Supplementary Information (SI) for ChemComm.

Supporting information

Controlled synthesis of silver/silicon hybrid nanostructure enables enhanced photocatalytic CO_2 reduction

Huai Chen[a,c*], Xuebiao Deng[a,c], Meiqi Lin[c], Huiqing Yuan[a,c], Ban Lan[a*], Yangyang Xiong[a,b*]

[a] Northeast Guangdong Key Laboratory of New Functional Materials, School of Chemistry and Environment, Jiaying University, Meizhou, 514015, P.R. China. E-mail: jyulb6@163.com

[b] School of Pharmaceutical Sciences, Zhejiang Chinese Medical University, Hangzhou, China. E-mail: xiong_yangyang@163.com

[c] MOE Laboratory of Bioinorganic and Synthetic Chemistry, Lehn Institute of Functional Materials, School of Chemistry, Sun Yat-sen University, Guangzhou, 510275, China. E-mail: chenh678@mail.sysu.edu.cn

Experimental Section

Chemicals. All chemicals used are commercially available and were used without any additional purification steps: trimethoxysilane (TriMOS, 95%), hydrofluoric acid (HF, 49% aqueous solution, electronic grade), 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%), Octene (99%), ethanol (95%), toluene (99.9%), trolamine (99%), acetonitrile (99%) and silver benzoate ($C_7H_5AgO_2$, 99.99%) were purchased from Aladdin Chemical Inc.

Preparation of oxide-embedded silicon nanocrystals (SiNCs). 63 mmol of TriMOS (7.7 mg) were carefully weighed in a nitrogen-filled glovebox and immediately transferred into a 100-mL Schlenk flask equipped with magnetic stirring under a nitrogen atmosphere. The flask was then placed in an ice bath to lower the temperature to approximately 0°C. 10 mL of nitric acid (90 mmol) and 10 mL of methanol (25 mmol) was then added into the flask and mixed under a continuous nitrogen flow. Clear, white gels formed within 5 min. The temperature was then gradually increased to room temperature, and the reaction mixture was allowed to sit undisturbed under a nitrogen atmosphere for 24 hours. Following the aging process, the product was isolated from the residual liquid by vacuum filtration and then transferred to a vacuum oven, where it was dried for 16 hours. The white, gel-like product transformed into a blue powder. Approximately 1 g of this powder was placed in a quartz reaction boat and transferred to a high-temperature tube furnace (Lindberg). The sample was heated from ambient temperature to a peak temperature of 1100°C at a rate of 18°C/min in a slightly reducing atmosphere (5% H_2 + 95% Ar). The sample was maintained at the processing temperature for 1 hour and then allowed to cool naturally to room temperature. The resulting amber-colored powder was manually ground using a mortar and pestle. The finely ground powders were then stored in a 20-mL vial under ambient conditions for further use.

Liberation of hydride-terminated SiNCs (H-SiNCs). A conventional HF-etching protocol was employed to release SiNCs from the SiO_2 matrix[1]. Approximately 0.5 g of the ground product was transferred to a polyethylene terephthalate beaker equipped with a Teflon-coated stir bar. To this beaker, 5 mL of ethanol and 5 mL of deionized water were added, forming a brown suspension under mechanical stirring. Subsequently, 5 mL of 48%–51% HF aqueous solution was introduced into the mixture under ambient conditions with continued mechanical stirring to initiate the etching reaction (extreme caution was exercised when handling the HF solution). After 1 hour of etching, the suspension colour gradually changed to orange. The H-SiNCs were extracted from the aqueous solution by multiple additions of toluene and then transferred to test tubes. The particles were isolated from the solution by centrifugation at 7000 rpm for 10 minutes and re-dispersed in acetonitrile and stored in vials for further use.

