Facile fabrication of AgBr/HCCN hybrids with Z-scheme heterojunction for efficient photocatalytic hydrogen evolution

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ABSTRACT

Constructing a Z-scheme heterojunction with enhanced photocatalytic hydrogen evolution for graphitic carbon nitride-based (g-C3N4) composites is challenging because integrating g-C3N4 with other semiconductors, without specific band structure design, typically results in type I or type II heterojunctions. These heterojunctions have lower redox ability and limited enhancement in photocatalysis. Herein, we select highly crystalline carbon nitride (HCCN) as a proof-of-concept substrate. For the first time, we develop a AgBr nanosphere/HCCN composite photocatalyst that features an all-solid-state direct Z-scheme heterojunction for visible-light photocatalytic hydrogen evolution. The electron transfer mechanism is initially studied from the band structures and Fermi levels of HCCN and AgBr. It is subsequently confirmed by X-ray photoelectron spectroscopy (XPS), and electron microscopy. The close heterojunction contact and the built-in electron field of the Z-scheme heterojunction promote the migration and separation of photogenerated electrons and holes in the composite photocatalyst. Due to the redistribution of charge carriers, the photocatalyst shows superior redox capability and a markedly enhanced hydrogen evolution performance compared to its individual components. Combining all the advantages, AgBr nanosphere/HCCN reached an apparent quantum efficiency (AQE) of 6 % under the illumination of 410 nm, which is 4 times higher than that of the single HCCN component.

1. Introduction

Carbon neutrality has become one of the most common goals for human society. As a sustainable and environmentally friendly technology, photocatalytic hydrogen production is considered an ideal way to achieve the aim of carbon neutrality. It is important not only for reducing the impacts of climate change but also for lowering the dependence on fossil fuels [1,2]. Since the discovery of photocatalytic hydrogen evolution reaction (HER) over graphitic carbon nitride (g-C3N4), [3] g-C3N4 has been intensively studied as a visible-light responsive photocatalyst due to its high abundance, non-toxicity, outstanding chemical stability, and ease of functionalization [4–6]. However, most existing g-C3N4 materials demonstrate moderate hydrogen evolution activity because of the sluggish surface reaction kinetics and rapid charge carrier recombination [7–9]. Combining g-C3N4 with other semiconductors to construct composite photocatalysts with heterojunction can efficiently boost their photocatalytic performance [10–13]. Fabricating heterojunction photocatalysts based on g-C3N4 combined with semiconductors such as TiO2, GdS, or ZnO can promote the separation of photoexcited charge carriers and extend the light-harvesting range of the semiconductor, thus enhancing its hydrogen evolution performance [14–17]. However, integrating g-C3N4 with these semiconductors without band structure engineering generally leads to type I or type II heterojunctions, only showing limited enhancement of photocatalysis [18]. This is because, in these types of heterojunctions, the photoexcited charge carriers driven by the internal
electric field migrate to the less negative conductive band (CB) and less positive valence band (VB). Compared to their components, such migration diminishes the redox potential of the composite photocatalysts, thereby constraining their enhancement of the performance in photocatalytic hydrogen evolution. Importantly, the Z-scheme heterojunction can provide superior redox capabilities that surpass those of the individual components of the composite photocatalyst. This structure also ensures more efficient charge carrier separation and a broader range of light absorption [17]. Therefore, developing g-C$_3$N$_4$-based composite photocatalysts with Z-scheme heterojunction through rational band structure design and controllable synthesis is highly desirable for achieving efficient photocatalytic hydrogen evolution under visible light.

Recently, silver halides, such as AgBr, have obtained widespread attention in the field of photocatalysis due to their visible light sensitivity and considerable photocatalytic performance [19–22]. Combining AgBr with other semiconductors to fabricate hybrid photocatalysts with type II heterojunction can enhance photocatalytic pollutant degradation and hydrogen evolution [19–22]. However, constructing a Z-scheme heterojunction between g-C$_3$N$_4$ and AgBr to enhance reduction activity is challenging. Owing to the unsuitable work function and band structure either results in the formation of a type II heterojunction with less redox potential or leads to a Z-scheme heterojunction with further enhanced oxidation ability, which only advances in photodegradation rather than hydrogen evolution [23–25]. To achieve a Z-scheme heterojunction with improved reduction ability, the Fermi energy, CB and VB of g-C$_3$N$_4$ have to be lower than those of AgBr. To the best of our knowledge, no reports so far have demonstrated the facial synthesis of materials and g-C$_3$N$_4$ for efficient photocatalytic hydrogen evolution. Lately, highly crystalline carbon nitride (HCCN) with abundant cyano groups has garnered plenty of attention, thanks to its novel photoelectrical and polymeric properties [26–32]. In these cases, the band structure and Fermi level of HCCN can be adjusted by modifying cyano groups and changing crystallinity or photoconversion. Additionally, we previously discovered that HCCNs show an electron storage capability [29–32]. These discoveries provide us with the possibility of adjusting the band structure of g-C$_3$N$_4$. Consequently, we selected HCCN as a proof-of-concept substrate material to fabricate a Z-scheme heterojunction heterostructural photocatalyst by assembling with AgBr nanosphere.

