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## Enhanced interface electric field in an all-solid-state Z-scheme Ag/AgCl/GCNT heterojunction for facilitating photocatalytic CO<sub>2</sub> reduction performance†

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**composites of g-C<sub>3</sub>N<sub>4</sub> nanotubes with anchored Ag/AgCl nanoparticles (AC/GCNT) were prepared using supramolecular self-assembly and an inert-atmosphere calcination method. The AC/GCNT-2 composites exhibits remarkably enhanced photocatalytic CO generation performance (25.10 μmol g<sup>-1</sup> h<sup>-1</sup>) without cocatalysts, hole scavengers, or an organic auxiliary agent, reaching a value 4.41 times that of GCNT materials (5.68 μmol g<sup>-1</sup> h<sup>-1</sup>).**

The continuous increase of the atmospheric CO<sub>2</sub> concentration can cause global warming, which can affect green-plant growth, ocean circulation directions, and the global distribution of water resources.<sup>1,2</sup> Simultaneously, CO<sub>2</sub> can be considered as a significant C1 resource for further resource utilization and energy development.<sup>3,4</sup> The strategy of CO<sub>2</sub> resource utilization can answer a double purpose: CO<sub>2</sub> emission reduction and clean energy generation.<sup>5</sup> The photocatalytic CO<sub>2</sub> reduction process can realize efficient conversion of solar energy and CO<sub>2</sub> into easily-stored and transportable chemical energy without being driven by other external energy, which is conducive to CO<sub>2</sub> resource conversion and utilization, and large-scale storage of clean energy.<sup>6,7</sup> Nevertheless, the conversion efficiency of the photocatalytic CO<sub>2</sub> reduction process is primarily affected by the high structural stability of the linear CO<sub>2</sub> molecule and the delayed dynamics of photogenerated-carrier migration.<sup>8</sup> Significantly, the construction of efficient photocatalysts is deemed the decisive factor for the

photocatalytic CO<sub>2</sub> conversion process, which relies on enhancing the solar-energy conversion efficiency.

Being a non-toxic and inexpensive raw materials, with a large active surface and controllable band structure, g-C<sub>3</sub>N<sub>4</sub> has attracted widespread attention and systematic research in the field of photocatalytic CO<sub>2</sub> reduction.<sup>9</sup> Nevertheless, attributed to their π-conjugated structure and non-metallic properties, the internal electric field (IEF) strength and CO<sub>2</sub> activation site numbers of g-C<sub>3</sub>N<sub>4</sub> materials should be further optimized *via* various modification strategies.<sup>10,11</sup> The construction of a heterogeneous interface on the surface of g-C<sub>3</sub>N<sub>4</sub> nanotube materials has gradually become a common strategy for enhancement of photocatalytic performance by forming efficient electron migration pathways and promoting the directional transport of photogenerated carriers.<sup>12,13</sup> The ability of g-C<sub>3</sub>N<sub>4</sub> nanotube materials to separate photogenerated electrons can be effectively enhanced through constructing heterogeneous interfaces on their surfaces *via* coupling with other photo-active materials, which realizes efficient photocatalytic conversion of CO<sub>2</sub>.

The morphologies of the GCNT materials, AgCl nanoparticles and AC/GCNT-2 composites were analysed using SEM and TEM measurements. As demonstrated in Fig. S1 (ESI†) and Fig. 1a and b, the GCNT materials exhibits a porous nanotube structure with a diameter of about 200 nm. Furthermore, the size of the AgCl materials obtained *via* a hydrothermal method is from 20 nm to 100 nm (Fig. 1c). As shown in Fig. S2 (ESI†) and Fig. 1d, the AC/GCNT-2 composites still maintains a porous nanotube morphology. Significantly, multitudinous nanoparticles with a diameter of 20 nm are uniformly dispersed on the surface of the AC/GCNT-2 composites. The selected area electron diffraction (SAED) pattern (Fig. 1f) of the AC/GCNT-2 composites indicates the presence of lattice diffraction fringes with spacings of 0.235 and 0.196 nm, corresponding to the Ag (1 1 1) and AgCl (2 2 0) crystalline surfaces, respectively, which demonstrates that Ag/AgCl nanoparticle-loaded GCNT materials were successfully prepared *via* hydrothermal and calcination methods.<sup>14,15</sup> As indicated in Fig. 1g–j, the four elements C, N, Ag and Cl uniformly appear on the surface of the AC/GCNT-2 composites, further demonstrating the uniform distribution of Ag/AgCl nanoparticles on the GCNT materials.