Radical initiated hydrosilylation for preparation of alkyl-passivated SiNCs (alkyl-SiNCs). Under a constant nitrogen flow, 1 mg of the radical initiator 2,2'-Azobis(2-methylpropionitrile) (AIBN, 4 μmol) and octene were added to the flask with mechanical stirring. The flask was then placed in an oil bath, and the temperature was gradually increased to 65°C. The hydrosilylation reaction was maintained at this temperature for 16 hours, resulting in a transparent orange solution. After the reaction, the solution was transferred into 1.5 mL centrifuge tubes (approximately 0.3 mL per tube). To each tube, approximately 1.2 mL of a 1:1 methanol/ethanol mixture was added, causing the formation of a cloudy yellow suspension. The precipitate was isolated by centrifugation at 17,000 rpm for 10 minutes using a high-speed centrifuge. The supernatant was decanted, and the particles were redispersed in a minimal amount of toluene. The suspension was then re-precipitated by adding the 1:1 methanol/ethanol mixture. This centrifugation and decanting process was repeated twice. Finally, the purified, functionalized SiNCs were redispersed in acetonitrile and stored in vials for further use.

Preparation of Ag@H-SiNCs. To the above-mentioned H-SiNCs dispersion (10 mg H-SiNCs), 200 μL of silver benzoate solution (2.3 wt%, acetonitrile) was added drop by drop and then stirred in room temperature. The reaction was maintained for 12 hours, resulting in a opaque black suspension. The sample was isolated by ultracentrifugation at 7000 rpm for 10 min. The supernatant was decanted, and the precipitate was redispersed in 20 mL of acetonitrile, followed by another round of centrifugation at 7000 rpm for 10 min. The redispersion/centrifugation/supernatant-removal procedure was repeated twice. Finally, the precipitate was dried in vacuum, stored in a glass vial under ambient conditions for further use.

Preparation of Ag@alkyl-SiNCs. To the above-mentioned Ag@alkyl-SiNCs dispersion (10 mg alkyl -SiNCs), 200 μL of silver benzoate solution (2.3 wt%, acetonitrile) was added drop by drop and then stirred in room temperature. The reaction was maintained for 12 hours, resulting in a transparent colloidal dispersion which is agree with alkyl-SiNCs. The sample was transferred into 1.5 mL centrifuge tubes (approximately 0.3 mL per tube). To each tube, approximately 1.2 mL of a 1:1 methanol/ethanol mixture was added, causing the formation of a cloudy yellow suspension.

The precipitate was isolated by centrifugation at 17,000 rpm for 10 minutes using a high-speed centrifuge. The supernatant was decanted, and the particles were redispersed in a minimal amount of toluene. The suspension was then re-precipitated by adding the 1:1 methanol/ethanol mixture. This centrifugation and decanting process was repeated twice. Finally, the purified Ag@alkyl-SiNCs were redispersed in acetonitrile and stored in vials for further use.

Photocatalytic CO_2 reduction performance. CO production via photocatalytic CO_2 reduction was carried out using a 50 mL sealed glass vial with magnetic stirring. Typically, 2 mg of powdery sample was suspended in 5 mL of a mixed solvent of TEOA and MeCN (v/v = 1/4) and formed a homogenous solution. The glass vial was pumped into CO_2 (99.999%) and then sealed before placing it onto the holder (5 cm above the light source), and the reaction lasted for a predesigned period at room temperature. The amount of produced CO was analyzed by an off-line gas chromatograph (FuLi Analytical Instrument Co., Ltd., GC9790 plus) equipped with a thermal conductivity detector and a nitrogen carrier. The light source was a white LED light setup (10 W, $\lambda = 450$ nm, PCX-50B/50 C, Beijing Perfect light Technology Co., Ltd.).