Herein, we propose the first AgBr nanosphere/HCCN composite photocatalyst (AgBr/HCCN) with all-solid-state direct Z-scheme heterojunction for visible-light photocatalytic hydrogen evolution. This composite photocatalyst was synthesized using a straightforward electrostatic self-assembly approach. The electron storage ability of HCCN enables a stable negative zeta potential for HCCN to construct an intimate contact with the AgBr nanosphere, facilitating the generated carrier transfer across the heterojunction interface. The work function (WF) and band structure of the HCCN and AgBr were investigated to explore the electronic transfer mechanism. In the presence of the inter-electric field of the Z-scheme heterojunction, generated electrons in HCCN tend to recombine with holes from the AgBr nanosphere, extending the lifetimes of electrons in AgBr and holes in HCCN. This elevates the redox ability of the hybrid photocatalyst. Furthermore, the formation of Z-scheme heterojunction is confirmed by X-ray photoelectron spectroscopy (XPS) and electron microscopes. The incorporation of AgBr nanosphere also amplifies the visible light-harvesting capability of HCCN, resulting in a 4-fold increase in the apparent quantum efficiency (AQE) under 410 nm illumination compared to pristine HCCN. In general, benefiting from the Z-scheme heterojunction, the AgBr nanosphere/CN photocatalyst exhibits a 5.4-fold enhancement in hydrogen evolution compared to the only HCCN component. This work is expected to open a new horizon in the design of efficient g-C$_3$N$_4$-based Z-scheme heterojunction semiconductors for photocatalysis and other applications.

2. Experimental

2.1. Materials

All chemical reagents were purchased from commercial suppliers and used without further purification. Deionized (DI) water was obtained through a laboratory pure water system. Methyl alcohol (CH$_3$OH, 99.9 %), lithium chloride (LiCl, Waterless, Analysis reagent (AR) grade), sodium chloride (NaCl, AR grade), potassium chloride (KCl, AR grade), melamine (C$_3$H$_6$N$_6$, 99 %), triethanolamine (TEOA, AR grade), cetyltrimethylammonium bromide (CTAB, ≥ 98 %) and sodium bromide (NaBr, 99.995 %) were from Sigma-Aldrich Co., Ltd. Silver nitrate (AgNO$_3$, ≥ 99.0 %) was purchased from Thermo Fisher Scientific Co., Ltd.

2.2. Catalyst preparation

2.2.1. Synthesis of g-C$_3$N$_4$ photocatalysts

The bulk g-C$_3$N$_4$ was synthesized by a typical thermal polymerization of triethanolamine [28–30]. In the procedure, 3 g melamine was placed in a 15 mL alumina boat with a lid. The powder was calcined at 550 °C for 4 h under a N$_2$ atmosphere in a tube furnace. The heating ramp was 5 °C/min. The product was bulk g-C$_3$N$_4$.

2.2.2. Synthesis of HCCN photocatalysts

Subsequently, the yellow bulk g-C$_3$N$_4$ (1.0 g) was ground with 0.55 g of KCl and 0.45 g of LiCl. The compound was heated at 100 °C for 30 min to eliminate the adsorbed water, then at 550 °C for 4 h at a 5 °C/min ramp under a N$_2$ atmosphere for further polymerization. The product was naturally cooled to room temperature and rinsed thoroughly with water to remove the lithium and potassium ions. Then the HCCN was collected by vacuum filtration and dried at 60 °C.

2.2.3. Fabrication of AgBr nanospheres

The AgBr nanospheres were prepared according to the previous reports [33]. Typically, 45.0 mg of CTAB and 0.5 mL of NaBr (10 mM) are magnetically stirred in a flask at 60 °C. After the complete dissolution of the components, 1.0 mL of AgNO$_3$ solution (10.0 mM) was rapidly injected into the solution and the reaction continued for 1 h. The obtained colloidal solution was washed by centrifugation at 6000 rpm for 10 min. The prepared AgBr nanospheres were dispersed in 1.5 mL of water to maintain the concentration at ~1.25 mg/mL. Analogously, 30 and 60 mg of CTAB were also used for the synthesis of AgBr nanospheres using the same procedure. The final products were labeled AgBr-CTABx (x = 30, 45, 60).

