

Ag@imidazolium functionalized polymeric yolk-shell hybrid nanoparticles for economical CO₂ photoreduction

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Materials and methods

Materials

Benzoyl peroxide (BPO), hydrofluoric acid, (methacryloxy)-propyltrimethoxysilane (MPS), Tetraethyl orthosilicate (TEOS) were purchased from Jinan Mingtu biotechnology Co. Ltd., 4-Vinyl benzyl chloride (VBC), divinylbenzene (DVB), 1-Methimidazole, hexamethyldisilamine potassium salt were purchased from Alfa Aesar and used without purification. Acetonitrile (analytical grade) was dried and purified by distillation. Sodium citrate, gallotannic acid, and silver nitrate aqueous solution (25 mM) were purchased from Tianjin Heowns Biochemical Technology Co. Ltd., China.

Preparation of Ag@SiO₂ nanoparticles

100 mL deionized water, 147 mg sodium citrate, and 4.3 mg gallotannic acid were added into round-bottomed flask. When the mixture was heated to boiling, 1 mL of silver nitrate aqueous solution (25 mM) was added into. After cooled down to room temperature, the mixture was centrifuged and washed to obtain the Ag nanoparticles with diameter of 20 nm. For the Ag nanoparticles with diameter of 40 nm or 60 nm, we modified the amount of the sodium citrate and gallotannic acid.

We then synthesized the MPS modified Ag@SiO₂ nanoparticles through a solution-gel method: after the obtained Ag nanoparticles were re-dispersed in 2.5 mL deionized water, 7.5 mL ethanol and 35 μ L TEOS were added into and stirred for 10 mins. After 0.3 mL of NH₃·H₂O was added into, the mixture was sealed and stirred for 6 hours. Then, 35 μ L of MPS was added into and stirred for 18 hours. Finally, the

obtained nanoparticles were centrifuged, washed, and dried.

Preparation of Ag@SiO₂-P(VBC-co-DVB) core-shell nanoparticles

100 mg MPS modified Ag@SiO₂ was dispersed in 30 mL ACN, 50 μL monomer VBC, 30 μL crosslinker DVB, and 8 mg initiator BPO were added into. The mixture was heated to boiling and kept heating until half of the solvent was steamed out. The resulting Ag@SiO₂-P(VBC-co-DVB) core-shell nanoparticles were centrifuged, washed, and dried.

Preparation of Ag@P(VBC-co-DVB) yolk-shell nanoparticles

With the Ag@SiO₂-P(VBC-co-DVB) core-shell nanoparticles in hand, we selectively etched off the SiO₂ shell to afford Ag@P(VBC-co-DVB) yolk-shell nanoparticles: the above mentioned Ag@SiO₂-P(VBC-co-DVB) core-shell nanoparticles were dispersed in 30 mL ethanol. Then, 1 mL hydrofluoric acid was added into and stirred overnight. After that, the resulting Ag@P(VBC-co-DVB) yolk-shell nanoparticles were centrifuged, washed, and dried.

Preparation of the iminazole functionalized Ag@P(IVBC-co-DVB) yolk-shell nanoparticles (AIDNPs)

40 mg of Ag@P(VBC-co-DVB) yolk-shell nanoparticles were dispersed in 20 mL toluene. After 23 mg 1-Methimidazole was added into, the mixture was heated to boiling and kept the reaction for 8 hours. Then, the resulting iminazole functionalized Ag@P(IVBC-co-DVB) yolk-shell nanoparticles (AIDNPs) were centrifuged, washed, and dried.

The corresponding hollow P(IVBC-co-DVB) nanoparticles were prepared

according to the same procedure mentioned above as the control nanoparticles.

Nanoparticles analysis and characterization

The particle size, morphology, and size distribution of the resulting nanoparticles were analysed by TEM (JEOL JEM-2100, Japan). All of the TEM size data reflected the averages of the particles, which were calculated by the formulae as the following.

$$U = D_w / D_n ,$$
$$D_n = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i} ,$$
$$D_w = \frac{\sum_{i=1}^k n_i D_i^4}{\sum_{i=1}^k n_i D_i^3}$$

where, U is the poly dispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, D_i is the particle diameter of the determined nanoparticles.

Fourier transform infrared spectra (FTIR) were carried out by a Bruker Alpha FTIR spectrometer over potassium bromide pellets and the diffuse reflectance spectra were scanned.