Carbon isotope tracer measurements. The isotope-labelling catalytic experiments using $^{13}CO_2$ molecules were performed under the same conditions. Briefly, 2 mg of powdery Ag@alkyl-SiNCs sample was suspended in a 50-mL glass vial with 5 mL of the mixed solvent containing TEOA and MeCN (volume ratio: 1:4). $^{13}CO_2$ (99.999%, Sigma) gas was purged three times (10 min for each purge period) to the glass vial to obtain a saturated $^{13}CO_2$ atmosphere. The gaseous products were analyzed using gas chromatography-mass spectrometry (GCMS-QP2010).

XRD measurements. XRD patterns were collected with a Rigaku Smart Lab diffractometer (Bragg-Brentano geometry, Cu Kα1 radiation, $\lambda = 1.54056$ Å). The spectra were scanned between 2θ ranges of 10–80° with an integration of 350 min.

XPS measurements and analyses. XPS measurements were carried out using Thermo Scientific KAlpha XPS system with a monochromatic Al Kα X-ray source (1486.7 eV, spot size: 400 μm). The electron kinetic energy was measured by an energy analyzer operated in the constant analyzer energy mode at 100 eV pass energy for elemental spectra. Casa XPS software (VAMAS) was used to interpret the high-resolution XP spectra. All spectra were internally calibrated to the C *1s* emission (284.8 eV).

Absorption measurements. The UV−vis absorption spectra were measured using a Shimadzu spectrometer (UV-3600) by samples solutions which diluted with specific amount of acetonitrile.

Electron microscopy studies. HAADF-STEM images and EDX results were acquired using an aberration-corrected 'cubed' Thermo Fisher Scientific Themis 60-300 microscope operated at an acceleration voltage of 200 kV with a probe current of ~50 pA for HAADF-STEM imaging with an energy dispersive spectrometer (EDS) under high vacuum condition.

Fourier-Transform Infrared Spectroscopy (FT-IR). FT-IR spectra of the samples were recorded by Nicolet/Nexus-670 FT-IR spectrometer in the region of 4000 - 400 cm-1 equipped with ATR transmission module.

Photoluminescence Measurements. Photoluminescence (PL) spectra of the AgNPs/SiNCs dispersions were recorded at room temperature using an FLS 980 spectrometer (Edinburgh Instruments) with a xenon lamp as a continuous wave light source. The excitation wavelength was set as 365 nm for all samples. For spectrally resolved PL decay measurements, ∼2 mL of SiNCs/chloroform solution was transferred in a quartz cuvette. The sample was pumped by a 405 nm laser (2 W/cm^2). The spectral resolution of this method is ∼ 6 nm. The laser pulse width and repetition rate were set between 100 and 500 μs and 0.5−10 kHz, respectively. The emitted photons were collected with a 10× 0.25 NA objective and sent to a 20 × 20 μm avalanche photodiode (Becker & Hickl, DPC-230) via spectrometer (Andor Shamrock 500).

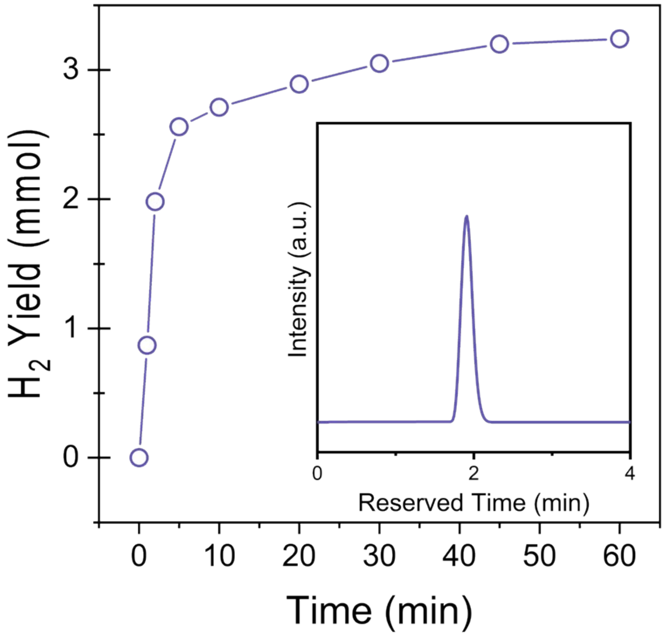

Fig. S1 | Hydrogen generation curves of H-SiNCs treated with silver benzoate. Inset: typical GC signal of H_2 after the elapsed time.

