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g-C₃N₄/ NiAl-LDH 2D/2D Hybrid Heterojunction for High-Performance Photocatalytic Reduction of CO₂ into Renewable Fuels

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ABSTRACT

2D/2D interface heterostructures of g-C_3N_4 and NiAl-LDH are synthesized utilizing strong electrostatic interactions between positively charged 2D NiAl-LDH sheets and negatively charged 2D g-C_3N_4 nanosheets. This new 2D/2D interface heterojunction showed remarkable performance for photocatalytic CO_2 reduction to produce renewable fuels such as CO and H_2 under visible-light irradiation, far superior to that of either single phase g-C_3N_4 or NiAl-LDH nanosheets. The enhancement of photocatalytic activity could be attributed mainly to the excellent interfacial contact at the heterojunction of g-C_3N_4/NiAl-LDH, which subsequently results in suppressed recombination, and improved transfer and separation of photogenerated charge carriers. In addition, the optimal g-C_3N_4/NiAl-LDH nanocomposite possessed high photostability after successive experimental runs with no obvious change in the production of CO from CO_2 reduction. Our findings regarding the design, fabrication and photophysical properties of 2D/2D heterostructure systems may find use in other photocatalytic applications including H_2 production and water purification.

KEYWORDS: layered double hydroxide, g-C_3N_4, CO_2 reduction, nanocomposite, photocatalysis

1. INTRODUCTION

One of the foremost challenges faced by today's human society is to conserve the environment for future generations, especially in light of concerns about global climate change related to rapid increase of atmospheric carbon dioxide (CO_2) levels. In addition to anthropogenic CO_2 emissions, human beings are also facing the ever-increasing challenge of the inevitable depletion of fossil fuel resources.[1-3] In this scenario, the development of novel technologies for the sustainable production of energy in an environmentally and economically feasible manner is urgently required. The conversion of CO_2 into renewable fuels by using clean and abundant solar energy, mimicking natural photosynthesis, has been regarded as one of the most compelling strategies that would not only reduce the atmospheric CO_2 levels but promises to fulfill the global energy demands.[4,5] Since the discovery of photoconversion of CO_2 to valuable fuels such as CH_3OH, CH_4, HCHO and HCOOH over semiconductor aqueous suspension by Inoue and co-workers in 1979,[6] great efforts have been made to construct more efficient and environmentally friendly catalysts to attain CO_2 photo-conversion more economically. However, the reduction of CO_2 is quite challenging owing to its thermodynamically inert and stable properties. Therefore, search for highly efficient and stable photocatalysts for CO_2 conversion, especially under solar light irradiation is a central challenge in this area of research.

In recent years, graphitic carbon nitride (g-C_3N_4), a metal-free conjugated polymer semiconductor has emerged as a promising alternative to the various traditional metal-containing photocatalysts, such as oxides,[7,8] sulfides,[9,10] and oxynitrides,[11] due to its fascinated properties such as high physicochemical stability, narrow band gap (2.7 eV), tunable electronic structure, low cost, non-toxicity, and most importantly, appropriate band edge potentials for water splitting and CO_2 photoreduction.[12-15] However, practical applications of pure g-C_3N_4 are still hindered by

several obstacles and shortcomings including rapid recombination of charge carriers, low specific surface area, and its low utilization efficiency of light quanta. With the aim to eradicate these obstacles, many attempts have been made to further improve the performance of pure g-C_3N_4 including electronic structure modulation,[16] combining it with other conducting materials,[14,17] constructing its heterojunction with other semiconductors,[18-21] and loading co-catalysts.[22,23] Among all the strategies, the construction of heterojunctions by combining two different semiconductors, particularly two-dimensional (2D) layered architectures with suitable conduction and valence band potentials is one of the most effective approaches to enhance the separation efficiency of photogenerated charge carriers during the photocatalytic process.[24-27] For instance, Xiang et al.[28] developed 2D/2D g-C_3N_4/grapheme heterostructures, and their photocatalytic activities were investigated for H_2 production under hole sacrificial agent. Very recently, Liu and co-workers[29] synthesized a 2D/2D $CdIn_2S_4$/mpg-C_3N_4 heterostructure for photocatalytic CO_2 reduction to generate methanol. Despite great efforts, the photocatalytic efficiency, particularly for CO_2 reduction without using a sacrificial agent, is still an open challenge due not only to slow redox chemistry but also issues related to the efficacy of CO_2 adsorption and electron transfer to CO_2.

In this work, we have successfully constructed a heterojunction between the negatively charged 2D g-C_3N_4 nanosheets and positively charged NiAl-layered double hydroxide (NiAl-LDH). Owing to the 2D layered configuration, band structure matching with favourable redox chemistry, basicity of surface hydroxyl groups, visible-light-absorption capability, NiAl-LDH is a great choice to be coupled with g-C_3N_4 to create 2D/2D intimate interface at the heterojunction with excellent charge carrier mobility with expected high CO_2 availability on the surface.[30-36] More attractively, as shown in this work, this heterostructure exhibits a high performance for

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photocatalytic CO_2 reduction under visible-light irradiation. Our results clearly establish that the coupling of 2D g-C_3N_4 nanosheets with basic 2D NiAl-LDH nanosheets plays a vital role in not only reducing charge recombination and improving the charge transfer but also improved CO_2 adsorption and electron transfer to CO_2. Moreover, NiAl-LDH coupled g-C_3N_4 nanosheets is a low cost material, which could be a potential candidate in practical applications such as photocatalytic CO_2 reduction without using a sacrificial agent. To the best of our knowledge, this is the first report on the use of the 2D layered junction between g-C_3N_4 nanosheets and NiAl-LDH for the visible-light-driven photocatalytic CO_2 reduction to generate solar fuels.

