An Antimonate Pyrochlore (H_{1.23}Sr_{0.45}SbO_{3.48}) for Photocatalytic Oxidation of Benzene: Effective Oxygen Usage and Excellent Activity

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Experimental Section

Material Synthesis.

Strontium antimonate were prepared by hydrothermal method. In typical procedure, 25 mL potassium pyroantimonate solution (containing 25 mmol Sb) was added dropwise into the 10 mL strontium chloride solution (containing 12.5 mmol Sr) with stirring. After the addition, 35 mL of water was poured into the container. The pH of the white slurry was adjusted to 4-9 by 1 mol/L KOH or HCl solution. Followed by 12 h stirring, the slurry was transferred into an autoclave and heated at 180 °C for 8 h. After a hydrothermal progress, the white precipitation was washed with distilled water to dissolve any unreacted raw material. Last, the white powders obtained were dried at 80 °C overnight.

Physical Characterization.

The crystal structures were determined by XRD using Cu Kα radiation (Bruker D8 Advance) at 25 °C. The step size is 0.02 degrees, and the scan speed is 2 seconds per step. Accurate lattice parameters were obtained by fitting the profile with GSAS^{S1}. The ultraviolet-visible diffuse reflectance spectra were measured by the diffuse reflection method using Varian Cary 500 Scan UV-visible system equipped with a Labsphere diffuse reflectance accessory. Particle sizes and surface morphology were observed with a field-emission transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN) at 200 kV. The elements were measured by scanning electron microscopy (SEM, Hitachi SU8010) equipped with EDS at 20 kV. The valences of elements were measured by

X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) at 3×10^{-10} mbar using Al K α X-ray beam (1486.6 eV).

Photocatalytic Activity Measurements.

The photocatalytic decomposition of gaseous benzene was conducted in a tubular reactor with a continuous-flow mode. The size of sieved photocatalyst particles are ranging from 0.21 to 0.25 mm. The light source is three UV lamps with a wavelength centered at 254 nm (Philips, TUV 4W/G4 T5). A vessel of benzene was immersed in an ice-water bath, and the oxygen was bubbled into to vessel. The mixing gas (oxygen and benzene) with benzene concentration 312 ppm was obtained at the outlet of the custom-designed vessel. Then the mixing gas was lead to the reactor with a flow rate of 20 mL/min. The temperature of the reactions was controlled at 35 °C by an air-cooling system for SSO-8 and 70 °C for P25. The components in effluent were analyzed by a gas chromatograph (HP7890, HP-FFAP capillary column 30m×0.32mm ID×0.25um, Porapak R packed column, FID, TCD, Agilent). The adsorption-desorption equilibrium of gaseous benzene on sample was obtained in the dark for 10 h before the activity measurement. In all experiment, the flow rate of the mixing gas was maintained at 20 mL/min. To change the GHSV, we varied the volume and quantity of photocatalyst.

Characterization of Photoelectrochemical.

Mott–Schottky (M-S) plots were measured in a three-electrode cell by using an electrochemical analyzer (CHI 660D) at different frequency with ac amplitude of 10 mV. The photocatlyst-coated FTO glass, a platinum wire, a Ag/AgCl electrode and 0.1 M sodium sulfate were used as the

working electrode, the counter-electrode, the reference electrode and the electrolyte, respectively. Impedance spectra were obtained in vacuum and H_2 atmosphere in the 1 Hz to 1 MHz frequency range with an ac perturbation of 700 mV. Cylindrical pellets of 10 and ~2 mm of diameter and thickness, respectively, were coated with Ag-paste on each side of the pellet.

Active Radicals Measurement.

The ESR measurements were carried out on a Bruker model A300 spectrometer at ambient temperature. The spectra were obtained with the microwave power 20 mW, frequency of 9.86 GHz and 3512 G central magnetic field. The light source is one UV lamp with a wavelength centered at 254 nm (Philips, TUV 4W/G4 T5). The spin trap 5-tertbutoxycarbonyl-5-methyl-1-pyrroline Noxide (BMPO) was used to verify the formation of superoxide and hydroxyl radicals. To further distinguish each ROS, DMSO and SOD were employed separately to test their scavenging effect on the ESR signal for hydroxyl radical and superoxide, respectively. The ESR spectra were obtained from samples containing 3 mg SSO-8 (or P25), 0.5 mL 25 mmol/L BMPO, 12 % DMSO (or 600 U/ml SOD).

