
Mass of the catalyst used:	15 mg

Based on Eq. S3, the quantum efficiency is 1.19%.

Reference

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