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Fig. 1 TEM images of (a) and (b) GCNT, (c) AgCl, (d) and (e) AC/GCNT-2 composites; (f) SAED image and (g)–(j) mapping images of AC/GCNT-2 composites.

As shown in Fig. 2a, a conspicuous diffraction peak situated at  $27.1^\circ$  has been observed in the X-ray powder diffraction (XRD) patterns of the GCNT materials, corresponding to the (0 0 2) crystalline plane of the g- $C_3N_4$  materials. Furthermore, the numerous diffraction peaks located in the XRD patterns of the AgCl materials match with those of cubic AgCl (PDF#85-1355). The diffraction peaks situated at  $38.1^\circ$ ,  $44.3^\circ$ ,  $64.5^\circ$ , and  $77.4^\circ$  in the XRD patterns of the AC/GCNT-*x* composites correspond to the PDF#87-0717 standard card, indicating the presence of elemental Ag in the AC/GCNT-*x* composites. Furthermore, the weak diffraction peaks corresponding to the AgCl materials are only observed in the AC/GCNT-3 composites, which indicates that further characterization should be carried out to verify the presence of AgCl in the other AC/GCNT-*x* composites. As indicated in Fig. 2b, the characteristic vibrational peaks in the FT-IR spectra of GCNT and the AC/GCNT-*x* composites, located at  $808\text{ cm}^{-1}$ ,  $1200\text{--}1700\text{ cm}^{-1}$ , and  $2200\text{ cm}^{-1}$ , can be attributed to triazine rings, conjugated C–N heterocyclic structures and  $\text{C}\equiv\text{N}$  groups in the GCNT materials.<sup>16–18</sup> A band in the region of  $1200\text{ to }1700\text{ cm}^{-1}$  for GCNT and the AC/GCNT-2 composites has been observed (Fig. S3, ESI<sup>†</sup>), which corresponds to disordered graphitic carbon–nitrogen vibrations.

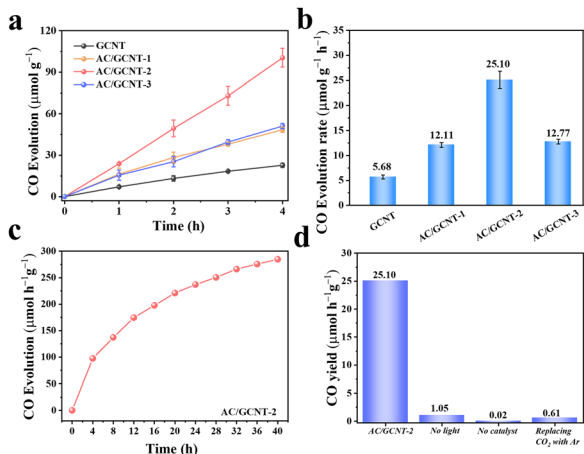
X-ray photoelectron spectroscopy (XPS) measurements were employed to investigate the chemical composition and elemental valence states of the GCNT and AC/GCNT-2 composites. As demonstrated in the C 1s high-resolution spectra of GCNT and the AC/GCNT-2 composites (Fig. 2c), three characteristic peaks are located at the binding energies of 284.8 eV, 286.7 eV, and 288.0 eV, which corresponds to C–C/C=C,  $\text{C}\equiv\text{N}$ , and N–C=N bonds, indicating that the Ag/AgCl nanoparticles loading has not caused an obvious impact on the basic structure of the GCNT materials.<sup>19</sup> The N 1s XPS spectra of GCNT and the AC/GCNT-2 composites (Fig. 2d) are Gaussian fitted to three characteristic peaks located at binding energies of 398.6 eV, 400.1 eV, and 401.1 eV, corresponding to the C–N=C bond in C–N heterocycles, and N–(C)<sub>3</sub> and C–N–H bonds.<sup>20,21</sup> Furthermore, the high-resolution Ag 3d spectrum of