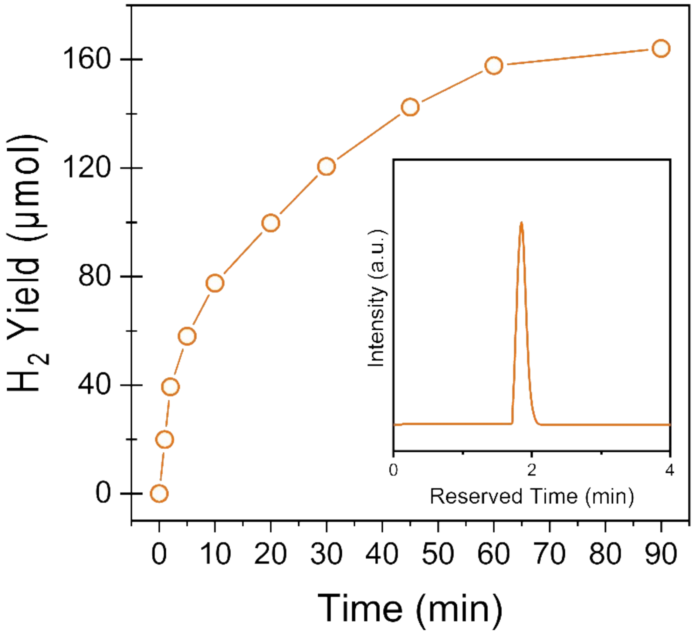

Fig. S2 | Hydrogen generation curves of alkyl-SiNCs treated with silver benzoate. Inset: typical GC signal of H_2 after the elapsed time.

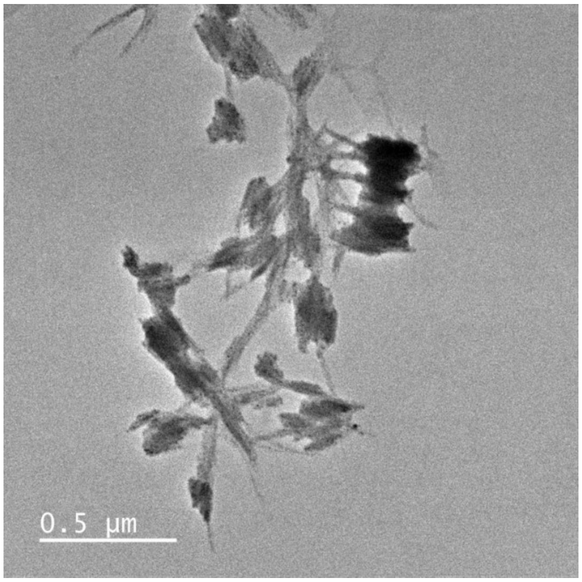

Fig. S3 | Additional HAADF-STEM images of Ag@H-SiNCs.

