Electronic Supplementary Material (ESI) for Dalton Transactions.
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Supplementary Information

Preparation of Au/ZrO_2

60 mg of ZrO_2 were dissolved in 45 mL of deionized water with sonication at room temperature for 10 min. Then 2.5, 5 and 7.5 mL of $HAuCl_4$ aqueous solution (10 mg/mL) and 5 mL of tannic acid aqueous solution (0.018 mol/L) were added into the above solution to form Au/ZrO_2 with different loading amount of Au. After being magnetically stirred for 0.5 h at room temperature, the mixture was then washed with water and ethyl for several times and dried under 60 ℃ for 12 h.[1]

Characterization Methods

Approximate 3 mg of samples masses were dissolved in 2 mL of aqua regia for 12 h. Then the solution was diluted to 20 mL. An inductively coupled plasma-atomic emission spectrometer (ICP-AES) on an Optima 7300 DV (PerkinElmer Corporation) was used to measure the mass of Au in the diluted solution and the concentration of Au was also obtained. Powder X-ray diffraction (XRD) patterns were collected on Philips X'pert Pro Super diffractometer with Cu Kα line (λ =1.5418 Å). Morphologies of Au/ZrO_2 samples were detected by transmission electron microscopy (TEM) and energy dispersive X-ray spectra (EDS) on the JEOL-2100F transmission electron microscope at the accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB MKII instrument equipped with a Mg Kα source (hυ = 1253.6 eV) where binding energy scales of all measurements were calibrated referencing C 1s to 284.5 eV. X-ray absorption near edge spectroscopy (XANES) and extended X-ray fine structure (EXAFS) spectra were collected at the beamline 1W2B of Beijing Synchrotron Radiation Facility (BSRF), China. Au L_3-edge EXAFS spectra and $k^2\chi(k)$ oscillations for Au foil and Au/ZrO_2 are listed in Figure S1 and Figure S2 respectively. The acquired EXAFS data were processed by the standard procedures ATHENA module implemented in the IFEFFIT software packages.

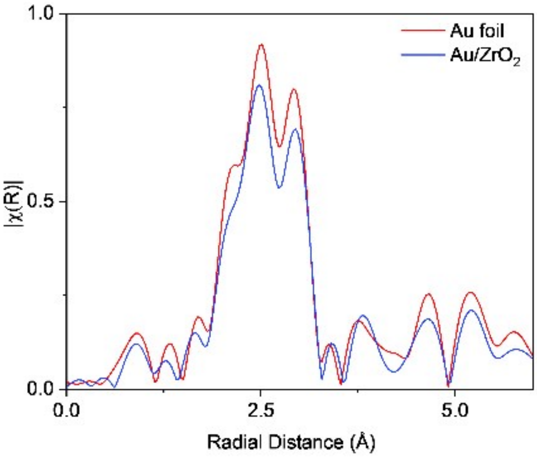

Figure S1. k^2-weighted FT spectra at the Au L_3-edge for Au foil and Au/ZrO_2.

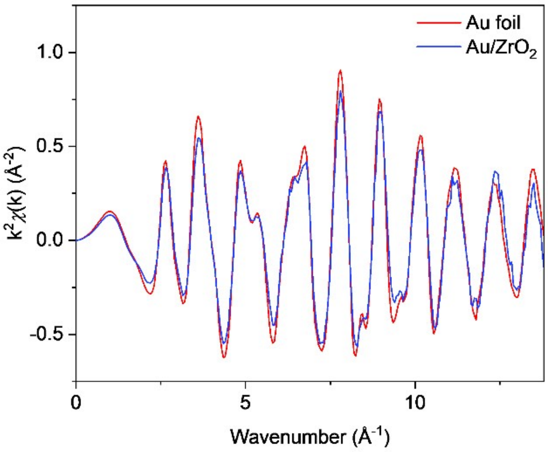

Figure S2. $k^2\chi$ (*k*) oscillations for Au foil and Au/ZrO_2.