2. EXPERIMENTAL SECTION

2.1 Materials. Nickel nitrate hexahydrate (Merck, AR grade), aluminum nitrate nonahydrate (Merck, AR grade), melamine (Sigma-Aldrich, 99.0%), ammonium fluoride (SDFCL, AR grade) and urea (SDFCL, AR grade) were used as received. All other chemicals used in this work were of analytical grade and used as-received without further purification. All aqueous solutions were prepared with Milli-Q water.

2.2 Method. The pure g-C_3N_4 nanosheets were synthesized according to a procedure described in our previous paper.[37] Initially, bulk g-C_3N_4 was synthesized by a simple thermal condensation method using melamine as a precursor. Approximately 10 g of melamine was placed in an alumina combustion boat and thermally treated at 550 °C for 2 h in a tube furnace with a heating rate of 5 °C min^{-1} under N_2 atmosphere. The obtained yellow agglomerates was ground into fine powder and collected for further use. The g-C_3N_4 nanosheets were synthesized by ultrasonic exfoliation of the obtained bulk g-C_3N_4 in water. About 100 mg of bulk g-C_3N_4 was dispersed in 250 mL of water, followed by ultrasonic treatment for 15 h. The obtained

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suspension was centrifuged at low rpm to separate the residual unexfoliated g-C_3N_4. Then the supernatant suspension was heated to remove water and the so-obtained pale yellow powder of g-C_3N_4 nanosheets was denoted as CN.

The flower-like pure NiAl-LDH was synthesized according to the reported synthesis procedure with some modifications mentioned below.[38] The g-C_3N_4/NiAl-LDH composites were synthesized by a one-step *in situ* hydrothermal method. In a typical process, a calculated amount of as-synthesized g-C_3N_4 nanosheets was dispersed in 80 mL of water and subjected to ultrasonication for 30 min. Then, $Ni(NO_3)_2.6H_2O$ (0.006 M) and $Al(NO_3)_3.9H_2O$ (0.002 M) were added into the above g-C_3N_4 suspension and ultrasonicated for another 10 min. Subsequently, NH_4F (0.016 M) and urea (0.04 M) were dissolved into the mixed solution and stirred for 30 min. The obtained suspension was thermally treated in a sealed Teflon-lined autoclave (100 mL) at 120 °C for 24 h. The resulting precipitate was washed with water several times until the pH reached 7 and dried in an oven at 60 °C overnight. A series of g-C_3N_4/NiAl-LDH 2D/2D composites with 5, 10, 15 and 20 wt.% NiAl-LDH to g-C_3N_4 were synthesized and denoted as CNLDH-5, CNLDH-10, CNLDH-15, and CNLDH-20, respectively. Pure NiAl-LDH was also synthesized by a similar procedure in the absence of g-C_3N_4, but without ultrasonication throughout the reaction.

2.3 Materials Characterization. X-ray diffraction (XRD) measurements were conducted on a Bruker D8-Advance X-ray diffractometer operating with Cu K_α radiation ($\lambda = 1.5418$ Å) over the 2θ range of 10−80°. The ultraviolet−visible diffuse reflectance spectra (UV−vis DRS) of samples were recorded over the range of 250−800 nm using a UV-3600, Shimadzu (UV−vis NIR spectrophotometer) equipped with an integrating sphere, and $BaSO_4$ was used as a reference. The Fourier transform infrared (FT-IR) spectra of the samples were recorded using a PerkinElmer

Spectrum 100 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. Photoluminescence (PL) spectra of the samples were conducted at room temperature on a steady state spectrofluorometer (SHIMADZU RF-6000) with an excitation wavelength of 365 nm. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were performed on a FEI Tecnai G^2 transmission electron microscope, operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI 5000 versaprobe instrument (ULVAC-PHI, Chigasaki, Japan) with monochromatic Al Kα X-ray radiation. The thermo-gravimetric analysis (TGA) was performed on a PerkinElmer Pyris Diamond TGA/DTA instrument. Nitrogen adsorption–desorption isotherms were carried out on a BELSORP-max, (Japan) equipment.

2.4 Photoelectrochemical Measurements. Photoelectrochemical measurements were carried out on an IVIUM Technologies electrochemical workstation with a standard three-electrode photoelectrochemical cell. 0.1 M Na_2SO_4 was used as the electrolyte solution. Indium Tin Oxide (ITO) deposited with photocatalyst served as a working electrode, while the counter and the reference electrodes were platinum wire and Ag/AgCl (in saturated KCl), respectively. Photocurrent measurements of the synthesized photocatalysts were examined for several on-off cycles of light irradiation by a 300 W Xenon arc lamp. The typical working electrode preparation was as follows: 20 mg of a powder sample was dispersed in 0.5 mL of ethanol and 20 μL of Nafion solution (5 wt%), and then ground well to make uniform slurry. The obtained slurry was then deposited as a thin film onto the ITO glass substrate, and the coated area was fixed at 1.0 cm^2. Finally, the coated ITO glass was dried at 80 °C to obtain a homogeneous film.