Oxygen Temperature Programmed Desorption (O₂-TPD).

The O₂-TPD experiments are performed on a fully automated chemisorption analyzer (autochem II 2920 instrumental). 0.1 g catalysts (the particle size 50-70 mesh) were pretreated under helium atmosphere at 180°C for 30 min followed by natural cooling until 50 °C under helium flow. Then, the adsorption process starts with a purge of 10% O₂/Ar at a flow rate of 25 ml/min⁻¹ for 30 min. Before the desorption process, the TCD and MS signal should be stable with the introduction of

helium into the tube at a flow rate of 40 ml/min⁻¹. Finally, the O₂-TPD test was initiated under helium atmosphere (40 mL/min⁻¹) from 50 °C to 800 °C at a ramp of 10° C/min⁻¹.

Tables

Table S1. Progress achieved in the photocatalytic oxidation of gaseous benzene in a fixed-bedreactor with continuous-flow gas mode at room temperature.

Sample (quantity)	Equilibrium concentration of benzene (flow rate)	atmosphere	Conversion ratio of sample/P25	Mineralization ratio of sample/P25	Light source	Year
H _{1.23} Sr _{0.45} SbO _{3.48} (0.36 g)	312 ppm (20 mL/min)	100% O ₂	100%/10%	74%/15%	Three 4W fluorescent UV bulbs(TUV 4W/G4 T5, Philips, 254 nm)	This work
SnO ₂ -Decorated ZnSn(OH) ₆ (0.1 g cat. + 1g SiO ₂)	250 ppm (20 mL/min)	100% O ₂	66%/9.7%	67.6%/87%	Four 6 W UV lamps (254 nm, TUV 6W/G6 T5, Philips)	2016 ⁸²
SrSn(OH) ₆ (0.4 g)	280 ± 20 ppm (20 mL/min)	100% O ₂	31%/12%	55%/27%	Three 4W fluorescent UV bulbs (TUV 4W/G4 T5, Philips, 254 nm)	2016 ^{S3}
TiO ₂ /ZSM-5 (0.5L)	25 ppm (1 L/min)	Air, 50% humidity	100%/60%	60%/47%	Two VUV lamps (4W, Sungreen), two 254 nm UV lamps (4W, Sungreen)	2016 ⁸⁴
SnO ₂ -Decorated MgSn(OH) ₆ (0.1 g cat. + 1g SiO ₂)	250 ppm (20 mL/min)	100% O ₂	89%/10%	68%/88%	Four 6 W UV lamps (254 nm, TUV 6W/G6 T5, Philips)	2015 ⁸⁵
ZnSn(OH) ₆ (0.3 g)	280 ± 20 ppm (20 mL/min)	100% O ₂	75%/5%	68%/24%	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2012 ⁸⁶
GaOOH (0.3 g)	210 ppm (20 mL/min)	100% O ₂	13%/5%	68%/-	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2010 ^{S7}
CaSb ₂ O ₅ (OH) ₂ (0.3 g)	420 ppm (20 mL/min)	100% O ₂	29%/4%	75%/20%	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2009 ⁵⁸
Cd ₂ Sb ₂ O _{6.8} (0.3 g)	210 ppm (20 mL/min)	100% O ₂	13%/3%	55%/-	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2009 ^{s9}
ZnSn(OH) ₆ (0.45 g)	252 ppm (20 mL/min)	100% O ₂	17%/8.5%	86%/30.8%	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2009 ^{S10}
Cd ₂ Ge ₂ O ₆ (0.45 g)	252 ppm (20 mL/min)	100% O ₂	46%/1.3%	85%/51%	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2009 ^{S11}
$Sr_2Sb_2O_7$ (0.3 g)	220 ppm (20 mL/min)	21% O ₂ , 79% N ₂	24%/4.2%	50%/37.8%	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2008 ^{S12}
β-Ga ₂ O ₃ (0.3 g)	450 ppm (20 mL/min)	21% O ₂ , 79% N ₂	42%/about zero	95%/-	Four 4 W UV lamps (Philips, TUV 4W/G4 T5, 254 nm)	2006 ^{S13}

