Supporting Information

Enhanced interface electric field in all-solidstate Z-scheme Ag/AgCl/GCNT heterojunction for facilitating photocatalytic CO₂ reduction performance

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Experimental Section

Experimental reagents

The chemicals hydroxylamine chloride (AR), AgNO₃ (AR), C₃H₆N₆ (98.0%), EtOH (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of photocatalysts

g-C₃N₄ nanotubes (GCNT) materials: 4.0 hydroxylamine chloride and 4.0 g melamine were injected in 60 mL deionized water. The supramolecular precursor was heated at 150 °C for 24 h in a reaction vessel lined with polytetrafluoroethylene. GCNT materials have been obtained by Ar atmosphere calcination in tube furnace at 520 °C with a heating rate of 5 °C min⁻¹, maintaining constant temperature for 4 h. No common hazards were note.

Ag/AgCl nanoparticles loaded g-C₃N₄ nanotubes (AC/GCNT) composites: Followed by the similar preparation method as GCNT materials: a certain amount of AgNO₃, 4.0 g hydroxylamine chloride, and 4.0 g melamine has been dispersed in 60 mL deionized water. AC/GCNT-1, AC/GCNT-2, and AC/GCNT-3 composites were prepared by the additive amount of AgNO₃ (0.5 g, 1.0 g, and 1.5 g).

AgCl nanoparticles: 1.0 g AgNO_3 and 4.0 g hydroxylamine chloride was dispersed in 60 mL of deionized water and heated at a constant temperature of 150 °C for 24 h.

Apparatus

X-ray powder diffraction (XRD) patterns were performed employing Shimadzu XRD-6000 instrument (Japan) to analyze the crystal structure of as-prepared photocatalysts. X-ray photoelectron spectroscopy (XPS) was used for analyzing the

chemical compositions of photocatalysts with Thermo Fisher DXR measurement (America). The morphology of as-prepared photocatalysts was analyzed by using a JEOL JSM-7800F scanning electron microscope (SEM, Japan) and JEOL JEM 2100F transmission electron microscope (TEM, Japan). The optical absorption performance of GCNT materials, AgCl nanoparticles, and AC/GCNT composites were measured by UV-vis diffuse reflectance spectra (UV-vis DRS) employing a Shimadzu UV3600 spectrophotometer (Japan). The photoelectrochemical (PEC) experiments were carried out with CHI760e electrochemical system (Chenhua Instrument Company, China). The photoluminescence (PL) spectra and PL decay were measured by QuantaMaster[™] 40 QuantaMaster & TimeMaster Spectrofluorometer (Photon Technology International, Inc., America). All FT-IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer (Thermo Fisher, America). *In-situ* FT-IR spectra were performed in the Praving Mantis DRIFTS accessory and reaction chamber.

Photocatalytic CO₂ reduction performance test

The photocatalytic CO_2 reduction performance of GCNT materials, and AC/GCNT composites were carried out with a PLS-SXE300D Xenon lamp source and Labsolar-6A all glass automatic on-line trace gas analysis system (Beijing Perfectlight Technology Co., Ltd.) under a constant temperature (5 °C) for preventing thermocatalytic effects. Firstly, 30 mg photocatalysts and 50 mL deionized water were injected into a 350 mL silicon reactor. The evacuation process of the silicon reactor was carried out to remove air. Then, CO_2 (99.999%) was bubbled into the silicon reactor, and the system pressure was maintained at 80 kPa pressure. Eventually, the products of the photocatalytic CO₂ reduction process were determined by Zhejiang Fuli GC-9790II.



Fig. S1 SEM images of GCNT materials.



Fig. S2 SEM images of AC/GCNT-2 composites.

The Raman spectra of GCNT materials and AC/GCNT-2 composites have been measured. As shown in Fig. S3, the band for characteristic vibrations of GCNT materials and AC/GCNT-2 composites have been found in the regions of 1200 to 1700 cm⁻¹, which corresponds to the disordered graphitic carbon-nitrogen vibrations.



Fig. S3 the Raman spectra of GCNT materials and AC/GCNT-2 composites.