2.5 Evaluation of Photocatalytic Activity. Photocatalytic activity of the synthesized samples for CO_2 reduction was evaluated in gaseous phase in a 250 mL stainless steel photoreactor with a

quartz window. A 300 W Xenon arc lamp was used as the light source with a UV cut-off filter ($\lambda \geq 420$ nm). In a typical process, 50 mg of the powder sample was placed into a photoreactor. Prior to irradiation, the reaction setup was vacuum-treated and purged with high purity CO_2 gas (5 ml/min) for 1 h, to remove air from the system. The high purity CO_2 gas was led to pass through a water bubbler to generate a mixture of CO_2 and water vapor. During the irradiation, 1 mL gaseous products from the reaction chamber were sampled at given time intervals (1 h) for subsequent quantitative analysis of products by using gas chromatograph (Shimadzu Tracera GC-2010 Plus) with Barrier Ionization Detector and He as a carrier gas. For reusability/stability test, the selected photocatalyst was collected after each run and refreshed by washing with water and heat treatment at 100 °C, and its photocatalytic activity was reevaluated under the aforementioned conditions.

The selectivity towards reactively-formed CO was simply deduced according to the following equation.[36]

$$CO\ Selectivity\ (\%) = \frac{2N_{CO}}{2N_{CO} + 2N_{H_2}} \times 100$$

In which N_{CO} and N_{H_2} stand for the yields of reactively-formed CO and H_2, respectively.

Apparent quantum yield (AQY) of the photocatalyst was calculated using the following equation according to previously reported works.[39-41]

$$AQY\ (\%) = \frac{the\ no\ of\ reacted\ electrons}{the\ no\ of\ incident\ photons} \times 100$$

$$= \frac{the\ no\ of\ evolved\ CO\ molecules\ \times 2}{the\ no\ of\ incident\ photons} \times 100$$

(AQY calculations are explained in the supporting information)

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3. RESULTS AND DISCUSSION

3.1. Formation Process and Characterization of g-C$_3$N$_4$/NiAl-LDH Heterojunctions. In the present study, the g-C$_3$N$_4$/NiAl-LDH nanocomposites are synthesized by a facile one-step *in situ* hydrothermal method and the formation process is schematically illustrated in **Scheme 1**. Initially, g-C$_3$N$_4$ nanosheets were obtained by ultrasonic exfoliation of the bulk g-C$_3$N$_4$ in water. After addition of Ni (NO$_3$)$_2$.6H$_2$O and Al (NO$_3$)$_3$.9H$_2$O to the ultrasonically dispersed g-C$_3$N$_4$ nanosheets, Ni^{2+} and Al^{3+} metal ions from the metal salts can be strongly bound onto the surface of negatively charged g-C$_3$N$_4$ nanosheets by electrostatic interactions. When urea and ammonium fluoride are added to the dispersion, a large amount of nuclei form and NiAl-LDH platelets grow onto the surface of g-C$_3$N$_4$ nanosheets under subsequent hydrothermal treatment. In this process, negatively charged g-C$_3$N$_4$ nanosheets could serve as nucleation sites for the *in situ* growth of NiAl-LDH sheets. As a result, restacking process of LDH sheets can be arrested effectively which leads to the 2D/2D assembly of g-C$_3$N$_4$ and NiAl-LDH sheets.[42,43] Moreover, zeta potential measurements were also conducted (in water) to investigate the interactions between these two semiconductors (**Figure S1**). A significant shift in the zeta potential of g-C$_3$N$_4$ was observed after the formation of nanocomposite with NiAl-LDH, which clearly indicates that the g-C$_3$N$_4$/NiAl-LDH nanocomposites could self-assemble through electrostatic interactions.

TGA analysis was performed to confirm the contents of NiAl-LDH in the synthesized g-C$_3$N$_4$/NiAl-LDH nanocomposites under N$_2$ atmosphere at a heating rate of 10 °C min^{-1}. As can be seen in **Figure S2**, the bare NiAl-LDH exhibits two significant weight loss regions. The first weight loss from 25 to 200 °C can be assigned to the evaporation of surface adsorbed and interlayer water molecules, while the second weight loss at temperature between 250 and 350 °C

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corresponds to the decomposition of the interlayer nitrate anions and de-hydroxylation of the brucite-like layers.[44-46] Besides, pure g-C_3N_4 decomposition starts at 550 °C and is completed at ~700 °C, which correspond to the burning of g-C_3N_4.[19] The general trend of thermal degradation of g-C_3N_4/NiAl-LDH samples is similar to bare NiAl-LDH and g-C_3N_4. However, when compared to bare NiAl-LDH, poor weight loss was observed over low temperature regions for g-C_3N_4/NiAl-LDH samples, which might be due to the scarcity of interlayer water molecules and nitrate anions owing to the self-exfoliation of LDH layers on g-C_3N_4 surface in the *in-situ* synthesis process. Regardless, the content of NiAl-LDH can be confirmed using the weight remainder after heating the samples over 800 °C. Therefore, the specific weight percentages of NiAl-LDH in the nanocomposites were found to be 4.2, 9.7, 13.8 and 18.5%, for CNLDH-5, CNLDH-10, CNLDH-15 and CNLDH-20, respectively.