X-ray photoelectron spectrometer (Mg as exciting source, ESCALAB MK II), and the X-ray diffractometer (2θ ranging from 10° to 90° , PERSEE, XD-3) were applied.

Photocurrent measurements were performed on a 300 W PLS-SXE 300D xenon lamp system equipped with filter. EIS was employed at a potential of 0.55 V from 0.01 Hz to 10 kHz with amplitude of 5.0 mV. Mott-Schottky curves were characterized on a frequency of 1.0, 1.5, and 2.0 kHz, respectively.

CO₂ photoreduction experiment

AIDNPs (5 mg) ultrasound dispersed in different solutions (10 mL) (pure 1,4-Dioxane, H₂O/1,4-Dioxane = 1:1, H₂O/1,4-Dioxane = 4:1, H₂O/1,4-Dioxane = 8:1, pure H₂O, or H₂O/ethanol = 1:1) were placed in quartz cuvette cell with 20 mL headspace. The solutions were bubbled with pure CO₂ for 5 mins and then illuminated (300 W Xe lamp) (365 nm UV-light, simulated sunlight (300 ~ 2600 nm), or visible light (420 ~ 800 nm)). At the preset time points (1 h, 2 h, 3 h, 4 h, 8 h, 12 h, 24 h), formic acid was detected and quantitated by ion chromatography and NMR according to the work curve. Meanwhile, the photochemical reactor headspace was analyzed by GC for H₂ or CO products.

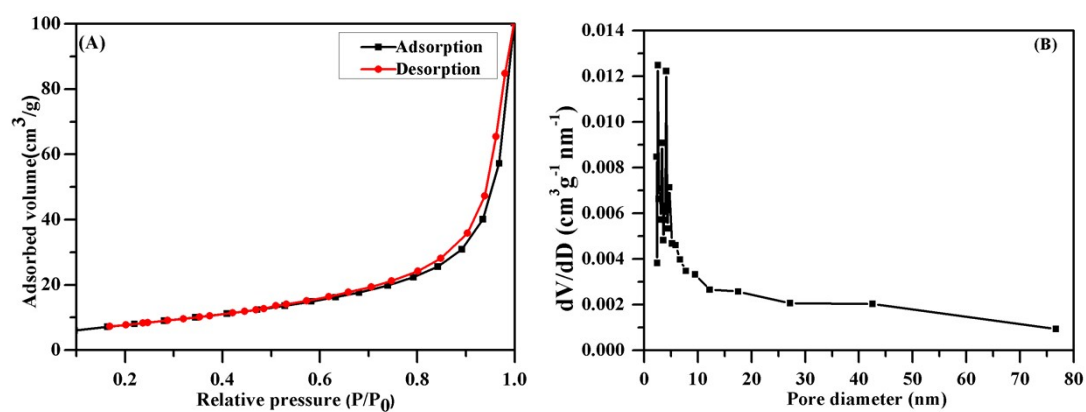


Figure S1. The N₂ adsorption–desorption isotherms (A) and the pore distribution diagram (B) of AIDNPs.

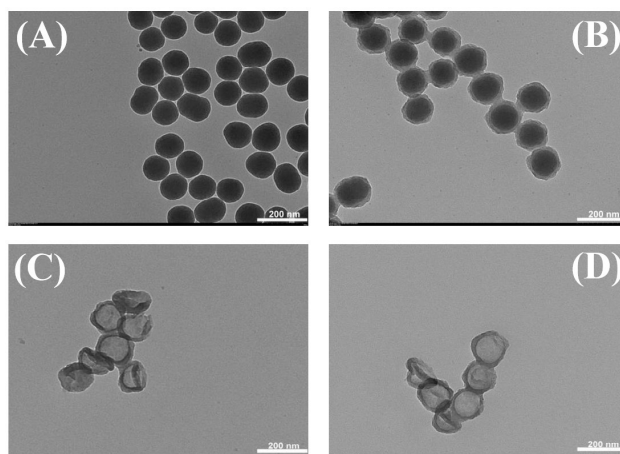


Figure S2. TEM pictures of SiO₂ nanoparticles (A), SiO₂-P(VBC-*co*-DVB) core-shell nanoparticles (B), Hollow P(VBC-*co*-DVB) nanoparticles (C), and Hollow P(IVBC-*co*-DVB) nanoparticles (D).