The transient photocurrent response and EIS measurements were performed on GCNT and AC/GCNT-2 composites for investigating the effect of Ag/AgCl nanoparticles introduction on the photogenerated carrier separation and migration process of AC/GCNT-2 composites. As indicated in Fig. S4a, the photocurrent responses intensity of AC/GCNT-2 composites are obviously higher than that of GCNT materials. The equivalent circuit diagram was inserted and simulated by Zveiw Software, where Rs, CPE1, Rct, and W0 represent solution resistance, interfacial capacitance, charge transfer resistance, and Warburg impedance, respectively. The test curve of EIS spectra is like the simulated results, demonstrating the reasonable equivalent circuit diagram has been constructed. The Rct value of GCNT materials and AC/GCNT-2 composites are 71.81 and 33.65 Ω , which is conducive to enhancing the interfacial electron transfer efficiency of the AC/GCNT-2 composites and providing more free electrons for participating in photocatalytic CO₂ reduction process of AC/GCNT-2 composites. The PL and TRPL spectra were performed on GCNT and AC/GCNT-2 composites for further investigating the carrier separation and migration efficiency of AC/GCNT-2 composites. As shown in Fig. S4c, the PL emission peak intensity of the AC/GCNT-2 composites are lower that of GCNT materials in the absorption range of 400 nm to 650 nm, indicating that the introduction of Ag/AgCl nanoparticles can significantly reduce the photogenerated carrier recombination rate of the AC/GCNT-2 composites. The TRPL decay curves of GCNT materials and AC/GCNT-2 composites have been analyzed and fitted. The fitting parameters has been attached in Table. S1. The average fluorescence lifetime (τ_{ave} , 3.97 ns) of the AC/GCNT-2 composites (Fig. S4d) is significantly shorter than that of the GCNT materials (2.22 ns), indicating that Ag/AgCl nanoparticles effectually enhances the carrier migration rate of the AC/GCNT-2 composites to realize the efficient utilization of photogenerated electrons for participating in photocatalytic CO₂ reduction process.

	$ au_1$	A1	$ au_2$	A2	τ_{ave}
GCNT	2.62 ns	2441.39	17.91 ns	237.34	3.97 ns
AC/GCNT-2	1.66 ns	1607.53	13.28 ns	79.02	2.22 ns

Tab. S1 The fitting parameter of TRPL decay curves



Fig. S4 (a) Transient photocurrents response, (b) EIS spectra, (c) PL spectra and (d) TRPL decay curves of GCNT materials and AC/GCNT-2 composites.

Photocatalyst	Catalyst	Light source	Performance	CO	Ref.
	Dosage (mg)		$(\mu mol \ g^{-1} \ h^{-1})$	Selectivity	
BON/CN-2	20	300 W Xenon lamp	14.84	100%	[R1]
Ni/S-CN-N	10	300 W Xenon lamp	11.72	75.6%	[R2]
Cu1/N2CV-CN	5	300 W Xenon lamp	11.12	98.50%	[R3]
0.7Ni-5OB-CN	100	300 W Xenon lamp	22.1	71.70%	[R4]
FeN ₄ /K-g-C ₃ N ₄	30	300 W Xenon lamp	20	99.60%	[R5]
PtCu-crCN	25	300 W Xenon lamp	11.74	80.70%	[R6]
Ni ₅ -CN	25	300 W Xenon lamp	8.6	88.10%	[R7]
0.7 at% P-PCN	30	300 W Xenon lamp	5.37	83.0%	[R8]
Cu-CCN	25	300 W Xenon lamp	3.086	100%	[R9]
AC/GCNT-2	30	300 W Xenon lamp	25.10	100%	This work

Tab. S2 Comparison of other C_3N_4 -based materials for photocatalytic CO_2 reduction.

The band energy (E_g) of AgCl and GCNT materials has been deduced by the empirical formula of $\alpha hv = A(hv - E_g)^{n/2}$, where the parameters α , hv, E_g , and A correspond to the light absorption coefficients, photon energy, band energy, and constants, respectively.¹⁰ The E_g of GCNT and AgCl materials is 2.81 eV and 3.27 eV (Fig. S5b, c), respectively. As shown in the Mott-Schottky plots of AgCl and GCNT materials (Fig. S5b, c), The flat-band potentials (E_{flat}) of the GCNT and AgCl materials is -0.84 V and -0.46 V (vs. NHE, pH = 7), respectively.¹¹ Meanwhile, the slope for the Mott-Schottky curves of both GCNT and AgCl materials is positive, which indicates GCNT and AgCl materials are n-type semiconductors. The conduction band (CB) potential (E_{CB}) of n-type semiconductor materials is more negative than E_{flat} , and the potential difference between E_{CB} and E_{flat} is 0.1 to 0.3 V. The difference 0.2 V has been applied to extrapolate E_{CB} of GCNT and AgCl materials, and E_{CB} of GCNT and AgCl materials is -1.04 V and -0.66 V. The relationship between E_g and valence band (VB) potential ($E_{\rm VB}$) and $E_{\rm CB}$ correspond with the equation $E_{\rm g} = E_{\rm VB} - E_{\rm CB}$,¹² and $E_{\rm VB}$ value of GCNT and AgCl materials is 1.77 V and 2.61 V, respectively. The free radical generation of GCNT and AC/GCNT-2 composites was investigated by electron spin resonance (ESR) spectroscopy analysis to probe the electron transfer process between