2.2.4. Preparation of AgBr/HCCN composites

In a typical procedure, 30 mg of HCCN was dispersed in 10 mL of methyl alcohol (10 v/v%) and sonicated for 3 min. The mixture was illuminated under a solar simulator for one minute to enhance electron accumulation. Subsequently, a given volume of AgBr nanosphere suspension (1.25 mg mL$^{-1}$) was slowly dropped into the solution under continuous stirring. The mixture of HCCN and AgBr nanosphere was stirred for 10 min to form a uniform suspension. The suspension was subjected to vacuum filtration. The collected powders were dried in an oven at 60 °C. The final products were named AgBr(x)/HCCN (where x = 0.5, 0.75, 1.0 w/w%), respectively.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the HCCN, AgBr nanosphere, and their hybrids were recorded on an X-ray diffractometer (Bruker D8 ADVANCE) using Cu K$_\alpha$ radiation (λ = 0.15406 nm) at a current of 40 mA and a voltage of 40 kV, during which the step size was 0.02° and dwell time per step was 1s. The microstructure and elemental mapping of AgBr/HCCN were characterized using a high-resolution field emission
scanning electron microscope (Zeiss LEO 1550) equipped with an energy-dispersive X-ray spectrometer (Oxford AZtec EDS). An FEI Titan Themis 2 microscope equipped with a spherical aberration-corrected probe and a SuperT X-ray detector was used to perform transmission electron microscopy (TEM), selected area electron diffraction (SAED), high-angle annular dark-field (HAADF) imaging using scanning TEM (STEM) mode, and energy dispersive X-ray spectroscopy (EDX). For sample preparation, the samples were dispersed in ethanol and sonicated for 1 min. A small drop of the resulting solution was then loaded onto a copper grid covered with a lacy carbon film. The UV – Vis reflectance spectra of the samples were recorded by an ultra-scanning electron microscope (Zeiss LEO 1550) equipped with an W. Sun et al. high-angle annular dark-field (HAADF) imaging under scanning TEM probe and a SuperX X-ray detector was used to perform transmission Themis 200 microscope equipped with a spherical aberration-corrected sample preparation, the samples were dispersed in ethanol and sonicated by a gold disk. The relationship between the work function with a relative humidity chamber. The nitrogen flow was maintained at following formula:

\[
WF = \frac{K}{N} = \frac{(1 - R)_{\infty}^2}{2R_{\infty}}
\]  

where \(F(R_{\infty})\) is the reflectance of an infinitely thick specimen, while \(K\) and \(N\) are the absorption and scattering coefficients, respectively. The steady-state photoluminescence (PL) spectra were recorded using a Raman spectrophotometer (Renishaw Co. Edinburgh FLS 980) with a confocal microscope and using a 405 nm laser at 1.0 %. X-ray photoelectron spectroscopy (XPS) and valence band XPS were performed using an X-ray photoelectron spectrometer (Kratos AXIS Supra®) equipped with a monochromatized Al-K\(\alpha\) X-ray source (1486.6 eV). All the binding energies were calibrated according to the C1s peak at 284.8 eV.

Fourier-transform infrared (FTIR) measurements were carried out on an FTIR spectrometer (IRTracer-100, SHIMADZU Co.) equipped with an attenuated total reflectance (ATR) setup at room temperature. The FTIR spectra were recorded from 4000 to 650 cm\(^{-1}\) with a 4 cm\(^{-1}\) resolution.

Electrochemical analysis was carried out in a conventional three-electrode cell using a Pt plate and a Ag/AgCl electrode as counter and reference electrodes, respectively. The working electrode was prepared on a fluorine-doped tin oxide (FTO) glass that had been cleaned by sonication in ethanol for 3 min and dried with nitrogen. The boundary of the FTO glass was protected using Scotch tape. The exposed area of the working electrode was 1 cm\(^2\). A 10 mg sample was dispersed in 1 mL of DI water by sonication to obtain a slurry. The slurry of samples was air-dried. The scotch tape was removed. The electrochemical impedance spectroscopy (EIS) was measured on an electrochemical workstation (VSP-300 electrochemical workstation from BioLogic, France) in the electrolyte containing 0.01 M K\(_2\)Fe(CN)\(_6\)/K\(_4\)Fe(CN)\(_6\) (1:1). The photocurrent response (applying −0.1 V bias vs Ag/AgCl electrode) was measured under the three-electrode cell in 0.5 M Na\(_2\)SO\(_4\) aqueous solution under dark condition.