Fig. 2 (a) XRD patterns of GCNT, AgCl and AC/GCNT-*x* composites, and (b) FT-IR spectra of GCNT and AC/GCNT-*x* composites; XPS spectra of GCNT and the AC/GCNT-2 composites: (c) C 1s, (d) N 1s, (e) Ag 3d and (f) Cl 2p.

the AC/GCNT-2 composites has been divided into two peaks located at binding energies of 367.4 eV and 373.6 eV, corresponding to the  $\text{Ag}^+$  of the AgCl materials. Furthermore, two peaks appear at binding energies of 368.1 eV and 374.1 eV, related to the  $\text{Ag}^0$  valence state, suggesting that Ag/AgCl nanoparticles are anchored in the structure of the AC/GCNT-2 composites.<sup>22,23</sup> As indicated in Fig. 2f, an obvious characteristic peak corresponding to  $\text{Cl}^-$  in the high-resolution Cl 2p spectra has not been observed in the GCNT materials, indicating that the  $\text{Cl}^-$  in  $\text{NH}_2\text{OH}\cdot\text{HCl}$  has not been introduced into the GCNT materials. Moreover, the characteristic peaks in the AC/GCNT-2 composites are located at the binding energies of 197.9 eV and 199.5 eV, and are related to the Cl 2p<sub>3/2</sub> and Cl 2p<sub>1/2</sub> orbitals of the AgCl materials.<sup>24,25</sup> The XPS analysis results further indicate that the Ag/AgCl nanoparticles were successfully loaded on the GCNT materials.

The photocatalytic  $\text{CO}_2$  conversion performance of the GCNT and AC/GCNT-*x* composite was investigated to evaluate the effect of Ag/AgCl particle introduction under conditions with pure water, no sacrificial agent, and no catalytic additive. The photocatalytic CO generation rate of the GCNT materials (Fig. 3a) reaches  $5.68\ \mu\text{mol g}^{-1}\text{ h}^{-1}$ , and AC/GCNT-*x* composite exhibit a significantly enhanced photocatalytic CO generation ability compared with that of the GCNT materials. The photocatalytic CO generation rates of the AC/GCNT-1, AC/GCNT-2, and AC/GCNT-3 composite reach 12.11, 25.10, and  $12.77\ \mu\text{mol g}^{-1}\text{ h}^{-1}$  (Fig. 3b), which are 2.13, 4.41, and 2.25 times higher than that of the GCNT materials. Compared with previous reports about other  $\text{C}_3\text{N}_4$ -based materials for photocatalytic  $\text{CO}_2$  reduction (Table S2, ESI<sup>†</sup>), AC/GCNT-2



**Fig. 3** (a) The photocatalytic CO evolution performance and (b) the photocatalytic CO evolution rate of the GCNT materials and AC/GCNT-*x* composites; (c) the stability of AC/GCNT-*x* composites for photocatalytic  $\text{CO}_2$  conversion; (d) the control experiments for the photocatalytic CO evolution rate of the AC/GCNT-2 composites.

composites possesses a high CO evolution rate and selectivity. The continuous photocatalytic  $\text{CO}_2$  reduction tests were performed on the AC/GCNT-2 composites to evaluate the reaction stability of the AC/GCNT-2 composites. As shown in Fig. 3c, the photocatalytic CO generation rate of the AC/GCNT-2 composites keeps a continuous increase in a 40 h continuous photocatalytic  $\text{CO}_2$  reduction

measurement, indicating that the AC/GCNT-2 composites possesses good  $\text{CO}_2$  reduction stability. The control experiments (Fig. 3d) indicate that light, the AC/GCNT-2 composites and injecting  $\text{CO}_2$  are indispensable reaction conditions for realizing photocatalytic  $\text{CO}_2$  conversion.