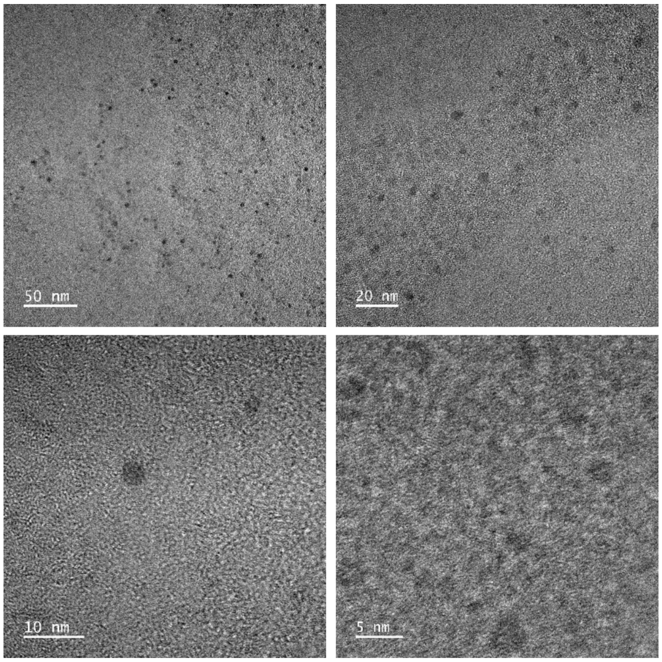

Fig. S4 | Additional HAADF-STEM images of Ag@alkyl-SiNCs in different resolution.

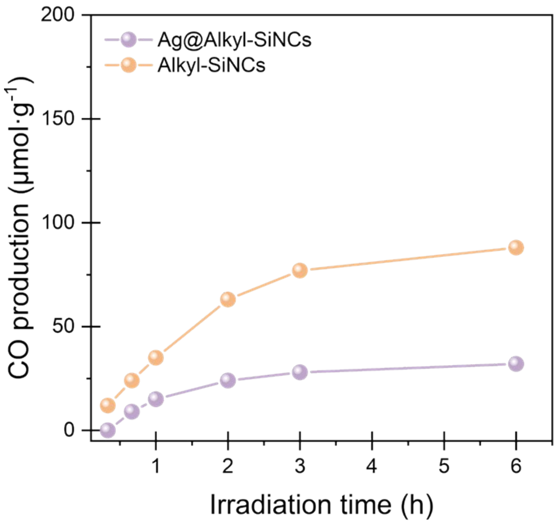

Fig. S5 | Comparison of the CO production performance of Ag@alkyl-SiNCs and pristine alkyl-SiNCs in CO_2 saturated solutions (8 mL acetonitrile; 2 mL TEOA; 2 mg catalyst; dark condition).

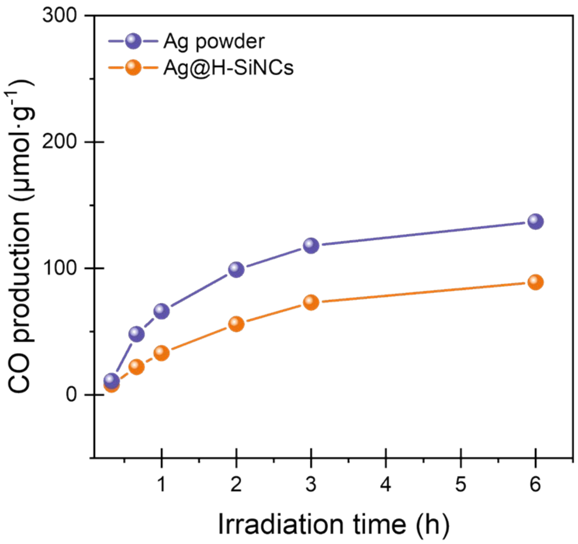

Fig. S6 | Comparison of the CO production performance of Ag-related control samples in CO_2-saturated solutions (8 mL acetonitrile; 2 mL TEOA; 2 mg catalyst) under blue LED irradiation (λ=450 nm).