Ag ₃ VO ₄ /TiO ₂ (1.7 g)	280 ppm (20 mL/min)	100% O ₂	95%/-	84%/-	500 W Xe-arc lamp simulated solar light $(320 < \lambda < 900 \text{ nm})$	2012 ⁸¹⁴
			40%/ -	60%/ -	500 W Xe-arc lamp visible light (450 <λ< 900 nm)	2012 ⁸¹⁴
BiVO ₄ /TiO ₂ (1.35 g)	260 ppm (20 mL/min)	100% O ₂	92%/18%	80%/25%	500 W Xe-arc lamp simulated solar light (320 <λ< 900 nm)	2011 ⁸¹⁵
			66.8%/0	52%/0	500 W Xe-arc lamp visible light (450 <λ< 900 nm)	2011 ⁸¹⁵
LaVO ₄ /TiO ₂ (1.2 g)	250 ppm (20 mL/min)	100% O ₂	57%/0	29%/0	500 W Xe-arc lamp visible light (450 <λ< 900 nm)	2009 ⁸¹⁶

Table S2. Crystallographic data of H1.23Sr0.45SbO3.48, obtained from Rietveldrefinements of X-ray diffraction.

Atom	Site	Х	У	Z	Occ.	U _(eq) (Å)
Sb ⁵⁺	16c	0	0	0	0.3	0.02689
Sb^{3+}	16c	0	0	0	0.7	0.02689
Sr^{2+}	32e	0.51896(10)	0.51896(10)	0.51896(10)	0.2287(5)	0.01816
O ²⁻	48f	0.31863(17)	1/8	1/8	1	0.025
O ²⁻	8b	3/8	3/8	3/8	0.970(6)	0.025

S.G.: Fd-3m (No. 227), a: 10.37 Å, Z: 16

Overall $R_p = 2.93\%$, *overall* $R_{wp} = 3.50\%$, *overall* $\chi 2 = 1.895$

Pyrochlore compounds with a general formula $A_2B_2O_7$ allows a wide variety of chemical substitutions at the A and B sites. Cations having higher ionic radii (~1Å) occupy the A sites, and the lower one (~0.6 Å) occupy the B sites. According to Fig. S1, there are three kinds of cation in this compound including Sb³⁺ (0.9 Å), Sb⁵⁺ (0.67 Å) and Sr²⁺ (1.18 Å). In consideration of the ion size, the Sr²⁺ occupy A sites, while Sb⁵⁺ occupy the B sites. In order to confirm the site of Sb³⁺ (0.9 Å), the ion exchange experiment is conducted according to the different stability of ion in the pyrochlore crystal. The weak interactions between B₂O₆ network and A₂O' chains leading to ion-exchange property taking place at A site. In the ion exchange experiment, 0.2 g SSO was disperse in 20 mL 1 mol/L NaNO₃ solution stirring 24 h. Then, 50 mL H₂S gas was led into the supernatant to detection of Sb³⁺ by forming the Sb₂S₃ precipitation. The supernatant keep transparent indicates that of Sb³⁺ is at B site.

Table S3. Quantum Yield (QY) of photocatalytic degradation of benzene over SSO-8 atdifferent GHSV

GHSVa	Illuminated	Quantity	Number of incident	CO_2	Number of produced	OYb
0115 (area		photons in 1s	concentration	CO ₂ in 1s	Q1
3333.1 h ⁻¹	6.39 cm ²	0.36 g	1.73×10 ¹⁷	1191 ppm	1.72×10 ¹⁵	29.7 %
4285.7 h ⁻¹	5.32 cm^2	0.3 g	1.44×10 ¹⁷	970 ppm	1.40×10 ¹⁵	29.1 %
6382.9 h ⁻¹	3.33 cm ²	0.19 g	0.90×10 ¹⁷	610 ppm	8.81×10 ¹⁴	29.4 %
7894.7 h ⁻¹	2.70 cm ²	0.15 g	0.73×10 ¹⁷	506 ppm	7.31×10 ¹⁴	30.0 %
11539.5 h ⁻¹	1.77 cm ²	0.10 g	0.48×10 ¹⁷	350 ppm	5.05×10 ¹⁴	31.5 %