The phase structure of the synthesized samples was investigated by XRD, and the results are displayed in **Figure 1**. The pure g-C_3N_4 material has two diffraction peaks at about 27.8° and 13.23° corresponding to the characteristic interlayer stacking of the conjugated aromatic systems and the in-planar structural repeating unit, respectively.[37] For pure NiAl-LDH, the reflections at 11.72°, 23.41°, 35.13°, 39.56°, 46.92°, 61.01°, and 62.43° are ascribed to the (003), (006), (012), (015), (018), (110), and (113) lattice planes, which can be indexed to the hexagonal NiAl-LDH (JCPDF22-0452). In the case of g-C_3N_4/NiAl-LDH heterostructures, a superimposition XRD pattern of g-C_3N_4 and NiAl-LDH is observed, and with the increase in NiAl-LDH content, the diffraction peaks of NiAl-LDH intensify gradually at the expense of g-C_3N_4 peaks, reflecting their respective contents in the g-C_3N_4/NiAl-LDH heterostructures. Moreover, after introduction of NiAl-LDH, the main peak of g-C_3N_4 (27.8°) in g-C_3N_4/NiAl-LDH composites slightly shifted

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from the original position and appeared with decreased intensities, which clearly indicates the coordination between the g-C_3N_4 and NiAl-LDH in g-C_3N_4/NiAl-LDH nanocomposites.

UV-vis DRS was performed to investigate the light response property of the synthesized photocatalysts, since the photocatalytic activity is relevant to the optical absorption characteristics. As shown in **Figure 2**, pure g-C_3N_4 displays a strong absorption edge located at 460 nm which corresponds to a band gap of ca. 2.7 eV. Bare NiAl-LDH exhibits mainly three absorption bands in the UV and visible-light regions, in which the first one is located from 200 to 300 nm, second one from 300 to 500 nm, and the third one from 600 to 800 nm. The intrinsic absorption band in the UV region (200 to 300 nm) could be assigned to ligand-to-metal charge transfer (LMCT) from the O 2p orbital to the Ni 3d t_{2g} orbital, while the bands from 300 to 800 nm are corresponding to d-d transitions, which are characteristics of Ni^{2+} ions in an octahedral geometry.[47,48] The absorption bands at 380 and 740 nm are attributed to spin-allowed transitions $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$, respectively, resulting from d^8 configuration of Ni^{2+} ions in an octahedral field. The other bands located at 420 and 645 nm are attributed to spin-forbidden transitions $^3A_{2g}(F) \rightarrow ^1T_{2g}(D)$ and $^3A_{2g}(F) \rightarrow ^1E_g(D)$, respectively.[49,50] A slight blue shift in the absorption edge was observed after the introduction of NiAl-LDH on g-C_3N_4, and with increasing NiAl-LDH content, the absorption edge was seen to shift towards the lower wavelength region. A similar kind of blue shift in the absorption edge is also observed in previous reports.[20,51] More remarkably, with an increase in the weight percentage of the NiAl-LDH on g-C_3N_4, a decrease in light absorption in the UV region (300 to 400 nm) and increase in the light absorption in the visible region (550 to 800 nm) was observed, which could be attributed to the strong interaction between g-C_3N_4 and NiAl-LDH in the resulting composites. The improved light absorption in the visible region can therefore provide more photogenerated

charge carriers required for the photocatalytic reactions, which can result in enhanced photocatalytic properties.

Figure 3 displays the FT-IR patterns of the synthesized g-C_3N_4, NiAl-LDH and g-C_3N_4/NiAl-LDH nanocomposites. For g-C_3N_4, the sharp and intense band at 805 cm^{-1} corresponds to the characteristic breathing mode of the s-triazine ring system, and the broad band at around 3200 cm^{-1} corresponds to the stretching vibrational modes of residual N–H components associated with uncondensed amino groups. Additionally, several bands in the 1200–1650 cm^{-1} region are assigned to the typical stretching modes of aromatic C–N heterocycles.[37] The bands at 3480 and 1635 cm^{-1} in the NiAl-LDH spectrum can be assigned to the O–H stretching and bending vibrations, respectively, and the strong band at 1365 cm^{-1} can be assigned to the bending vibrations of NO_3^- ions intercalated in the lamellar structure.[46] The other bands below 800 cm^{-1} are attributed to the translational modes of metal–oxygen (Ni–O and Al–O) and metal–oxygen–metal (Ni–O–Al) bands.[52,53] It should be noted that the FT-IR spectra of g-C_3N_4/NiAl-LDH composites consists of all the characteristic bands of g-C_3N_4 along with the broad shoulder band at 3480 cm^{-1}, which originates from the stretching vibrations of O–H groups existing in NiAl-LDH. Moreover, after the addition of NiAl-LDH, the bands at 885 cm^{-1} showed a blue shift, which is consistent with the UV-vis DRS observations. These results clearly demonstrate the effect and existence of NiAl-LDH on g-C_3N_4 through the interfacial electrostatic interactions. Such strong interactions between the semiconductors are clearly of significance to the charge transfer and can induce a synergistic effect to enhance the photocatalytic activity.