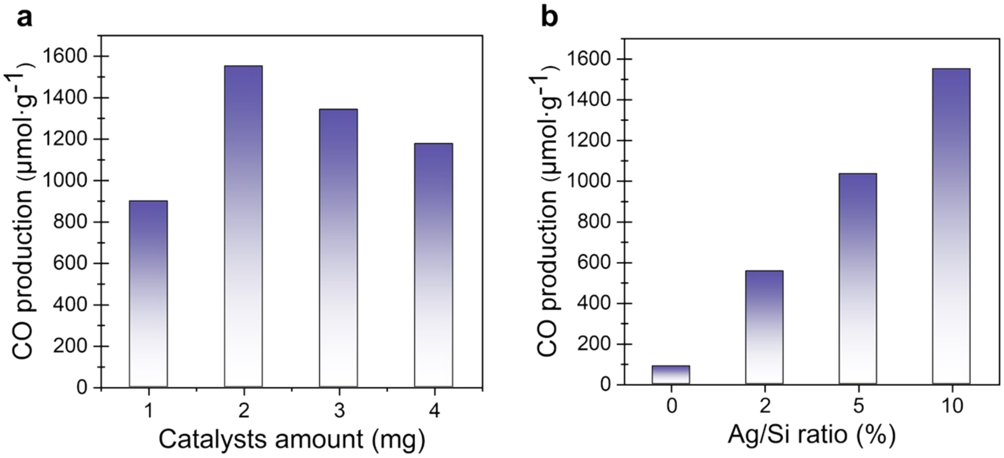

Fig. S7 | Photocatalytic investigation on Ag@alkyl-SiNCs. The influence on (a) catalyst usage; and (b) Ag/Si ratio in Ag@alkyl-SiNCs.

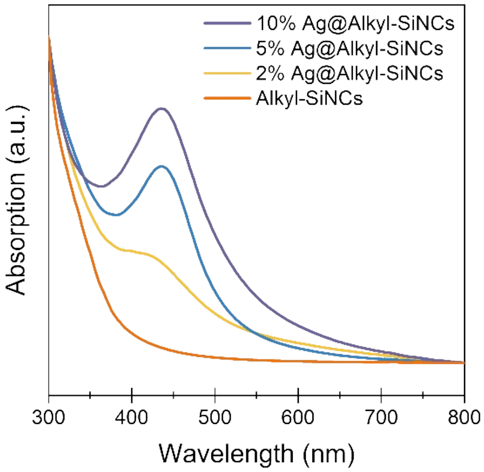

Fig. S8 | UV-vis spectra of pristine SiNCs and Ag@Alkyl-SiNCs with different Ag/Si ratio.

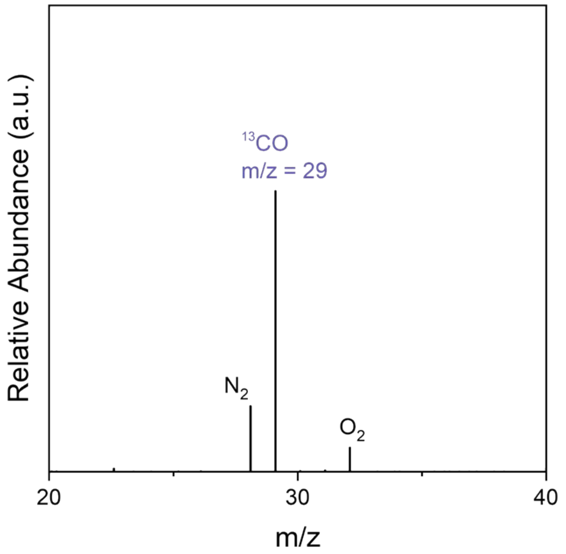

Fig. S9 | Gas chromatography-mass spectrometry (GC-MS) analysis of ^{13}CO generated from the photocatalytic reduction of $^{13}CO_2$ by Ag@alkyl-SiNCs. The component of O_2 and N_2 may result from the gas leakage by injection.

References

1. R. J. Clark, M. Aghajamali, C. M. Gonzalez, L. Hadidi, M. A. Islam, M. Javadi, Md H. Mobarok, T. K. Purkait, C. J. T. Robidillo, R. Sinelnikov, A. N. Thiessen, J. Washington, H. Yu, J. G. C. Veinot, *Chem. Mater.* 2016, 29, 80.