GCNT and Ag/AgCl nanoparticles. As indicated in Fig. S5a, four DMPO-•O₂⁻ signal peaks with equal spacing and approximate area appear in the ESR spectra of both GCNT and AC/GCNT-2 composites after illumination, indicating that $\bullet O_2^-$ occurs in both GCNT and AC/GCNT-2 composites under light conditions. The intensity of DMPO- \circ O₂⁻ signal peaks is higher than that of the GCNT material, indicating that the AC/GCNT-2 composites have stronger ability of $\bullet O_2^-$ radicals generation.¹³ The characteristic signal peaks corresponding to •OH radicals have been not observed in the GCNT material under either dark or light conditions, and the demonstrable DMPO-•OH signal peaks appear in the ESR spectra of AC/GCNT-2 composites under light condition (Fig. S6b), which indicates that AC/GCNT-2 composites possess photoexcited •OH generation ability.¹⁴ Based on the ESR results and energy band position analysis, the possible electron migration path within the AC/GCNT composites is explored. The Evac of Ag substance is -4.26 eV according to the previous reports.⁶ So, E_{NHE} , pH = 7 of the elemental Ag is -0.59 V based on formula: $E_{\text{vac}} = -E_{\text{NHE, pH}=0}$ -4.44 and $E_{\text{NHE, pH}=7} = E_{\text{NHE, pH}=0} - 0.059 \text{ pH}$, which is more positive than E_{CB} position for GCNT and AgCl materials.¹⁵

Based on ESR spectra, the obvious DMPO- \cdot O₂⁻ and DMPO- \cdot OH signals have been observed. If the possible electrons transfer path between GCNT, Ag and AgCl materials follow type II heterojunction, the photogenerated electrons on Ag can reduce CO₂ to CO. The required potential for \cdot OH generation ($E_{OH^-/\cdot OH} = 1.99$ V) is more negative than E_{VB} position of AgCl materials (1.77 V). The holes from AgCl to GCTN materials don't match the potential requirement of \cdot OH generation. According to energy band structure, type II heterojunction based on Ag, GCNT and AgCl might not meet the requirements redox potential for \cdot OH generation. Based on the energy band position distributions of GCNT, Ag and AgCl materials, the possible electrons transfer path between GCNT, Ag and AgCl materials follow all-solid-state Z-scheme transfer route. Under illumination conditions, the holes in VB position of GCNT materials and the electrons in CB position of AgCl materials migrates the Ag element, respectively. E_{CB} (-1.04 V) of GCNT materials is more negative than the required potential of CO generation (${}^{E_{\text{CO}_2/\text{CO}}} = -0.53 \text{ V}$) and the $\cdot \text{O}_2^-$ generation (${}^{E_{\text{O}_2} \cdot \text{O}_2}^- = -0.33 \text{ V}$)¹⁶, which endows the photogenerated electrons in CB position of GCNT materials with stronger reducing ability for reducing CO₂ and O₂ to CO and $\cdot \text{O}_2^-$, corresponding to the obvious DMPO- $\cdot \text{O}_2^-$ signal peaks appearing in ESR spectra of AC/GCNT composites. Furthermore, the E_{VB} position of AgCl materials (2.61 V) is more negative than the required potential for \cdot OH generation ($E_{\text{OH}^-/\cdot\text{OH}} = 1.99 \text{ V}$). So, the holes in VB position of AgCl materials with strong oxidizing ability can oxidize OH⁻ to \cdot OH, which corresponds to the obvious DMPO- \cdot OH signal peaks appearing in ESR spectra of AC/GCNT composites. Therefore, the construction of all-solid-state Z-scheme heterojunction can realize IEF strength and the effective utilization of photogenerated electrons at CB position of GCNT materials, which is conducive to enhancement of the CO generation rate of AC/GCNT composites.



