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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

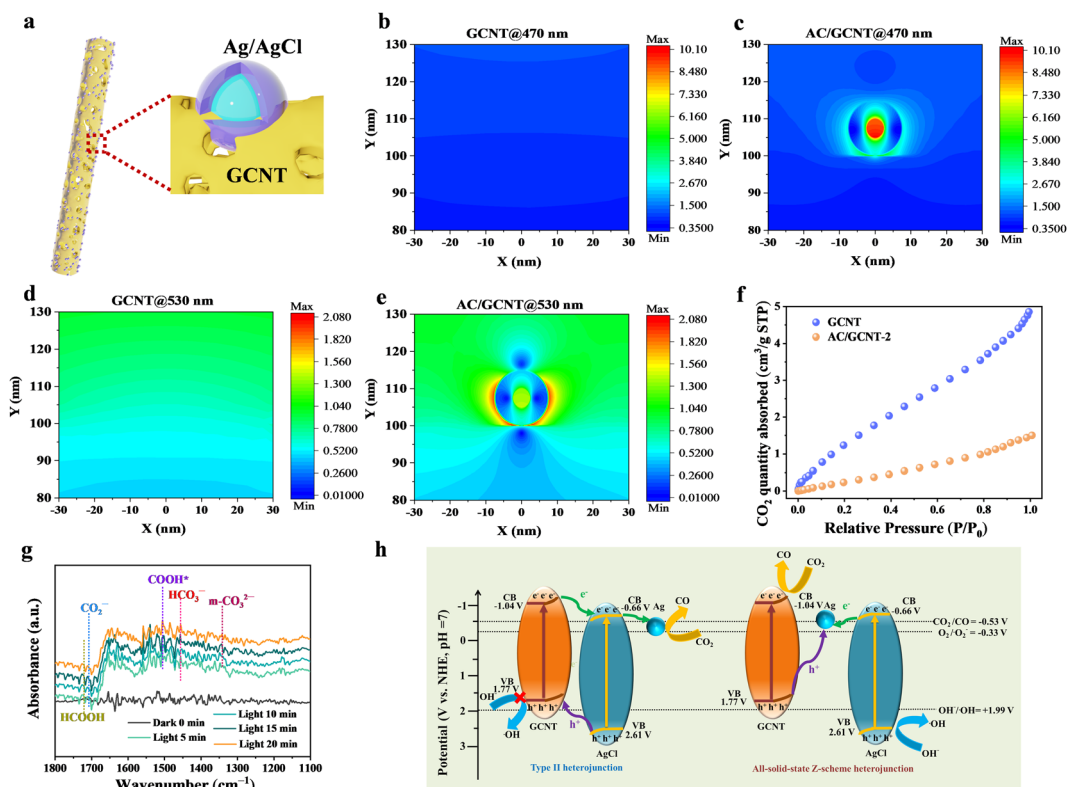


**Fig. 3** (a) The photocatalytic CO evolution performance and (b) the photocatalytic CO evolution rate of the GCNT materials and AC/GCNT-*x* composites; (c) the stability of AC/GCNT-*x* composites for photocatalytic  $\text{CO}_2$  conversion; (d) the control experiments for the photocatalytic CO evolution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

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