The work functions of g-C\(_3\)N\(_4\), HCCN, and AgBr nanospheres were measured using a Kelvin probe system (RHC040, KP Tech Ltd) equipped with a relative humidity chamber. The nitrogen flow was maintained at 6 L/min. The data collecting rate was 1 dpot 30 points. 500 dots were recorded for each sample. The work function of the tip was 4.77 eV and corrected using a gold disk. The relationship between the work function (WF) and the contact potential difference (CPD) can be calculated by the following formula:

\[
WF = -WF_{\text{tip}} + CPD
\]

Using the following formula to convert the WF to Fermi energy (\(E_F\)) in terms of normal hydrogen electrode (NHE):

\[
E_F = -WF_{\text{tip}} + 4.44 \text{eV} - E_{\text{NHE}}
\]

2.4. Photocatalytic H\(_2\) production

The activity of AgBr nanospheres on HCCN (AgBr/HCCN) and pristine HCCN powder was measured for photocatalytic hydrogen production. The measurement was carried out under side illumination in a glass reaction tube (25 mL). A 100 W Solar Simulator Xenon lamp (94011A, LCS-100, Newport Co., Ltd.) was equipped with an AM1.5G air mass filter to provide Class A spectral performance based on current applicable standards at one Sun irradiance output. The produced gas in the headspace was analyzed using a gas chromatograph (GC, PerkinElmer Autosystem XL) with a CarbonPLOT P7 column and a thermal conductivity detector (TCD), using argon as the carrier gas. 3 wt%Pt (in theory) as a co-catalyst was deposited on the photocatalyst by in situ photo-deposition using chloroplatic acid as a Pt source. The hybrid photocatalyst (3 mg) was dispersed in 10 mL of aqueous solution containing 25.0 mg NaCl and TEOA (10 v/v%) as the hole-scavenging agent. The mixture was sealed and purged with argon for 30 mins. Subsequently, the mixture was irradiated with simulated sunlight while stirred. The samples after HER are named AgBr (x)/HCCN/Pt (where x = 0.5, 0.75, 1.0 w/w%). The apparent quantum efficiency (AQE) under different wavelengths was evaluated by placing a series of bandpass filters (410, 460, 500, and 540 nm) with a full width at a half-maximum of 10 nm in the optical path of the solar simulator. The light intensity was obtained with a pyranometer (THORLABS PM160, Thorlabs, Inc.). The AQE was calculated according to the following equation:

\[
AQE = \frac{2n(H_2)^*}{n(hv)} \times 100\% = \frac{r \times N_A \times K \times h \times c}{P \times S \times \lambda} \times 100\%
\]

where \(r\) is the rate of photocatalytic hydrogen production (mol/s), \(N_A\) is Avogadro number (6.022 × 10\(^{23}\)), \(K\) is the number of transferred electrons, which is 2 for hydrogen evolution, \(h\) is Planck’s constant (6.626 × 10\(^{-34}\) J-s), \(c\) is the speed of light (3 × 10\(^{8}\) m/s), \(P\) is the power density of the incident monochromatic light (W/m\(^2\)), \(S\) is the irradiated area to produce hydrogen (which is around 5.5 cm\(^2\)), and \(\lambda\) is the wavelength of the incident monochromatic light (m). The measured power density and corresponding AQE results are shown in Table S1.

The photoactivity of the AgBr/HCCN was assessed by prolonging the hydrogen evolution over several cycles. When evaluating the HER stability only using NaCl as the salt, the reaction conditions were the same as described above. After the first cycle (3 h), the catalyst was collected by filtration, and the reaction solution was replaced with a fresh one. For HER stability measurements involving NaCl, KCl, and LiCl, 25.0 mg of KCl and LiCl were added to 10 mL of an aqueous solution containing 25.0 mg NaCl and TEOA (10 v/v%). In the first three cycles, the photocatalytic reaction system was refilled with argon every three hours. After the first three cycles, for each cycle, the catalyst was recycled by filtration, and the reaction solution was replaced with a fresh one.

3. Results and discussion

3.1. The formation and band structure of AgBr/HCCN photocatalyst

The AgBr/HCCN photocatalysts were fabricated by an electrostatic self-assembly method. The zeta potential of pristine HCCN was −13 mV (Fig. S1). However, the HCCN nanoparticles could store photogenerated electrons [29,32]. As shown in Fig. 1a, upon illumination, the HCCN nanoparticles were photogenerated electrons, generating a negatively charged surface. As a result, the zeta potential of the HCCN increased to −35 mV after 2 min of illumination (Fig. S1). This phenomenon matches well with our previous study [32]. The AgBr nanosphere was synthesized using a micellar method, where cetyltrimethylammonium bromide (CTAB) was used as a stabilizing agent. The traces of CTAB molecules remain on the AgBr nanosphere, providing a net positive surface charge (ζ = +60.0 mV, Fig. S1). A proportion of AgBr nanosphere was added dropwise to the HCCN suspension with continuous stirring. Finally, a stable hybrid AgBr/HCCN photocatalyst with close contact was
achieved through the electrostatic assembly of the AgBr nanosphere onto the HCCN surfaces.