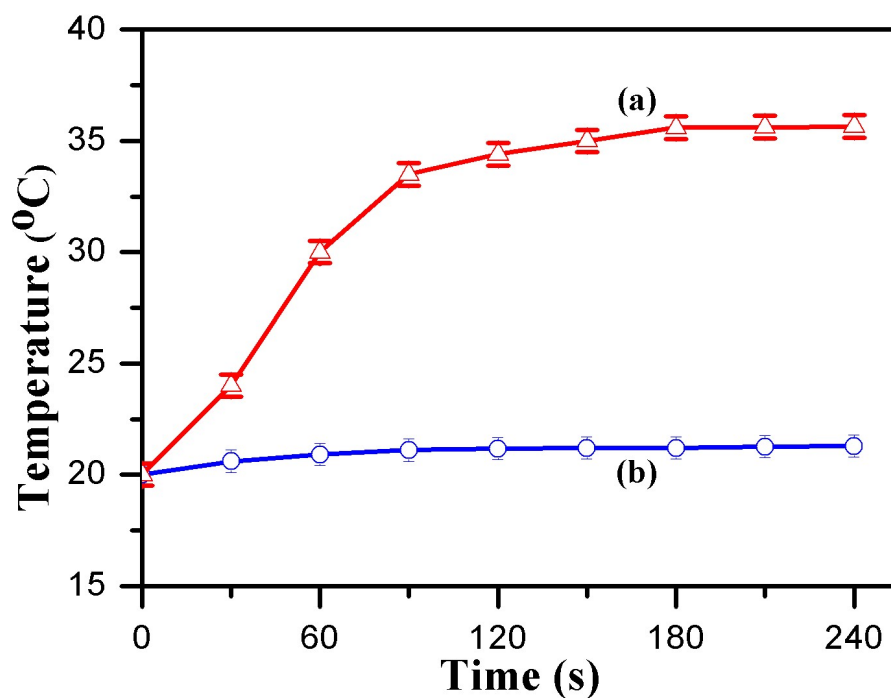


Figure S3. The variation curves in temperature of the AIDNPs (a) and the corresponding hollow P(IVBC-*co*-DVB) nanoparticles without Ag core (b) in H₂O (20 μg/ml) under NIR laser (830 nm) at 2.0 W/cm² for 4 min with an initial temperature of 20 °C.