The transient photocurrent response, electrochemical impedance spectroscopy (EIS) results, photoluminescence (PL) spectra and time-resolved PL (TRPL) decay curves (Fig. S4a-d, ESI<sup>†</sup>) of the GCNT materials and AC/GCNT-2 composites indicate that the AC/GCNT-2 composites possesses enhanced photo-generated-electron migration efficiency.<sup>26</sup> The distribution model for the electric field was constructed to further elaborate on the IEF enhancement mechanism of the AC/GCNT composites between the GCNT materials and Ag/AgCl nanoparticles (Fig. 4a). As indicated in Fig. 4b and d, a uniform surface electric field distribution has been observed in the GCNT materials, which demonstrates that the electronic transmission efficiency of the GCNT materials needs to be further strengthened.<sup>27</sup> As demonstrated in Fig. 4c, a “hot spot” is significantly observed in the centre position of the Ag/AgCl nanoparticles and a remarkable enhanced electric field distribution appears in the interface of the GCNT materials and Ag/AgCl nanoparticles at 470 nm, which indicates that the introduced Ag/AgCl nanoparticles can effectively increase the IEF intensity. Furthermore, the “hot spot” appears at the periphery of the Ag/AgCl nanoparticles at 530 nm, which strengthens the



**Fig. 4** (a) The schematic diagram of the AC/GCNT-2 composites; the COMSOL simulation results of the GCNT materials at (b) 470 nm and (d) 530 nm, and the AC/GCNT-2 composites with the excitation light wavelength at (c) 470 nm and (e) 530 nm; (f) the  $\text{CO}_2$  adsorption isotherm of GCNT and the AC/GCNT-2 composites; (g) *in situ* FT-IR spectra for the photocatalytic  $\text{CO}_2$  reduction process of the AC/GCNT-2 composites; (h) schematic illustration of the possible charge transfer mechanism in the AC/GCNT composites.

IEF between the GCNT materials and Ag/AgCl nanoparticles to accelerate electron transport to CO<sub>2</sub> reduction sites. Accordingly, the simulation of the electric field distribution shows that the introduction of Ag/AgCl nanoparticles can achieve efficient migration and utilization of electrons for participation in catalytic CO<sub>2</sub> conversion.

The CO<sub>2</sub> adsorption performance of a photocatalyst is perceived as a considerable evaluation factor for determining the promotion mechanism of the photocatalytic CO generation rate. As indicated in Fig. 4f, the maximum value of CO<sub>2</sub> quantity adsorbed for the GCNT materials is 4.86 cm<sup>3</sup> per g STP, which reaches 3.23-fold that of the AC/GCNT-2 composites (1.50 cm<sup>3</sup> per g STP), further demonstrating that the determining factor is the strengthening of the IEF by heterojunction construction rather than CO<sub>2</sub> adsorption performance. The investigation of intermediate generation in the photocatalytic CO<sub>2</sub> reduction process using *in situ* spectroscopy possesses high research significance and scientific value for analysing the photocatalytic CO<sub>2</sub> reduction process. As observed in Fig. 4g, in the *in situ* FT-IR spectra, the intensity of the vibrational peaks corresponding to *m*-CO<sub>3</sub><sup>2-</sup> (1347 cm<sup>-1</sup>), HCO<sub>3</sub><sup>-</sup> (1455 cm<sup>-1</sup>), COOH\* (1517 cm<sup>-1</sup>), CO<sub>2</sub><sup>-</sup> (1713 cm<sup>-1</sup>), and HCOOH (1735 cm<sup>-1</sup>) intermediates gradually increases with temporal evolution, indicating that the photogenerated electrons continuously interact with CO<sub>2</sub> adsorbed on the AC/GCNT-2 composites to generate reaction intermediates.<sup>28</sup> The energy band structure of the AgCl and GCNT materials has been analysed using  $(\alpha h\nu)^2$  vs.  $h\nu$  curves<sup>29</sup> (Fig. S5a and b, ESI<sup>†</sup>) and Mott-Schottky plots (Fig. S5c and d, ESI<sup>†</sup>). Based on electron spin resonance (ESR) spectra (Fig. S6a and b, ESI<sup>†</sup>) and work-function calculations (Fig. S7a–c, ESI<sup>†</sup>), an all-solid-state Z-scheme charge transfer mechanism formed by the Ag, AgCl and GCTN materials has been proposed, as shown in Fig. 4h. The TEMPO quenching (Fig. S8a and b, ESI<sup>†</sup>) and Kelvin probe force microscopy (KPFM) images (Fig. S9a–d, ESI<sup>†</sup>) further indicate that the AC/GCNT-2 composites possesses high oxidation–reduction ability and spatial distribution of photogenerated carriers.

