Electronic Supplementary Information (ESI)

A highly efficient and stable $Ag/AgIO_3$ particles for photocatalytic reduction of CO_2 under visible light

Zhiqiao HE, Da WANG, Huiying FANG, Jianmeng CHEN and Shuang SONG*

College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, People's Republic of China

* Corresponding author:

Shuang SONG

Tel.: 86-571-88320726; Fax: 86-571-88320276.

E-mail: ss@zjut.edu.cn

Experimental Section

Preparation and characterization of the catalysts

$AgIO_3$ powder was prepared by solid-state ion-exchange method. KIO_3 (1.51 g) and $AgNO_3$ (1.20 g) were mixed thoroughly in a mortar until uniform solid particles were formed. The resulting white precipitate was washed with deionized water to dissolve any unreacted raw material. To prepare the $Ag/AgIO_3$ particles, 50 mL of 3.5 mM hydrazine hydrate was added dropwise with vigorous stirring to 100 mL of aqueous $AgIO_3$ dispersion. The resulting brown suspension was then washed with deionized water several times and finally dried at 60 °C for 24 h. Theoretically, the catalyst has an $Ag:AgIO_3$ molar ratio of 1:9. A reference photocatalyst of $N\text{-}TiO_2$ was prepared by following the procedure reported by Kontos and coworkers.[S1]

$Ag/AgIO_3$ particle formation was confirmed by X-ray diffraction (XRD, Thermal ARL X-ray diffractometer, Thermo, France) using Cu Kα radiation (45 kV and 40 mA). Measurements were done in the 2θ range of 10° to 80° at a scanning speed of 2° min^{-1} at room temperature. Surface morphologies of the synthesized particles were observed under a scanning electron microscope (SEM, S-4800, Hitachi, Japan) and a transmission electron microscope with 0.20 nm point resolution (Tecnai G2 F30 S-Twin, Philips-FEI, Netherlands) at an acceleration voltage of 300 kV. Surface electronic states were analyzed by X-ray photoelectron spectra (XPS) on a PHI 5000C ESCA system (Perkin-Elmer, USA) equipped with a polychromatic Mg Kα radiation source operated at 1253.6 eV. Diffuse reflectance spectra were measured using a UV-vis spectrometer (TU-1901, Pgeneral, China). The specific surface area, which was based on nitrogen adsorption, was measured by using a gas adsorption analyzer (ASAP 2010 Analyzer, Micromeritics, USA) according to the Brunauer–Emmett–Teller (BET) method. The Mott–Schottky plot was obtained on a electrochemical workstation (CHI 660D, Shanghai Chenhua, China) using a standard three-electrode cell with a pressed tablet of $AgIO_3$ as working electrode, a platinum plate as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The electrolyte was an aqueous 0.1 M Na_2SO_4 solution, which was purged with nitrogen before measurements. Mott–Schottky experiments were done by measuring the frequency response at 10 Hz.

Photocatalytic reaction

Photocatalytic reduction of CO_2 was carried out in a stainless steel reactor (8 cm inner diameter, 5.5 cm inner height, and 260 mL effective capacity) equipped with an

O-ring sealed quartz window at the top to admit light. A 500 W Xe arc lamp (Beijing Electric Light Sources Research Institute, China) positioned 20 cm above the vessel was used as a source of simulated solar light. To obtain visible light, UV light was removed by inserting a UV cutoff filter (wavelength > 400 nm) across the light path. In our experiment, the light flux entering the reactor was determined to be 2.551×10^{-6} einstein min^{-1} cm^{-2} by using a visible-light radiometer (FZ-A, Beijing Normal University, China). A self-contained water jacket was connected to a circulating water bath thermostated at 25 ± 1 °C. In a typical run, 0.3 g of powdered catalyst was evenly dispersed on glass fiber (4 cm × 4 cm) that was placed in the photoreactor facing the quartz window. Prior to irradiation, compressed CO_2 (99.99%, Hangzhou Jingong Special Gas Co., Ltd., China), whose flow was regulated by a mass flow controller, was bubbled through a water reservoir to presaturate the CO_2 with water (~3.2% H_2O, v/v). After the CO_2 was purged for 30 min, the gas valves on both sides of the reactor were closed to seal the reactor and the Xe lamp was switched on. Magnetic stirring was used to agitate the mixture of CO_2 and water vapor during irradiation. At preset intervals, gaseous samples from the vessel were taken by a 1 mL gastight syringe (P/N 5190-1531, Agilent, USA) and then manually injected into a gas chromatography (GC).