The morphologies and microstructures of pure g-C_3N_4, NiAl-LDH and g-C_3N_4/NiAl-LDH nanocomposites were investigated by TEM and HR-TEM. The TEM image of pure NiAl-LDH (**Figure 4**a) exhibits 3D flower-like morphology consisting of plenty of ultrathin nanoflakes. As

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expected, g-C$_3$N$_4$ possessed a 2D sheet-like structure with irregular orientation (**Figure 4**b), which indicates the successful exfoliation of bulk g-C$_3$N$_4$. Interestingly, in the case of g-C$_3$N$_4$/NiAl-LDH nanocomposites (CNLDH-10), the flower-like morphology of NiAl-LDH disappears; however, a number of ultrathin 2D LDH sheets are well grown on the surface of g-C$_3$N$_4$, which demonstrates the successful self-assembly of g-C$_3$N$_4$ and NiAl-LDH by electrostatic interactions (**Figures 4**c – e). This clearly indicates that, during the *in situ* growth process both g-C$_3$N$_4$ and NiAl-LDH nanosheets strongly interact with each other due to the their opposite surface charges and these interactions subsequently contribute to avoid the restacking of NiAl-LDH nanosheets in the nanocomposite samples. Besides, the HR-TEM image (**Figure 4**f) exhibits lattice fringes corresponding to the interplanar distance of 0.32 and 0.26 nm, which can be ascribed to the (002) plane of g-C$_3$N$_4$ and (012) plane of NiAl-LDH, respectively.[35,54] Additionally, EDS elemental mapping images (**Figure S3**) further confirm that the g-C$_3$N$_4$/NiAl-LDH heterojunction (CNLDH-10) was composed of C, N, Ni, Al and O elements. The homogenous distribution of the component elements in the CNLDH-10 heterojunction clearly demonstrates that both g-C$_3$N$_4$ and NiAl-LDH phases are indeed fully mixed and intimately contacted, rather than existing as separate aggregates in the CNLDH-10 heterojunction.

The XPS spectra were conducted to analyze the detailed chemical status of the pure and composite photocatalysts. As observed from **Figure S4**, the survey XPS spectrum of the CNLDH-10 sample exhibits the peaks corresponds to C, N, Ni, Al, and O elements, revealing the presence of g-C$_3$N$_4$ and NiAl-LDH in the composite. For pure g-C$_3$N$_4$, the N 1s spectrum can be deconvoluted into three peaks located at the binding energies of 398.4, 399.6, and 400.9 eV, which are ascribed to sp2 hybridized nitrogen in triazine rings (C−N=C), bridged tertiary nitrogen N−(C)$_3$ groups, and amino functional groups (N−H), respectively (**Figure 5**a). The C 1s

spectrum in **Figure 5**b can be fitted by two peaks, attributed to C−C at 284.5 eV and N=C−N at 288.1 eV.[16,54] Besides, the Ni 2p spectrum (**Figure 5**c) for pure NiAl-LDH consists of two peaks with the binding energies of 856.2 and 873.8 eV, corresponding to Ni $2p_{3/2}$ and Ni $2p_{1/2}$, respectively, in agreement with the Ni^{2+} oxidation state, and the additional satellite peaks indicate the presence of a high-spin divalent state of Ni^{2+} in the sample.[55,56] Additionally, the high resolution Al 2p spectrum (**Figure 5**d) confirms the Al^{3+} oxidation state in the pure NiAl-LDH.[57] For the $g-C_3N_4$/NiAl-LDH nanocomposites, a significant increase in the binding energies of Ni $2p_{3/2}$ and Ni $2p_{1/2}$, and a small decrease in the C 1s binding energy were observed compared to the pure reference materials. However, no such shift in the binding energies of N 1s and Al 2p were observed for the pure and composite samples. The increased and decreased binding energies of Ni 2p and C 1s suggesting the strong electron transfer between $g-C_3N_4$ and NiAl-LDH, and the similar phenomenon was also observed in previous reports.[36,58]

3.2. Photocatalytic CO_2 Reduction Activities of the $g-C_3N_4$/NiAl-LDH Heterojunctions. The photocatalytic activities of all synthesized $g-C_3N_4$/NiAl-LDH photocatalysts, including pure $g-C_3N_4$ and NiAl-LDH were evaluated under visible-light illumination and the results are displayed in **Figure 6**. Carbon monoxide was found to be the main and direct product of CO_2 reduction reaction and no other carbonaceous products were observed. However, other products such as H_2 and O_2, which are generated from the water (vapor) splitting, were also detected. During the evaluation of photocatalysts, controlled experiments in the absence of light irradiation or catalysts were also conducted, and the results revealed that no reduced products could be detected, illustrating that light irradiation and photocatalysts are essential for photocatalytic CO_2 reduction reactions. Moreover, neither CO, nor other products can be detected by introducing CO_2 into the reaction system without water vapor or introducing N_2 instead of CO_2 into the

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reaction system under light irradiation, clearly demonstrating that CO was solely originated by the reduction of CO_2 with water vapor over the photocatalysts under the visible-light illumination.

Figure 6a shows the evolution of CO as a function of illumination time on all the synthesized photocatalysts under visible-light irradiation. As expected, pure g-C_3N_4 exhibited a minimal generation of CO, attaining a total yield of 0.39 μmol for 5 h, due to rapid recombination of photogenerated charge carriers. Moreover, in this photocatalytic process g-C_3N_4 also generated significant amounts of H_2 and O_2 through water (vapor) splitting owing to its suitable band edge potentials for both the water reduction and oxidation reactions. Besides, pure NiAl-LDH exhibits a low photocatalytic activity for CO_2 reduction, in which the amount of generated CO is only 0.23 μmol for 5 h.