^aGHSV: gas hourly space velocity

^bQY: Quantum Yield

Table S4. Quantum Yield	(QY) of	photocatalytic	degradation	of benzene over P25
L	$\langle \cdot \cdot \rangle$			

GHSV	Illuminated area	Quantity	Number of incident photons in 1s	CO ₂ concentration	Number of produced CO ₂ in 1s	QY
2970.3 h ⁻¹	7.17 cm ²	0.3 g	1.94×10 ¹⁷	60 ppm	8.6×10 ¹³	1.32 %

Figures



Figure S1. The XPS of Sb3d, O1s, and Sr 3d of SSO-8.

The binding energies of Sb $3d_{3/2}$ of Sb₂O₃ and Sb₂O₅ are 539.29 and 540.29 eV, respectively. The obtained spectra were assigned to Sb³⁺ and Sb⁵⁺ according to the above binding energies. The binding energy of 530.04, 531.31 and 532.41 eV are corresponding to the lattice oxygen, adsorbed oxygen and surface hydroxyl, respectively^{S17}. Thus, the adsorbed oxygen on the surface of SSO-8 is abundant.



Figure S2. The corner sharing SbO₆ octahedron and interpenetrating Sr₂O' (side view). Gray balls stand for the site of 32e (filling or unfilling with Sr²⁺ ions); the blue balls stand for the O²⁻ ions at 48f; the red balls stand for the site of 8b (filling or unfilling with O²⁻ ions). Sb⁵⁺ ions are in the middle of SbO₆ octahedron (16c).



Figure S3. XRD patterns and BET specific area of strontium antimonate synthesized at 180 °C for 8 h. The values behind the hyphen stand for the pH values of the synthesis conditions.



Figure S4. Photocatalytic activity of SSO synthesized at different pH values (GHSV ~4000 h^{-1}).



Figure S5. The irradiation of the light source.

For the Quantum yield (QY) calculation, the following equation is used.

 $\frac{number of electrons transferring}{number of incident photons} = \frac{number of CO_2 molecules \times 30}{number of incident photons} \times 100\%$ x =

Where 30 is the number of electrons transferring when the reaction (1) take place once^{S18}:

$$C_6 H_6 + 7.5 O_2 = 6 C O_2 + 3 H_2 O \tag{1}$$

The light intensity of the benzene decomposed reactions was measured by a spectrometer (Spectrilight TM III). The radiation source is three germicidal lamps (254 nm wavelength output). The spectrum of the light source is shown in Figure S3. Thus, number of incident photons in 1s is calculated using the following equation:

ber of incident photons in
$$1s = \lambda = 250 \frac{A \cdot I(\lambda)}{hv}$$

Numł

Where I(λ) is the radiant illuminance at λ , λ is the wavelength, A is the irradiating area, h is the Planck constant, v is the frequency of light. Because the band edge of SSO-8 is at 272 nm, the total number of photons which can be used by SSO-8 is the UV light with wavelength shorter than 272 nm. The irradiating area (A) is 6.39 cm², the Planck constant (*h*) is 6.626×10^{-34} J•s, the Integral I(λ) ranging from 250 nm to 272 nm is 21174.33 μ W/cm². The number of incident photons in 1s is 1.73×10^{17} .

$$\operatorname{ced} \operatorname{CO}_{2} \operatorname{in} 1 \operatorname{s} = r_{CO_{2}} \times 1 \operatorname{s} = \frac{1}{6} \times \left[\frac{dN_{CO_{2}}}{dt}\right] \times 1 \operatorname{s}$$

Number of produced CO₂ in 1s

$$=\frac{1}{6} \times \left[\frac{N_0 dn_{CO_2}}{dt}\right] \times 1s = \frac{1}{6} \times \left[\frac{N_0 d([CO_2] \cdot \frac{V}{V_m}}{dt}\right] \times 1s = \frac{1}{6} \times \left[\frac{N_0 d([CO_2] \cdot \frac{V}{V_m}}{dt}\right] \times 1s$$

 $\frac{1}{6} \times \left[\frac{dN_{CO_2}}{dt}\right]$ is the reaction rate; N_{CO_2} is the number of the CO₂; [CO₂] is the concentration of CO₂; the Avogadro constant (N₀) is $6.02 \times 10^{23} mol^{-1}$; the molar volume of gas (Vm) is 22.4 L·mol⁻¹; V is the gas volume, and is calculated by 20 mL·min⁻¹×dt. When the concentration of CO₂ is 1191 ppm, the number of produced CO₂ in 1s is 1.72×10^{15} , the number of electrons transferring is 5.16×10^{16} .