Table S1 QY of photoreduction of CO_2 over $Ag/AgIO_3$ particles under monochromatic light of various wavelengths.

wavelength (nm)	incident photon flux (einstein min^{-1} cm^{-2})	product yield (μmol g^{-1})		QY (%)
		CH_4	CO	
430	1.832×10^{-7}	2.07 ± 0.22	n. d.	0.23 ± 0.024
460	2.791×10^{-7}	3.51 ± 0.20	0.60 ± 0.070	0.25 ± 0.016
490	3.403×10^{-7}	4.33 ± 0.43	0.64 ± 0.086	0.26 ± 0.026
520	3.226×10^{-7}	4.83 ± 0.51	0.71 ± 0.041	0.31 ± 0.032
550	3.389×10^{-7}	4.56 ± 0.63	0.64 ± 0.082	0.28 ± 0.038
580	4.275×10^{-7}	5.57 ± 0.86	0.92 ± 0.132	0.27 ± 0.018
610	3.059×10^{-7}	2.90 ± 0.16	0.47 ± 0.072	0.20 ± 0.012
700	1.285×10^{-7}	0.87 ± 0.11	n. d.	0.14 ± 0.017

Photocatalytic action spectra were obtained by using monochromatic light (light

width, ±15 nm) from a Xe lamp with a monochromator. The irradiation intensity of monochromatic light below the entrance window of the photoreactor is shown in Table S1. The incident photon flux at the wavelength range of 430–700 nm was in the range of 1.285–4.275 × 10^{-7} einstein s^{-1} cm^{-2}.

The quantum yield (QY) for CO_2 reduction was obtained based on the molar production of carbon-containing compounds, according to eqn (S1):

QY = number of moles of electrons reacted/number of moles of incident photons (S1)

The turnover number (TON) is defined as the number of product molecules of the system over the number of active sites exposed to light at a certain time.

Methods of sample analysis

CO was analyzed by GC on an Agilent 7890B (USA) equipped with a thermal conductivity detector and an HP-PLOT MoleSieve column (30 m × 320 μm × 12 μm). CH_4 was analyzed by GC on a Shimadzu 2014 (Japan) equipped with a flame ionization detector and an RTX-1701 capillary column (30 m × 250 μm × 25 μm).

Calculation of the TON under visible-light irradiation

The Ag/$AgIO_3$ catalyst has an Ag:$AgIO_3$ molar ratio of 1:9. Since the molar masses of $AgIO_3$ and Ag are 282.77 and 107.87 g mol^{-1}, respectively, we can convert the Ag: AgIO3 mole ratio into mass ratio according to eqn (S2)

$(1 \times 107.87)/(9 \times 282.77) = 0.042386$ (S2)

The densities of $AgIO_3$ and Ag are 5.525 and 10.49 g cm^{-3}; thus, the Ag:$AgIO_3$ volume ratio is

$(0.042386 \times 5.525)/10.49 = 0.022324$ (S3)

The SEM image shows that the $AgIO_3$ sheets have a thickness of ~150 nm and that the Ag particles have an average diameter ~30 nm. Thus, the number of Ag particles per square centimeter of $AgIO_3$ is approximately

$$\frac{0.022324}{(\frac{4}{3}\times\pi\times(\frac{30}{2})^3)}/(\frac{1}{150}\times 2) = 1.1843\times10^{10}\ \text{cm}^{-2} \quad \text{(S4)}$$

Considering that the photocatalysts were equally dispersed on the 16 cm^2 glass fiber, the number of Ag particles that are effective for photocatalytic reduction of CO_2 is

$$1.1843 \times 10^{10} \times 16 = 1.8949 \times 10^{11} \quad \text{(S5)}$$

Each Ag atom exposed to visible light may be regarded as a potential active site. Since the estimated length of the unit-cell edge of the face-centered cubic Ag crystal is 0.40772 nm, the number of irradiated active sites is

$$[1.8949 \times 10^{11} \times 4 \times \pi \times (30/2)^2 \times 2]/(2 \times 0.40772^2) = 3.2213 \times 10^{15} \quad \text{(S6)}$$

Thus, the total number of moles of active sites is

$$3.2213 \times 10^{15}/6.0221 \times 10^{23} = 5.3549 \times 10^{-3}\ \mu\text{mol} \quad \text{(S7)}$$

The total CH_4 and CO yields on $Ag/AgIO_3$ catalyst under visible-light irradiation after 240 min are 7.32 and 0.89 μmol, respectively. Consequently, The TON for CH_4 is

$$7.32/5.3549 \times 10^{-3} = 1367$$

and the TON for CO is

$$0.89/5.3549 \times 10^{-3} = 167$$

Reference

S1 A. I. Kontos, A. G. Kontos, Y. S. Raptis and P. Falaras, *Phys. Status. Solidi-R*, 2008, **2**, 83.