Importantly, after forming the 2D/2D heterostructure of g-C_3N_4 with NiAl-LDH, the obtained g-C_3N_4/NiAl-LDH photocatalysts exhibited remarkable photocatalytic activity for CO evolution. As shown in **Figure S5**, the rate of CO evolution increased with increasing the NiAl-LDH content in the g-C_3N_4/NiAl-LDH nanocomposites, reaching a highest rate of 8.2 μmol $h^{-1}g^{-1}$ for the case of NiAl-LDH content of 10 wt.% (CNLDH-10), which is more than five times that for pure g-C_3N_4 (1.56 μmol $h^{-1}g^{-1}$) and almost nine times higher than that for NiAl-LDH (0.92 μmol $h^{-1}g^{-1}$). Notably, the CO selectivity for CNLDH-10 photocatalyst is almost 82%. As shown in **Figure 6**b and c, the synthesized composites not only exhibited remarkable enhancement in the generation of CO but also exhibited significant enhancement in the generation of H_2 and O_2. It is also worth noting that all the samples displayed (CO + H_2):O_2 products stoichiometry close to 2:1, since both CO_2 reduction to CO, and H_2O reduction to H_2 are 2e- processes, whereas H_2O oxidation is a 4e- process. However, when the NiAl-LDH content increased beyond its optimum

level (~10 wt.%) in the g-C_3N_4/NiAl-LDH composites, a decrease in the reduction products rate was observed. This can probably be attributed to the following reasons: (1) excessive amount of NiAl-LDH may cover the active sites on the surface of g-C_3N_4, and (2) at a very high content of NiAl-LDH, there is a good chance of the development overlapped (self-aggregated) NiAl-LDH sheets in the sample which reduces the density of g-C_3N_4/NiAl-LDH heterojunctions. Hence, an optimized content of NiAl-LDH is crucial for optimizing the photocatalytic activity of g-C_3N_4/NiAl-LDH composites.

The impact of surface area on CO_2 photoreduction activities of all the samples was investigated using nitrogen adsorption-desorption measurements. As can be seen **Figure S6**, pure g-C_3N_4 nanosheets possesses higher specific surface area (S_{BET} = 106.9 m^2/g) in comparison with NiAl-LDH (S_{BET} = 28.5 m^2/g) and also the higher CO_2 photoreduction activity. It was found that when NiAl-LDH introduced into g-C_3N_4 nanosheets, the specific surface areas of g-C_3N_4/NiAl-LDH composites were similar to that of g-C_3N_4, but their CO_2 photoreduction activities are apparently different. This clearly demonstrates that there should be another key factor other than surface area that influences the CO_2 photoreduction activities of the present nanocomposites significantly. As such, the variation in the photoreduction activities of these nanocomposites is mainly rely on the efficient separation of photogenerated electron-hole pairs which resulted by the intimate interface between g-C_3N_4 and NiAl-LDH. This is further investigated by the CO_2 photoreduction results of a physical mixture of g-C_3N_4 and NiAl-LDH (denoted as CNLDH-10 PM in **Figure 6**a, b, and c). Clearly, physically mixed CNLDH-10 PM (10 wt% NiAl-LDH on g-C_3N_4) composite showed poor CO evolution activity (2.84 μmol $h^{-1}g^{-1}$), indicating the absence of strong electrostatic interactions between the g-C_3N_4 and NiAl-LDH.

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Additionally, the photocatalytic activity of the presented 2D/2D system was also compared with the commercial P25 reference catalyst, which showed rather negligible photocatalytic CO evolution due to the rapid charge carrier recombination, low CO_2 absorptivity, and improper conduction band (CB) potential to drive CO_2 reduction.[36] Notably, the photocatalytic CO evolution activity of the CNLDH-10 composite is also higher than the various $g-C_3N_4$-based photocatalysts reported previously, such as $g-C_3N_4/BiOBr/Au$,[59] $BiOI/g-C_3N_4$,[60] $g-C_3N_4/C$,[61] $g-C_3N_4/Bi_2WO_6$,[62] and other photocatalysts, for example $rGO-Ag-CdS$,[63] $I-TiO_2$,[64] PbS QD's$/Cu/TiO_2$,[65] $Au@SrTiO3$,[66] and so on.

Furthermore, **Figure 6**d displays an action spectrum of CNLDH-10 catalyst, which exhibits the wavelength-dependent AQY values on account of CO production using appropriate band-pass filters. It can be seen that the AQY values of CO production are essentially dependent on the incident wavelength that matches well with the absorption in the optical spectrum of the CNLDH-10 catalyst. Moreover, action spectrum reveals higher AQY values in the 400-450 nm wavelength regions; whereas very low AQY values observed after the wavelength of 500 nm. These results clearly indicate that the inter-band transitions of $g-C_3N_4$ predominantly lead to the CO_2 photoreduction of the CNLDH-10 catalyst. The significant AQY values obtained in this study are 0.39% at 400 nm, and 0.21% at 420 nm, respectively. Notably, the AQY values of the present system at 400 and 420 nm are indeed higher than the other state of the art CO_2 reduction photocatalysts.[67-70]

Reusability and stability are critical issues for the long-term use of a photocatalyst in practical applications. In order to investigate the photostability of the synthesized $g-C_3N_4/NiAl-LDH$ nanocomposites, four cycling CO_2 photocatalytic reduction experiments were performed over CNLDH-10 under the same experimental conditions. Each run was conducted with the periodic

replacement of fresh CO_2 and water vapor. As shown in **Figure 7**, the photocatalytic CO

evolution of CNLDH-10 was decreased to 1.79 μmol after four successive experimental runs

(~20 h), retaining over 86% of its original activity (2.05 μmol) under the visible-light irradiation.