In summary, composites of g-C<sub>3</sub>N<sub>4</sub> nanotubes with anchored Ag/AgCl nanoparticles (AC/GCNT) were successfully constructed. The high-performance directional migration of photogenerated electrons endows the AC/GCNT composites with a high photocatalytic CO<sub>2</sub> reduction rate (25.10 μmol g<sup>-1</sup> h<sup>-1</sup>), which is 4.41 times that of the GCNT materials (5.68 μmol g<sup>-1</sup> h<sup>-1</sup>). The photogenerated carrier migration path in the all-solid-state Z-scheme AC/GCNT heterojunction formed by the Ag/AgCl nanoparticles and GCNT materials has been revealed by ESR spectra and energy band structure analysis. The simulation of the electric field distribution using COMSOL software and the CO<sub>2</sub> adsorption isotherms of GCNT and the AC/GCNT-2 composites indicate that an intensified IEF strength has a crucial function, rather than CO<sub>2</sub> absorption performance. This manuscript inspires the construction of all-solid-state Z-scheme heterojunctions and contributes a research reference for g-C<sub>3</sub>N<sub>4</sub>-based composites for photocatalytic CO<sub>2</sub> conversion processes.

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## Data availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of interest

There are no conflicts to declare.

## References

- 1 H. S. Baker, R. J. Millar, D. J. Karoly, U. Beyerle, B. P. Guillod, D. Mitchell, H. Shioyama, S. Sparrow, T. Woollings and R. A. Myles, *Nat. Clim. Change*, 2018, **8**, 604–608.
- 2 R. G. Hilton and J. A. West, *Nat. Rev. Earth Environ.*, 2020, **1**, 284–299.
- 3 E. Orsi, P. I. Nickel, L. K. Nielsen and S. Donati, *Nat. Commun.*, 2023, **14**, 6673.
- 4 X. L. Zhu, H. B. Zong, C. J. V. Pérez, H. H. Miao, W. Sun, Z. M. Yuan, S. H. Wang, G. X. Zeng, H. Xu, Z. Y. Jiang and G. A. Ozin, *Angew. Chem., Int. Ed.*, 2023, **62**, e202218694.
- 5 J. T. Dong, S. N. Ji, Y. Zhang, M. X. Ji, B. Wang, Y. J. Li, Z. G. Chen, J. X. Xia and H. M. Li, *Acta Phys. -Chim. Sin.*, 2023, **39**, 2212011.
- 6 B. Wang, H. L. Chen, W. Zhang, H. Y. Liu, Z. K. Zheng, F. C. Huang, J. Y. Liu, G. P. Liu, X. W. Yan, Y.-X. Weng, H. M. Li, Y. B. She, P. K. Chu and J. X. Xia, *Adv. Mater.*, 2024, **36**, 2312676.
- 7 L. N. Li, G. P. Liu, S. Q. Cao, J. T. Dong, B. Wang, Y. B. She, J. X. Xia and H. M. Li, *Appl. Catal., B*, 2024, 124904.
- 8 J. T. Dong, J. Z. Zhao, X. W. Yan, L. N. Li, G. P. Liu, M. X. Ji, B. Wang, Y. B. She, H. M. Li and J. X. Xia, *Appl. Catal., B*, 2024, **351**, 123993.
- 9 Q. Q. Lu, K. Eid, W. P. Li, A. M. Abdullah, G. B. Xu and R. S. Varma, *Green Chem.*, 2021, **23**, 5394–5428.