Photocatalytic activity measurement

All the measurements were carried out in a totally dark room. 10 mg catalyst powder was dispersed into 80 mL of deionized water after sonication for 1 h and then the mixture was transferred into a cylinder Pyrex glass container with the size of 8 cm (diameter) × 12 cm (height). 20 mL of triethanolamine was added as sacrifice reagent. CO_2 passed through the at the flow rate of 60 mL/min for an hour. Then the container was sealed. A 300 W Xe-lamp (PLS-SXE 300, Beijing perfectlight Co. Ltd, China) was placed vertically above the container as the light source. Reaction temperature was kept at 298 K by a flow of cooling water during the reaction.400 rpm magnetic stirring was used in the reduction of CO_2 to ensure the homogeneity of aqueous suspension without sedimentation. One AM 1.5G filter was added to simulate solar illumination conditions with the light density of $100mW/cm^2$ and estimate the performance of catalysts. A 420 nm cutoff filter was added to remove the ultraviolet to estimate the performance of catalysts in visible light region. After the radiation, 1 mL of resultant gas was brought out and injected into a gas chromatograph (GC-2014, Shimadzu) equipped with three channels. The first channel with one flame ionization detector (FID1) used to detect CO and another channel with FID2 was used to detect CH_4. The last channel with thermal conduction detector was sued to detect H_2. However, no H_2 has been detected in the experiment. Temperatures of vaporization chamber, chromatographic column are 150℃, 60℃ respectively. Ar gas was used as carrier gas.[2] Chromatograms of products of the CO_2 reduction of 4.4 % wt Au/ZrO_2under simulated solar illumination ($\lambda > 300$ nm) are listed in Figure S2 as one example.

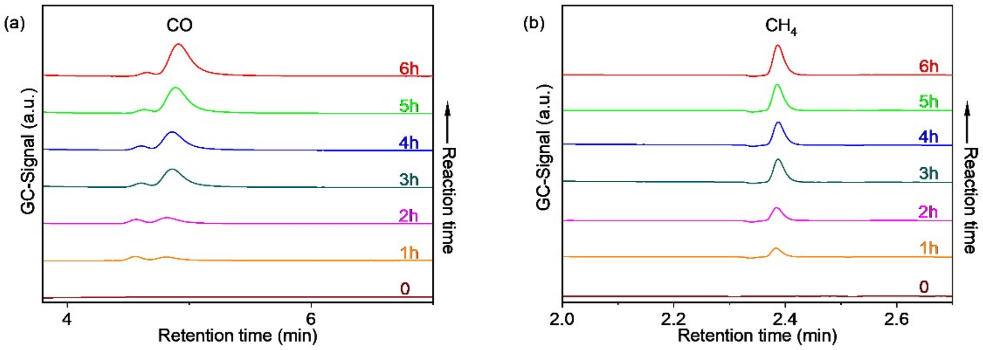

Figure S3. Detection of gaseous products of photocatalytic CO_2 reduction on 4.4 % wt Au/ZrO_2 under simulated solar illumination (λ>300 nm). (a) Chromatograms of CO detected by FID1. (b) Chromatograms of CH_4 detected by FID2.

The quantum efficiency was measured under the 300 W Xe-lamp with band-pass filters of full width at half maximum (FWHM) which equals 15 nm. The intensity of radiation was determined by an optical power meter (PM100D, Thermal Powermeter Head, THORLABS).

Photoelectrochemical measurement

All photoelectrochemical measurements were carried out in a typical three-electrode system with an electrochemical workstation (Model CHI760D, CH instruments, Inc, Austin,TX) and at room temperature. A Pt plate was used as the counterelectrode and saturated Ag/AgCl was as the reference electrode. Na_2SO_4 (0.5 mol/L) aqueous solution was utilized as the electrolyte. To prepare the working electrode, 4 mg electrocatalyst and 30 μL Nafion solution (5 wt%) were ultrasonically dispersed in 1 ml water/ethanol (vol : vol = 3 : 1) solution to form a homogeneous ink uniformly dropped onto a 1×2 cm fluorine-doped tin oxide (FTO) substrate. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an a.c. voltage with 5 mV amplitude in a frequency range from 100 kHz to 100 MHz. The bias of the photocurrent tests was 0.3 V. A Xe arc lamp (300 W) with a 420 nm filter was utilized as the light source for the photocurrent tests.[3,4]

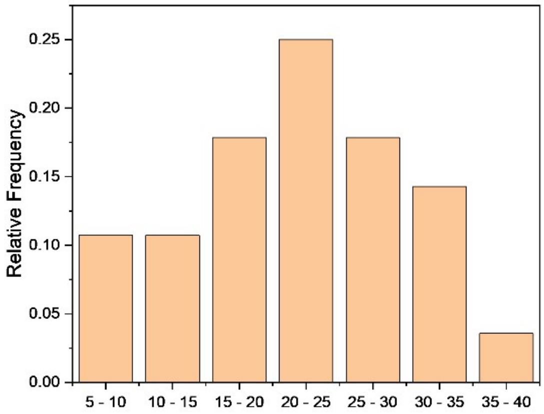

Figure S4. Diameters distribution of loaded Au nanoparticles of 4.4 % wt Au/ZrO_2.