A slight depletion in the activity may originate from the inevitable loss of the catalyst during the

recycling runs. The results indicate that LDH was firmly attached to the $g-C_3N_4$ substrate during

the *in situ* synthetic process, owing to their opposite surface charges. Subsequently,

immobilization of LDH on $g-C_3N_4$ surface can not only enhance the photocatalytic CO_2 reduction

performance, but also improves the stability of the catalyst during the photocatalytic

reactions.[33,71] **Figure S7** shows a comparison of the XRD patterns of CNLDH-10 sample before

and after the photocatalytic reaction and no obvious peak change in the XRD patterns was

observed, suggesting the structural stability of the composites during the photocatalytic reaction

process. Moreover, the TEM image (**Figure S7**) of the reused sample also clearly demonstrated

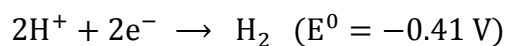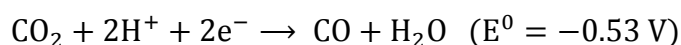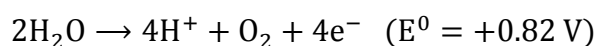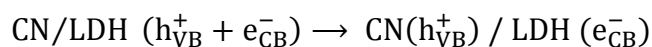that the morphology of the CCG-10 photocatalyst did not change significantly after the reaction.

3.3. Photocatalytic Mechanism in the $g-C_3N_4$/NiAl-LDH Heterojunction System. In order

to investigate the photocatalytic mechanism for the enhanced photocatalytic CO_2 reduction by

the $g-C_3N_4$/NiAl-LDH heterojunctions, PL spectra of the photocatalysts were recorded. As

shown in **Figure 8**a, all the photocatalysts show a broad PL emission peak centered at around

460 nm, which corresponds to the band-band PL due to the recombination of photogenerated

charge carriers of $g-C_3N_4$. It can be found that the PL emission intensities reach the maximum

value for pure $g-C_3N_4$ and decrease significantly with the introduction of NiAl-LDH, clearly

demonstrating that the recombination of the photogenerated electron-hole pairs in $g-C_3N_4$ has

been effectively inhibited after the heterojunction formation with NiAl-LDH. The CNLDH-10

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sample exhibits the least PL emission intensity i.e., the lowest recombination rate, which agrees well with its highest photocatalytic activity as mentioned above.

To provide further evidence to support the efficient photogenerated charge carriers separation of the present system, photoelectrochemical measurements were performed. **Figure 8**b shows reproducible and stable photocurrent responses to on-off cycles in the pure and composite samples. Notably, the CNLDH-10 photocatalyst exhibited the highest photocurrent response in comparison with those of pure $g-C_3N_4$ and NiAl-LDH, which can be attributed to the existence of a strong interface between $g-C_3N_4$ and NiAl-LDH, where photogenerated charge carriers could be efficiently separated. The greater transfer efficiency of charge carriers lead to the remarkable photocatalytic activity of $g-C_3N_4$/NiAl-LDH nanocomposites.

In addition, the valence band (VB) and CB positions of $g-C_3N_4$ and NiAl-LDH were investigated by valence band XPS (VB-XPS). As shown in **Figure 9**, the VB edge positions of $g-C_3N_4$ and NiAl-LDH are determined to be 1.38 and 1.62 eV, respectively. Based on the band gaps of $g-C_3N_4$ (2.7 eV) and NiAl-LDH (2.32 eV), the CB edge positions are calculated to be -1.32 eV and -0.7 eV for $g-C_3N_4$ and NiAl-LDH, respectively. Therefore, it could be concluded that the CB minimum of NiAl-LDH is lower than that of $g-C_3N_4$, while the VB maximum of $g-C_3N_4$ is higher than that of NiAl-LDH. Based on the above results, the photocatalytic mechanism for the $g-C_3N_4$/NiAl-LDH nanocomposites is proposed and schematically illustrated in **Figure 10**. Upon visible-light irradiation, both $g-C_3N_4$ and NiAl-LDH can be excited to generate the electrons and holes in CB and VB, respectively, since their band gap energies lie in the visible region. The excited electrons on the CB of $g-C_3N_4$ could pass across the heterojunction into the CB of NiAl-LDH, while the formed holes on the VB of NiAl-LDH can pass through the heterojunction into the VB of $g-C_3N_4$. Such promoted charge separation or suppressed charge

recombination results in mutual activation of both g-C$_3$N$_4$ and NiAl-LDH. The resultant holes in

the VB of g-C$_3$N$_4$ and those transferred from the VB of NiAl-LDH can oxidize the chemisorbed

water molecules on the surface of g-C$_3$N$_4$ to generate O$_2$ and protons. At the same time, the

enriched electrons on the CB of NiAl-LDH could be trapped by the CO$_2$ to generate CO under

the assistance of the protons, as explained by the following equations.

$$CN/LDH + h\vartheta \rightarrow CN/LDH \ (h^+_{VB} + e^-_{CB})$$

$$CN/LDH \ (h^+_{VB} + e^-_{CB}) \rightarrow CN(h^+_{VB}) / LDH \ (e^-_{CB})$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \ (E^0 = +0.82 \ V)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \ (E^0 = -0.53 \ V)$$

$$2H^+ + 2e^- \rightarrow H_2 \ (E^0 = -0.41 \ V)$$

4. CONCLUSIONS

In summary, g-C$_3$N$_4$/NiAl-LDH heterojunctions were synthesized by an *in situ* hydrothermal

method which established a strong interface system due to the 2D/2D assembly of positively

charged NiAl-LDH sheets and negatively charged g-C$_3$N$_4$ nanosheets. The resulting 2D/2D g-

C$_3$N$_4$/NiAl-LDH heterojunctions exhibited excellent performance for photocatalytic CO$_2$

reduction under visible-light irradiation. The optimum g-C$_3$N$_4$/NiAl-LDH heterojunctions

showed the highest CO production rate of 8.2 μmol h^{-1}g^{-1}, which is 5 times higher than that of

pure g-C$_3$N$_4$ and 9 times higher than that for pure NiAl-LDH. The high performance of this new

2D/2D composite material is ascribed mainly to the synergistic effect between g-C$_3$N$_4$ and NiAl-

LDH, including strong interfacial contact due to 2D/2D assembly, suppressed recombination,

improved separation, and efficient transfer of excited charge carriers. More importantly, the

heterojunctions were highly photostable even after successive experimental runs, without any

obvious change in the activity.