Fig. 1 b presents the UV–vis diffuse reflectance spectra of the as-prepared HCCN and AgBr nanosphere. Both HCCN and AgBr nanosphere exhibit a strong visible-light absorption with a band edge at around 470 nm. As shown in the inset, the band gaps of the HCCN and AgBr nanosphere calculated using the Kubelka–Munk equation are 2.67 and 2.73 eV, respectively. The reflectance spectrum of bulk g-C$_3$N$_4$ was also recorded, revealing a band gap of 2.73 eV (see Fig. S2). Compared to g-C$_3$N$_4$, the decreased band gap of the HCCN means an enhanced light absorption. The VB positions of HCCN and AgBr nanosphere were measured by valence band X-ray photo-electron spectroscopy (VB XPS), as shown in Fig. 1c. The directly measured VBs of HCCN and AgBr nanosphere are 2.20 and 1.05 eV, respectively. The VBs of HCCN and AgBr nanosphere, relative to the normal hydrogen electrode, were calculated using the following formula:

$$E_{VB, NHE} = \phi + E_{VB, XPS} - 4.44 \text{ eV}$$

(3)

where $E_{VB, NHE}$ is the potential vs. normal hydrogen electrode, $E_{VB, XPS}$ is the VB value from VB XPS, and $\phi$ is the work function of the XPS instrument, which is 4.50 eV here [34,35]. Thus, $E_{VB, NHE}$ of HCCN, and AgBr nanospheres were calculated to be 2.26 and 1.11 eV, respectively. According to the above results, the conduction band (E$_{CB}$) of the two semiconductors can be calculated by the relationship: $E_{CB} = E_{VB} - E_g$. The band structures are summarised in Fig. 1e. Based on the staggered band structures, it is possible to generate either type II or Z-scheme heterojunction. To fully identify the type of heterojunction, the direction of electron flow within the two semiconductors has to be elucidated. The work functions (WFs) of the two semiconductors determine the migration direction of electrons between them [36]. Therefore, a scanning kelvin probe was adopted to measure the WFs of the HCCN and AgBr nanosphere. As shown in Fig. 1d, the WFs of HCCN and AgBr nanosphere are 5.13 and 4.97 eV, respectively. The WFs of HCCN and AgBr nanosphere, relative to the normal hydrogen electrode, were calculated by the relationship: $E_{WF} = E_{F, HCCN}$ and $E_{WF} = E_{F, AgBr}$ corresponding to $E_{NHE}$ are 0.69 and 0.53, respectively. (Please see the experimental section for the conversion). Moreover, $E_{F, g-C3N_4}$, $E_{VB}$, and $E_{CB}$ of g-C$_3$N$_4$ were calculated to be 0.92 eV, 2.26 eV, and $-0.47$ eV, respectively (Please see Fig. S3 and S4). Compared to g-C$_3$N$_4$, the HCCN

Fig. 1. (a) Schematic illustration of fabricating AgBr/HCCN hybrid photocatalyst by electrostatic self-assembly. (b) UV–vis diffuse reflectance spectra (the inset is the band gap calculated by Kubelka–Munk equation), (c) VB XPS, and (d) work functions of HCCN and AgBr nanosphere. (e) Electron transfer and photocatalytic reaction mechanism of the composite.
shows a slightly higher Fermi energy (0.69 eV) and lower CB (-0.41 eV), further facilitating the extraction of the photoelectrons from HCCN to AgBr and the generation of Z-scheme heterojunction [37]. Given the evidence, it is logical to suggest that the electrons in the AgBr/HCCN photocatalysts migrate following the Z-scheme mechanism. As shown in Fig. 1e, electrons in the AgBr nanosphere will spontaneously flow to HCCN, because the WF of HCCN is larger than that of the AgBr nanosphere. After reaching an equilibrium of $E_F$, an internal electric field (IEF) will be established between the HCCN and AgBr nanosphere with a direction from AgBr to HCCN, leading to upward and downward band bending for AgBr and HCCN, respectively. The photoexcited electrons of HCCN recombine with the holes of AgBr, leaving the electrons in the CB of AgBr and holes in the VB of HCCN with higher redox potentials. Ultimately, electrons in the CB of AgBr reduce $\text{H}^+$ ions to produce $\text{H}_2$, while holes in the VB of HCCN consume the sacrificial agents.