Therefore, the QY of SSO is 29.7 %.



Figure S6. The conversion and mineralization ratio of C_6H_6 over SSO-8 at different GHSV (4285.7-11538.5 h⁻¹).



"**Figure S7.** The XRD and XPS patterns of SSO-8 sample before and after the photocatalytic reaction. a. The XRD patterns. b. Survey-scan XPS spectra. c. High-resolution XPS spectra of Sr 3d orbitals. d. High-resolution XPS spectra of Sb 3d and O1s orbitals."



Figure S8. The conversion ratio and mineralization ratio of C_6H_6 over SSO-8, ZnSn(OH)₆, Ga₂O₃, and P25 (GHSV ~12000 h⁻¹)



Figure S9. Conversion ratio and mineralization ratio of benzene over SSO-8 and P25 in different atmosphere (GHSV ~4000 h⁻¹)



Figure S10. Conversion ratio and mineralization ratio of benzene over SSO-8 and P25 in anaerobic atmosphere (O₂:N₂=0:100, GHSV ~4000 h⁻¹), water vapor was added after 12 h reaction.



Figure S11. Band position of SSO-8. a. The ultraviolet-visible diffuse reflectance spectrum. b. Mott–Schottky (M-S) plots. c. The schematic drawing of redox potentials of SSO-8^{S19}.

It is known that the optical absorption of materials near the band edge follow: $F(R)E = A(E-Eg)^{n/2}$, where F(R), E, A and n are band gap, diffuse absorption coefficient, photon energy, proportionality constant and an integer (n = 1, 2, 4, 6), respectively. The relation between the diffuse absorption coefficient and the band gap energy can be described by $(F(R)E)^{1/2} = A(E-Eg)$. $(F(R)E)^{1/2}$ had a linear relation with E. In the equation, n decides the characteristics of the transition in the material (n=1, direct absorption; n=4, indirect absorption). The results reveal that the indirect band gap of SSO-8 is 4.1 eV.

Mott–Schottky (M-S) plots are used to measure the type and the flat band of semiconductors. The slope of the Mott-Schottky plot increases with the potential indicating that SSO-8 is an n-type semiconductor. The conduction band and valence band position is at -0.5 V and 3.6 V vs. Ag/AgCl (-0.3 V and 3.8 V vs. standard hydrogen electrode). Therefore, the band structure of SSO-8 is suitable for the production of •OH (•OH/H₂O 2.27 V vs. SHE, pH=7), $O_2^{\bullet-}$ ($O_2/O_2^{\bullet-}$ -0.28 V vs. SHE, pH=7).



Figure S12. a. The O_2 -TPD profiles for SSO-8. b. The desorption of H_2O from SSO-8 with different pretreated temperature.



Figure S13. The influence of water vapor to oxidation of benzene in O_2 atmosphere over SSO-8 and P25 (GHSV ~4000 h⁻¹).



Figure S14. Impedance spectra of SSO-8 and P25 in different atmosphere.

To comparison the proton conductivity between SSO-8 and P25, impedance spectra of the two photocatalysts are conducted in H_2 atmosphere and vacuum. The conductivity of P25 shows no difference between H_2 atmosphere and vacuum. However, conductivity of SSO-8 in H_2 atmosphere is higher than that in vacuum. That means the protons can diffuse in the bulk of SSO-8. It has been demonstrated that the proton conducting property contributes to form more OH groups in the 1D channel of pyrochlore by transferring protons via single OH bond forming in the crystal^{S20} (particularly with O_2^- ions on 48f sites). In other words, SSO-8 acts as a "container" of hydroxyl groups.

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