- 10 X. X. Lv, X. M. You, J. Y. Pang, H. Zhou, Z. J. Huang, Y. F. Yao and X. L. Wang, *Chem. Commun.*, 2024, **60**, 4652–4655.
- 11 S. Hu, P. Z. Qiao, X. L. Yi, Y. M. Lei, H. M. Hu, J. H. Ye and D. F. Wang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202206579.
- 12 L. Chen, H. Y. Li, H. M. Li, W. S. Qi, Q. Zhang, J. Zhu, P. Zhao and S. D. Yang, *Appl. Catal., B*, 2021, **318**, 121863.
- 13 W. H. Liu, S. Q. Hu, Y. Wang, B. B. Zhang, R. Y. Jin and G. S. Hu, *Nanoscale Res. Lett.*, 2019, **14**, 108.
- 14 S. Bera, S. Ghosh and R. N. Basu, *J. Alloys Compd.*, 2020, **830**, 154527.
- 15 F. Wang, Z. Li, H. H. Wang, M. Chen, C. B. Zhang, P. Ning and H. He, *Nano Res.*, 2022, **15**, 452–456.
- 16 D. B. Nimbalkar, P. V. R. K. Ramacharyulu, S. R. Sahoo, J. R. Chen, C. M. Chang, A. N. Maity and S. C. Ke, *Appl. Catal., B*, 2020, **273**, 119036.
- 17 Z. J. Liu, L. Wang, P. F. Liu, K. R. Zhao, S. Y. Ye and G. X. Liang, *Food Chem.*, 2021, **357**, 129753.
- 18 L. X. Ma, Y. P. Gao, B. Q. Wei, L. Huang, N. Zhang, Q. Weng, L. Zhang, S. Z. Liu and R. B. Jiang, *ACS Catal.*, 2024, **14**, 2775–2786.
- 19 W. Luo, Y. L. Li, J. S. Wang, J. C. Liu, N. Zhang, M. D. Zhao, J. S. Wu, W. Y. Zhou and L. Z. Wang, *Nano Energy*, 2021, **87**, 106168.
- 20 Y. Dai, W. R. Peng, Y. Ji, J. Wei, J. H. Che, Y. Q. Huang, W. H. Huang, W. M. Yang and W. Z. Xu, *J. Food Sci.*, 2024, **89**, 8022–8035.
- 21 Q. Li, Y. Q. Jiao, Y. Q. Tang, J. Zhou, B. G. Wu, B. J. Jiang and H. G. Fu, *J. Am. Chem. Soc.*, 2023, **145**, 20837–20848.
- 22 D. Sun, Y. Zhang, Y. F. Liu, Z. G. Wang, X. C. Chen, Z. Y. Meng, S. F. Kang, Y. Y. Zheng, L. F. Cui, M. L. Chen, M. D. Dong and B. Hu, *Chem. Eng. J.*, 2020, **384**, 123259.
- 23 R. Qiao, M. M. Mao, Y. J. Zhong, J. Q. Ning and Y. Hu, *Inorg. Chem.*, 2015, **54**, 9033–9039.
- 24 Y. T. Yu, Z. J. Zhu, F. Chen, T. Y. Ma and H. W. Huang, *Adv. Mater.*, 2024, **36**, 2413835.
- 25 F. R. Guo, C. L. Mao, C. Liang, P. Xing, L. H. Yu, Y. Shi, S. B. Cao, F. Y. Wang, X. Liu, Z. H. Ai and L. Z. Zhang, *Angew. Chem., Int. Ed.*, 2023, **62**, e202314243.
- 26 S. Bera, S. Ghosh, T. Maiyalagan and R. N. Basu, *ACS Appl. Energy Mater.*, 2022, **5**, 3821–3833.
- 27 D. Sun, J. Mao, H. L. Wei, Q. Zhang, L. Cheng, Z. L. Yang and P. W. Li, *ACS Appl. Mater. Interfaces*, 2022, **14**, 28021–28032.
- 28 J. Xie, Z. L. Lu, Y. Feng, J. G. Huang, J. D. Hu, A. Z. Hao and Y. L. Cao, *Nano Res.*, 2024, **17**, 297–306.
- 29 J. J. Lai, L. J. Ding, Y. Liu, C. H. Fan, F. H. You, J. Wei, J. Qian and K. Wang, *Food Chem.*, 2023, **423**, 136285.