Fig. S5 (a) UV-Vis DRS spectra of GCNT, AgCl and AC/GCNT-x composites; $(\alpha hv)^2$ vs. *hv* curves of (b) GCNT and (c) AgCl materials; Mott-Schottky plots of (d) GCNT and (e) AgCl materials; (f) the illustration for energy band structure of GCNT and AgCl materials.



Fig. S6 ESR spectra for (a) DMPO- \cdot O₂⁻ and (b) DMPO- \cdot OH for GCNT and AC/GCNT-2 composites.

For demonstrating electron direction in constructed AC/GCNT composites, the work function (Φ) of AgCl, Ag and GCNT is calculated by the DFT method, which can explore the energy difference between the Fermi level and vacuum level of AgCl, Ag and GCNT. As demonstrated in Fig. S7a-c, the Φ value of GCNT, Ag and AgCl are 4.28, 4.62, and 5.71 eV, respectively, revealing GCNT possess higher Fermi level than that of Ag and AgCl and the Fermi level of the Ag is in the middle of GCNT and pristine AgCl. Ascribed to the more negative $E_{\rm F}$ of GCNT materials compared with that of AgCl materials, the interaction between AgCl and GCNT materials triggers off the interface electrons spontaneously transfer from GCNT materials to AgCl materials until interface electrons balance. When the interface electrons achieve dynamic balance, electrons would transfer from the interface of GCNT materials to form a depletion layer leading to the reduction of electron density, and electrons simultaneously would accumulate in the interface of AgCl materials to create an accumulation layer result in the increase of the electron density. The interface electron transfer process is conducive to achieving the upward band bending of GCNT materials and inverse band bending of AgCl materials. Subsequently, the interfacial electric field has been established from AgCl materials to GCNT materials at the contact interface for triggering off the continuous electrons flow from GCNT materials to AgCl materials. Furthermore, AC/GCNT composites are photoexcited to form photoinduced electron-hole pairs under illumination conditions, which promotes the directional migration of electrons from the

VB position of AgCl and GCNT materials to the CB position of AgCl and GCNT materials. Meanwhile, the photogenerated electrons are retained in the CB position of AgCl materials and the photoinduced holes accumulate at the VB position of GCNT materials, which can maximize the oxidation-reduction ability and enhance photoexcited electrons separation and transfer efficiency. Accordingly, a Z-scheme electron transfer route has been supposed between of GCNT materials and AgCl materials. The schematic illustration of possible charge transfer mechanism has been revised as **Fig. R2**.



Fig. S7 (a-c) calculated work functions of GCNT, Ag and AgCl; (d, e) energy band diagram of AC/GCNT composites before and after contact; (f) Charge transfer pathway of AC/GCNT composites.

To further verify the Z-scheme transfer path, ESR spectra by the quenching of TEMPO for analyzing the reducibility of photogenerated electrons (H_2O , Ar) and the oxidability of holes (acetonitrile, Air). As indicated in Fig. R6, AC/GCNT-2 composites exhibit obvious ESR spectra for the quenching of TEMPO, which indicates AC/GCNT-2 composite possess enhanced oxidation-reduction ability. If the transfer path follows type II heterojunction based on Ag, GCNT and AgCl, photogenerated electrons and hold would transfer to situation with low oxidation-reduction ability. So, the following measurement further proves that the possible charge transfer mechanism

in AC/GCNT composites is all-solid-state Z-scheme heterojunction.



Fig. S8 ESR spectra for (a) e^{-} and (b) h^{+} for GCNT and AC/GCNT-2 composites.

To investigate the driven force of photogenerated carriers on the sample, the Kelvin Probe force microscopy (KPFM) measurements of GCNT and AC/GCNT-2 composites has been performed. As shown in S9a, b, the potential difference between the GCNT materials and the FTO substrate is 66.8 mV under illumination. The potential difference between the AC/GCNT-2 composites and the FTO substrate is 98.7 mV under illumination, which is significantly higher than that of GCNT materials. KPFM measurements indicates that the interface electric field can be constructed by Z-scheme transfer path between Ag, AgCl and GCNT materials to accelerate photoelectrons transfer.



Fig. S9 the interfacial potential difference distribution of (a, b) GCNT and (c, d) AC/GCNT-2 composites in light.

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