3.2. Crystallography and morphology

Fig. 2a shows the XRD patterns of the as-prepared HCCN, AgBr nanosphere, and the composite AgBr/HCCN photocatalyst. Specifically, the peaks at 8° and 28° correspond to the (1 0 0) and (0 0 2) crystal planes of HCCN [29]. AgBr nanosphere shows its characteristic peaks (JCPDS No. 06-0438). Besides, two diffraction peaks located at 38° and 77.4° show on the pattern of AgBr nanosphere, which can be assigned to (1 1 1) and (3 1 1) planes originating from crystalline Ag, respectively (JCPDS No. 65-2871) [38]. The low-intensity peaks of Ag were visually enhanced by the base 10 logarithm transformation for the y-axis of AgBr nanosphere (see Fig. S5, the XRD pattern of AgBr without any process). As expected, the characteristic diffraction peaks of both HCCN and AgBr nanosphere are observed in the hybrid AgBr nanospheres/HCCN. The intensity of characteristic peaks of AgBr increases with the concentration of AgBr nanosphere in the XRD patterns of AgBr/HCCN (Fig. S6), implying the successful combination of HCCN and AgBr nanosphere. A typical transmission electron microscopy (TEM) image of the prepared HCCN is presented in Fig. 2b. Matching with other reports, the as-prepared HCCN consists of small irregular nanosheets. The distance measured from the distinct lattice fringe is 0.98 nm, corresponding to the (1 0 0) plane spacing of HCCN [39]. Fig. 2c shows the SEM image of the AgBr nanosphere. The AgBr nanosphere exhibits a smooth surface with a predominant diameter ranging between 350 and 450 nm. (the size distribution graph is inserted in Fig. 2b). The loading of the AgBr nanosphere was clearly shown using a backscattered electron detector (BSD) in SEM. As shown in Fig. 2d, the AgBr nanospheres are dispersed on the surface of HCCN, showing a brighter image than HCCN because of its heavier atomic mass. In Fig. S7, the AgBr nanosphere shows no obvious change after its combination with HCCN in a highly magnified image, demonstrating that the mildness of the electrostatic self-assembly method can preserve the morphology of each component. Platinum (Pt), serving as an effective co-catalyst, was deposited by in situ photodeposition, using chloroplatinic acid as a Pt source. The location of Pt will provide direct evidence for revealing the mechanism of electron migration between the HCCN and AgBr nanosphere. Therefore, the energy dispersive X-ray (EDX) mapping and TEM were used to observe AgBr/HCCN after Pt deposition. As shown in Fig. 2e, the AgBr nanospheres still maintain the original morphology but with a rougher surface, which was caused by Pt deposition. As shown in Fig. 2f-k, the AgBr nanosphere contains the elements of Pt, Ag, Br, C, and N. The C and N surrounding the AgBr nanosphere originate from the HCCN. Significantly, the Pt element is found to be selectively deposited on the AgBr nanosphere, indicating the execution of a Z-scheme rather than a type II electron transfer mechanism in this system.

3.3. Surface chemical state analysis

An intimate contact between the two components of a heterojunction photocatalyst facilitates the transfer of charge carriers. FTIR spectra were recorded to analyze the chemical bonds of the as-prepared samples (Fig. S8). The characteristic peaks of $\text{C}=$ and heterocycles of HCCN at
2181 cm\(^{-1}\) and 1578 cm\(^{-1}\) shift to a lower wavenumber at 2179 cm\(^{-1}\) and 1576 cm\(^{-1}\), respectively. This is due to the interaction between HCCN and the AgBr nanosphere, which weakens their bond strength [40]. The interaction indicates the close contact between the two components. (a detailed analysis can be found in Fig. S8).

The chemical states of the as-prepared samples were further investigated using X-ray photoelectron spectroscopy (XPS) to observe any changes in the surface chemical environment. Fig. 3a shows the high-resolution C 1s XPS spectra of the HCCN and AgBr/HCCN. The C 1s peak in HCCN was deconvoluted into three peaks at 284.8, 286.2, and 288.1 eV, which correspond to adventitious carbon (C–C), C–NH\(_x\) (x = 1, 2) species on the edges of heptazine units and C atoms in the heptazine skeleton (N–C=N), respectively [41–43]. Compared with HCCN, the C 1s peaks of AgBr/HCCN associated with the species of C–NH\(_x\) and N–C=N shift to 286.4 and 288.2 eV, respectively, indicating an interaction between the HCCN and AgBr nanosphere. The formation of the Z-scheme heterostructure results in the withdrawal of electrons from HCCN, leading to a decrease in electron density and a shift of the peaks towards higher binding energy. In addition, the increased relative peak intensity at 286.4 eV of AgBr/HCCN could result from the C-N bond of the traces of CTAB. As depicted in Fig. 3b, the N 1s XPS spectra exhibit four types of nitrogen species with peaks located at 398.5, 400.3, 401.0, and 403.6 eV, corresponding to the nitrogen atom in C–N=C, N–C\(_3\), C\(_2\)N–C–N–H, and the charging effect of the heterocycles from HCCN, respectively [41–43]. Analogous to C 1s spectra, the peaks of nitride species of AgBr/HCCN shifted to a higher binding energy, demonstrating a decrease in the electron density of HCCN in the composite. The Ag 3d XPS spectra exhibit three distinct peaks at 284.8, 286.2, and 288.1 eV upon deconvolution. Meanwhile, the Br 3d XPS spectra display peaks at 367.6 and 373.6 eV. Compared with the single component AgBr, the binding energy of Ag and Br species in the AgBr/HCCN shifted toward the lower binding energy, reflecting an increased electron density in the AgBr. These results further confirm the Z-scheme electron migration in AgBr/HCCN and the intimate contact between the two components. Additionally, the peak of K 2s, shown in the Ag 3d XPS spectra, originates from the synthesis of HCCN. This is also reflected in the XPS survey spectrum (Fig. S9).