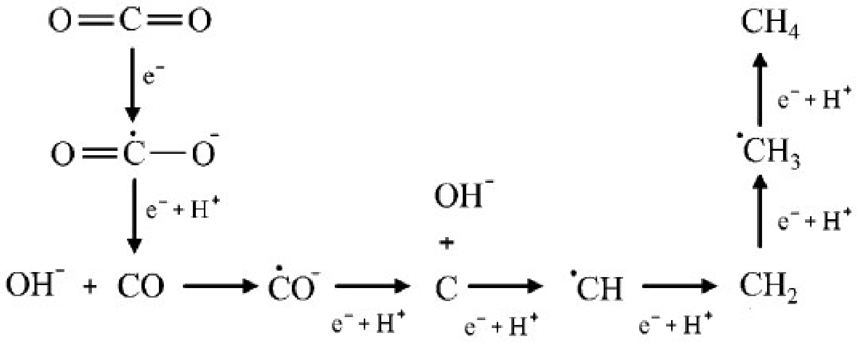

Figure S5. The carbene pathway for CO and CH_4 generation in the gas-phase CO_2 photoreduction

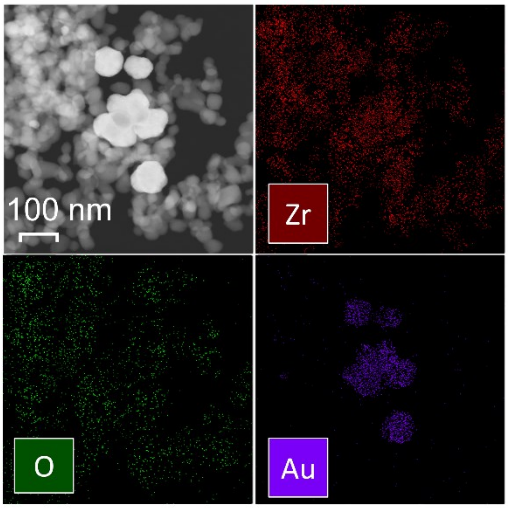

Figure S6. Element mapping of 6.3% wt. Au/ZrO_2

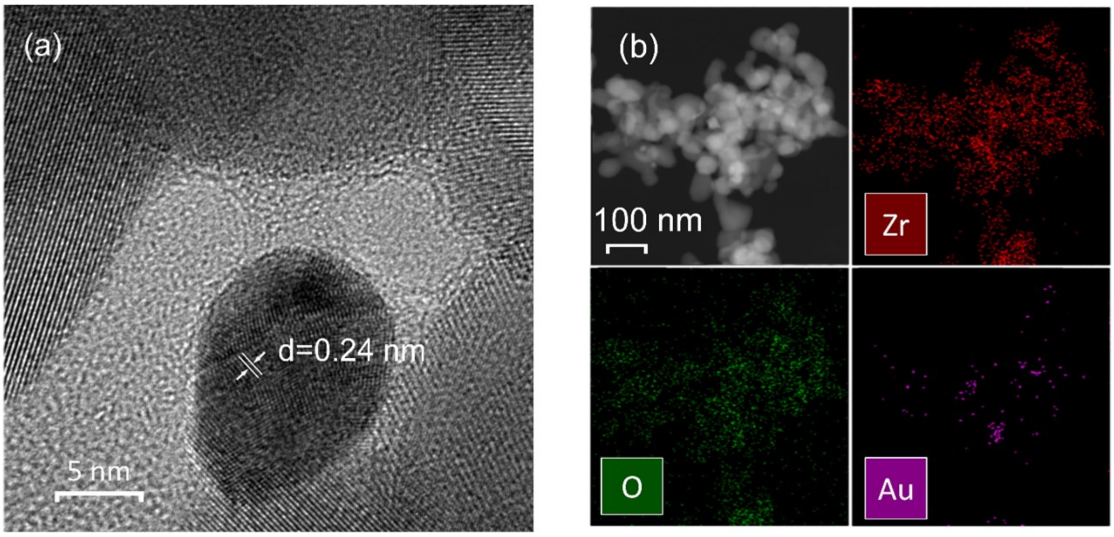

Figure S7. (a) HRTEM of 4.4% wt. Au/ZrO_2 after 24 hours. (b) TEM and element mapping of 4.4% wt. Au/ZrO_2 after 24 hours.

Reference

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