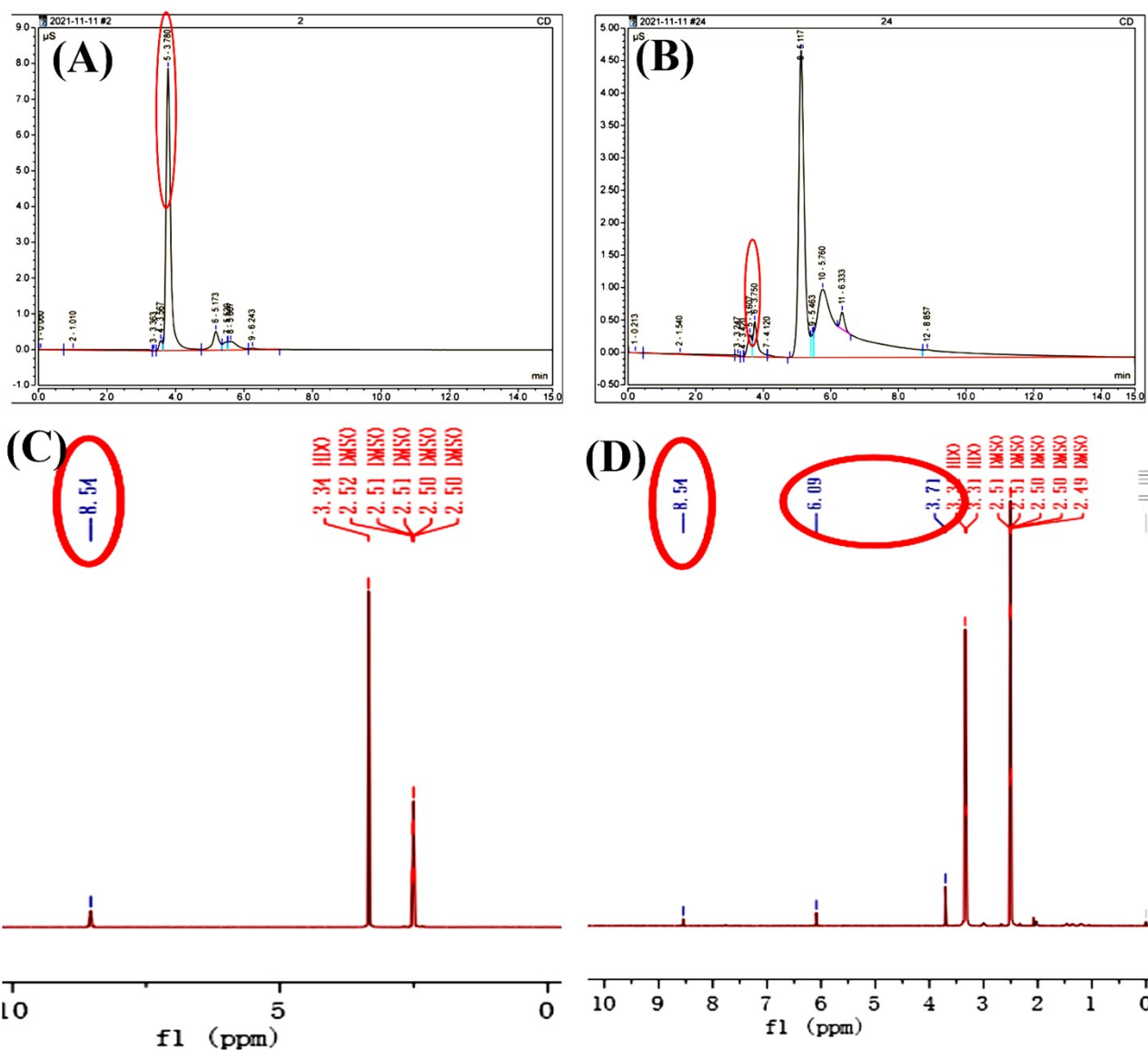


Figure S4. The control (A, C) and the experimental data (B, D) of the HCOOH by ion chromatograph analysis (A, B) or $^1\text{H-NMR}$ analysis (C, D) in DMSO. (In ion chromatograph, peak at 3.780 min was the HCOOH; In $^1\text{H-NMR}$, δ at 8.54 was the characteristic H spectrum, δ at 6.09 and 3.71 was the characteristic H spectrum of 1,3,5-Trimethoxybenzene as internal standard compound)

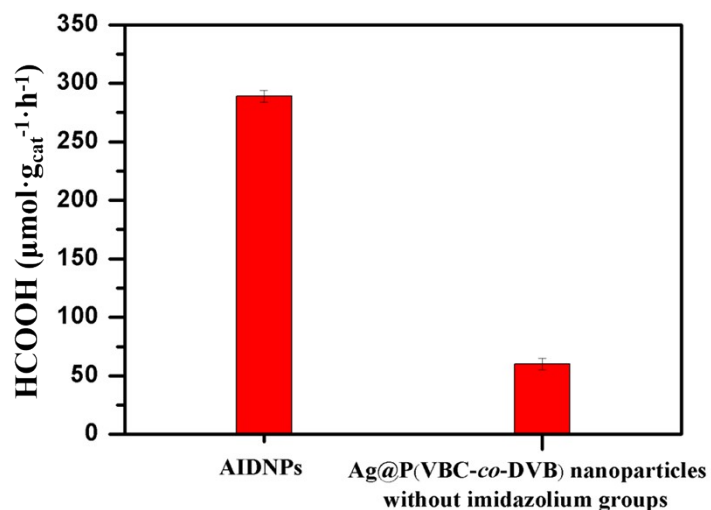


Figure S5. The HCOOH yield of AIDNPs and the yolk-shell Ag@P(VBC-co-DVB) nanoparticles without imidazolium groups in the H₂O/1,4-dioxane (4/1, v/v) under visible light (420 ~ 800 nm).