3.4. Physical and photoelectrochemical properties

Brunauer–Emmett–Teller (BET) was used to study the surface properties of the HCCN and AgBr/HCCN. According to the adsorption–desorption isotherm linear plots shown in Fig. S10, pure HCCN, and AgBr/HCCN, both demonstrate type-IV adsorption isotherms, reflecting the presence of mesopores. In detail, the surface areas of HCCN and AgBr/HCCN are 15.78 and 21.54 m\(^2\)/g, respectively. AgBr/HCCN composite also shows a higher total pore volume than bare HCCN (Table S2). Both the results suggest that the introduction of AgBr nanospheres can improve the pore volume and surface area of the composite, facilitating the interaction of the photocatalysts and the reactants. Fig. 4a presents UV–Vis diffuse reflectance spectra of the as-prepared HCCN, AgBr nanosphere, and their composites. The
absorption edges of the AgBr nanosphere, HCCN, and the AgBr(x)/HCCN samples mostly coincide around 470 nm. For the AgBr nanosphere sample, a broad and shallow absorption peak emerges around 520 nm which is due to the localized surface plasmon resonance (LSPR) absorption of the AgBr nanosphere. As the loading of AgBr nanosphere increases the composite photocatalysts demonstrate an enhanced absorption at 500 nm, which is visible as a shoulder tailing off of the band edge. It is well known that the effective generation and separation of photoexcited charge carriers are essential for improving photocatalytic efficiency. Photoluminescence (PL) spectra were recorded to study the separation of charge carriers. As can be seen in Fig. 4 b, the HCCN shows the strongest PL intensity with the characteristic peak at 550 nm, while the AgBr nanosphere exhibits the peak at 575 nm with a low PL intensity. The PL intensities of the AgBr/HCCN composites initially decrease and then increase as the loading amount of the AgBr nanosphere increases. The AgBr (0.75 %)/HCCN demonstrates the lowest PL intensity among the composite photocatalysts, reflecting the optimal separation of photo-excited electrons and holes. Compared to HCCN, the AgBr/HCCN shows a distinct quenching of the PL intensity, indicating that the Z-scheme electron transfer substantially improves the separation of charge carriers. Transient photocurrent response measurements of the as-prepared samples were performed to evaluate the interfacial charge transfer by coating the samples on fluorine-doped tin oxide (FTO) glass. Specifically, the photocurrent is generated by the diffusion of photogenerated electrons to the conductive surface of FTO while holes are consumed by the hole acceptor in the electrolyte [44,45]. Fig. 4c clearly shows that, among all the samples, AgBr/HCCN exhibits the highest photocurrent, indicating that the migration of photoinduced electron-hole pairs in AgBr (0.75 %)/HCCN is more efficient than that in pure HCCN and g-C3N4. Moreover, electrochemical impedance spectroscopy (EIS) was further recorded under dark conditions to investigate the resistance of the composite photocatalyst to conveying charge carriers to the targeted reactive sites [46]. Generally, a material that can easily transfer photoexcited electrons, displays a smaller semicircle in the Nyquist plot. As shown in Fig. 4d, AgBr/HCCN shows the smallest arc radius, suggesting much lower electron-transfer resistance than the pristine HCCN. Both the transient photocurrent response and the EIS measurement indicate a significant enhancement in the photoelectrochemical properties of HCCN upon the fabrication of a Z-scheme heterojunction with AgBr nanosphere.

3.5. Photocatalytic HER performance and stability of the AgBr/HCCN photocatalysts

The photocatalytic HER activities of AgBr/HCCN composites were evaluated under AM1.5G irradiance using a solar simulator. Before the photocatalytic hydrogen evolution was tested, the optimal conditions for the photocatalytic hydrogen evolution were explored (see Fig. S11). The corresponding HER efficiencies are shown in Fig. 5a. As the content of the AgBr nanosphere increased, a volcano-shaped trend in the activity was observed. The optimum loading content of the AgBr nanosphere is 0.75 w/w% of the HCCN, and the corresponding HER activity is 20.1 mmol g⁻¹ h⁻¹, which is 5.4 times higher than that of the pristine HCCN (3.7 mmol g⁻¹ h⁻¹). The HER activity of pure AgBr was measured, but no hydrogen was detected. To further elucidate the influence of the heterojunction interface between HCCN and AgBr nanosphere on the photocatalytic HER performance, a reference reaction was conducted. Specifically, after Pt deposition on HCCN (HCCN/Pt), 0.75 w/w% of
AgBr nanosphere was mixed with the HCCN/Pt suspension (HCCN/Pt + AgBr (0.75 %)). Triethanolamine could neutralize the zeta potential of HCCN/Pt by inducing a positive zeta potential through the hydrolysis-produced N\textsuperscript{+} groups [47]. This diminished the likelihood of forming close contact between the HCCN/Pt and AgBr nanosphere. As a result, the photocatalytic HER activity of this sample is 6.3 mmol g\textsuperscript{-1} h\textsuperscript{-1}. Compared to AgBr (0.75 %)/HCCN, the decreased hydrogen evolution activity of HCCN/Pt + AgBr (0.75 %) implies that the intimate contact of the heterojunction contact is relevant to the photocatalytic activity. The wavelength-dependent HER activities of AgBr (0.75 %)/HCCN and pristine HCCN were explored under different monochromatic illumination, and the results are listed in Table S1. As shown in Fig. 5 b, the apparent quantum efficiency (AQE) for hydrogen evolution over AgBr (0.75 %)/HCCN and pristine HCCN under 410, 460, and 500 nm are 6.0, 1.3, 0.1 %, and 1.5, 0.3 and 0.1 %, respectively. The hydrogen evolution trend of AgBr (0.75 %)/HCCN matches well with its optical absorption. The identical AQE under 500 nm indicates that the enhanced photocatalytic activity of AgBr (0.75 %)/HCCN benefits from the generation of Z-scheme heterojunction, instead of the LSPR effect of AgBr nanosphere. Compared with similar systems, this work shows a significant enhancement in photocatalytic hydrogen evolution (Table S3). The photocatalytic stability of AgBr/HCCN was studied by continuously running the catalyst for multiple cycles under different reaction conditions. As shown in Fig. 5 c, firstly, the photocatalytic HER of AgBr/HCCN was measured, when NaCl was added as the only salt. Before the second round of HER, the photocatalyst was recycled via vacuum filtration, and the reaction solution was also renewed. Even though, the activity of the second cycle reaction dropped to around one-third of the first cycle. This may be caused by the leaking of potassium (K) or lithium (Li) from the HCCN, which agrees with another report [48]. To prevent the loss of K\textsuperscript{+} or Li\textsuperscript{+} in HCCN, a specific amount of KCl and LiCl was added to the reaction system to maintain the concentration of these ions. As shown in Fig. 5d, during the initial 5 cycles of reactions, the photocatalytic stability of AgBr/HCCN significantly improved, reaching 80 % of the activity observed in the first cycle (without adding extra TEOA or salt). Furthermore, AgBr/HCCN could be thoroughly recovered through recycling and replacing the reaction solution with a fresh one, reflecting the good photostability of AgBr/HCCN (please see the fourth and fifth cycles). The slight decrease in hydrogen evolution rate as a function of irradiation time in each cycle is attributed to the continuous consumption of TEOA, while the small fluctuation in cyclic hydrogen generation between the cycles is due to experimental error and limited gas circulation in the small reactor (Fig. S12.).

3.6. Morphology and surface chemical state properties after HER

In Fig. S13, the survey XPS spectrum of the AgBr (0.75 %)/HCCN after HER shows that Pt co-catalysts were introduced into the composite photocatalyst (AgBr (0.75 %)/HCCN/Pt). In comparison to AgBr (0.75 %)/HCCN before HER, AgBr (0.75 %)/HCCN/Pt (the one after HER) exhibits a slightly decreased intensity of K in the survey XPS spectra, indicating the loss of a small amount of K ions during HER (Fig. S13b).
This observation is consistent with the results of the photocatalytic stability test. Besides, no other obvious change was observed, revealing the stability of the components during the photocatalytic reaction. Fig. S14 depicts that the binding energy peaks in the C 1s, N 1s, Ag 3d, and Br 3d XPS spectra of AgBr (0.75 %)/HCCN/Pt show minor shifts, indicating an interaction between Pt and the composite (see supporting information for details). The similar binding energy with AgBr (0.75 %)/HCCN attests to the interface stability of the heterojunction during photocatalytic HER. Furthermore, the Pt 4f spectrum of AgBr (0.75 %)/HCCN/Pt was deconvoluted, yielding two pairs of doublets: 4f\(_{/2}\) positions at 70.7 and 72.2 eV, and 4f\(_{/2}\) positions at 74.0 and 75.5 eV. These can be ascribed to metallic Pt\(^0\) and oxidized Pt\(^{2+}\), respectively, as depicted in Fig. S14D [9,37]. The morphology of AgBr (0.75 %)/HCCN after photocatalytic HER was studied by SEM (Fig. S15) and no significant alteration was observed. Pt as a co-catalyst selectively deposited on the AgBr nanospheres driven by the Z-scheme heterojunction, which was in accordance with TEM EDX mapping (Fig. S2). The XPS and SEM characterizations performed after the photocatalytic reaction not only confirm the proposed Z-scheme heterojunction electron transfer mechanism but also demonstrate the stability of AgBr (0.75 %)/HCCN under illumination.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2024.159292.

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