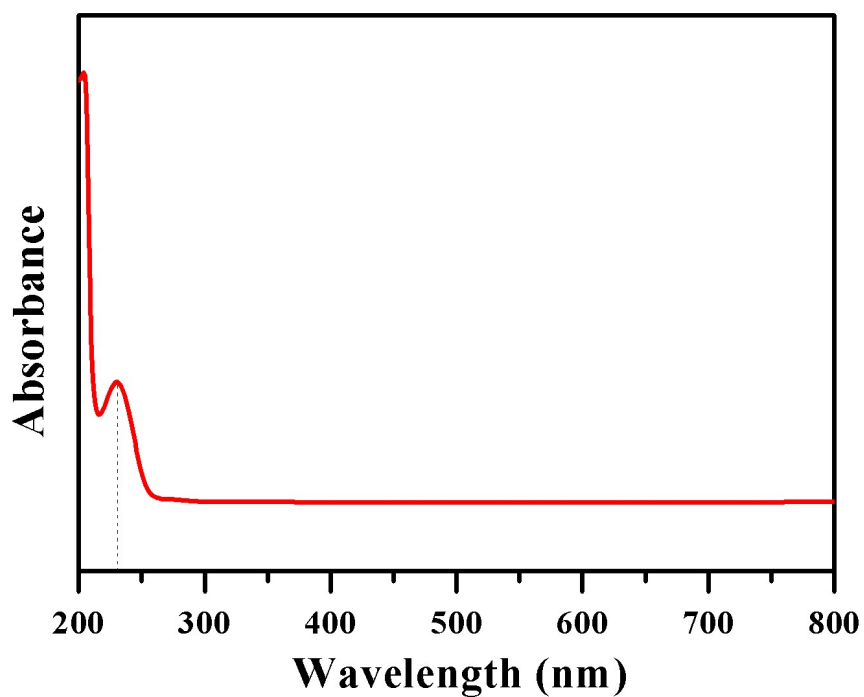


Figure S6 The UV-visible spectral absorption curve of the 1,4-dioxane.

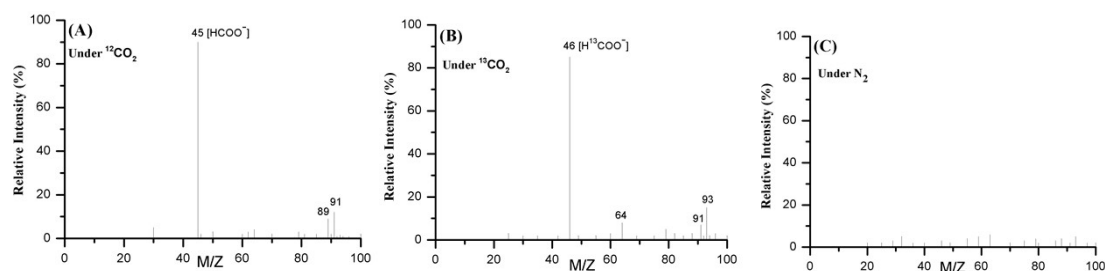


Figure S7. Mass spectral signals obtained from the photo-reduction under $^{12}\text{CO}_2$ (A), $^{13}\text{CO}_2$ (B), or N_2 (C).

Table S1. The faradaic efficiency (FE) of HCOOH (FE_{HCOOH}) and H_2 (FE_{H_2}), as well as the required CO_2 reduction conditions.

Entry	FE_{HCOOH} (%)	FE_{H_2} (%)	$\text{FE}_{\text{HCOOH}}/\text{FE}_{\text{H}_2}$	Photosensitizer and sacrificial reagent	Ref
1	75	5	15	No need	This work
2	64	5	13	Need sacrificial reagent	23
3	70	6	12	No need	24
4	-	-	-	Need photosensitizer and sacrificial reagent	25
5	90	10	9	Electro-catalysis	26

References

- 23.** B. Shan, S. Vanka, T.T. Li, L. Gautier, M.K. Brennaman, Z. Mi, T. J. Meyer. *Nat. Energy*, **2019**, 4, 290-299.
- 24.** W. Dong, I.A. Navid, Y. Xiao, J. W. Lim, J.L. Lee, Z. Mi. *J. Am. Chem. Soc.*, **2021**, 143, 10099-10107.

25. A.C. Ghosh, A. Legrand, R. Rajapaksha, G.A. Craig, C. Sasso, G. Balázs, D. Farrusseng, S. Furukawa, J. Canivet, F.M. Wisser. *J. Am. Chem. Soc.*, **2022**, 144, 8, 3626-3636.
26. Z.H. Zhu, B.H. Zhao, S.L. Hou, X.L. Jiang, Z.L. Liang, B. Zhang, B. Zhao. *Angew. Chem. Int. Ed.*, **2021**, 60, 23394-23402.
27. N. Li, J.J. Liu, J.W. Sun, B.X. Dong, L.Z. Dong, S.J. Yao, Z. Xin, S.L. Li, Y.Q. Lan. *Green Chemistry* **2020**, 22, 5325-5332.