ASSOCIATED CONTENT

Supporting Information

Zeta potential measurements; TGA spectra; EDS spectrum and corresponding elemental mapping images; XPS survey spectrum; Photocatalytic CO, H_2 and O_2 evolution rates graph; N_2 adsorption–desorption isotherms; TEM and XRD of fresh and reused photocatalyst.

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Figure Captions

Scheme 1. Schematic illustration of the synthesis process of g-C$_3$N$_4$/NiAl-LDH hybrid heterojunctions.

Figure 1. XRD patterns of the synthesized g-C$_3$N$_4$, NiAl-LDH, and g-C$_3$N$_4$/NiAl-LDH heterojunctions.

Figure 2. UV–vis DRS of g-C$_3$N$_4$, NiAl-LDH, and g-C$_3$N$_4$/NiAl-LDH heterojunction samples.

Figure 3. FT-IR spectra of g-C$_3$N$_4$, NiAl-LDH, and g-C$_3$N$_4$/NiAl-LDH heterojunction samples.

Figure 4. TEM images of (a) NiAl-LDH, (b) g-C$_3$N$_4$, (c, d and e) CNLDH-10, and (f) HRTEM image of the CNLDH-10 heterojunction.

Figure 5. XPS profiles of (a) N 1s, (b) C 1s, (c) Ni 2p, and (d) Al 2p of g-C$_3$N$_4$, NiAl-LDH and CNLDH-10 samples.

Figure 6. Time-dependent (a) CO, (b) H$_2$, and (c) O$_2$ amounts generated over all the synthesized photocatalysts (Conditions: 50 mg catalyst and 300 W Xenon lamp with a UV cut-off filter ($\lambda \geq$ 420 nm)). (d) An action spectrum of AQY on account of CO production by CNLDH-10 photocatalyst (blue plot), along with DRS of CNLDH-10 (green curve).

Figure 7. Reusability studies of CO evolution over CNLDH-10 heterojunction.

Figure 8. (a**)** PL spectra and (b) transient photocurrent responses of g-C$_3$N$_4$, NiAl-LDH, and g-C$_3$N$_4$/NiAl-LDH heterojunction photocatalysts.

Figure 9. Valence band XP spectra of g-C$_3$N$_4$ and NiAl-LDH samples.

Figure 10. Schematic illustration of the proposed mechanism for CO$_2$ photoreduction in the g-C$_3$N$_4$/NiAl-LDH heterojunctions.

Figures

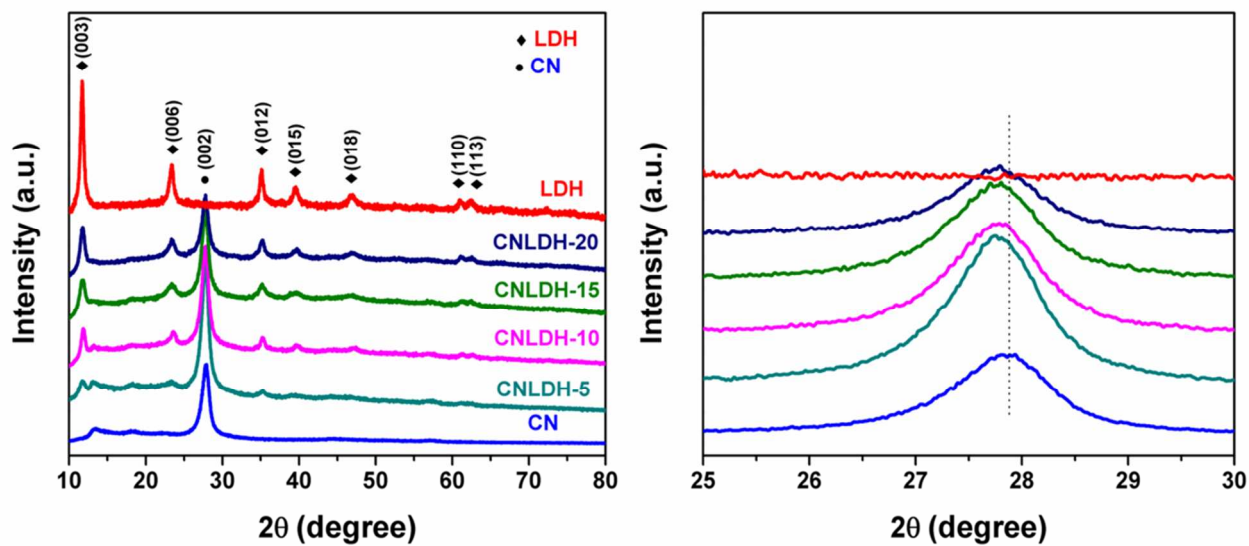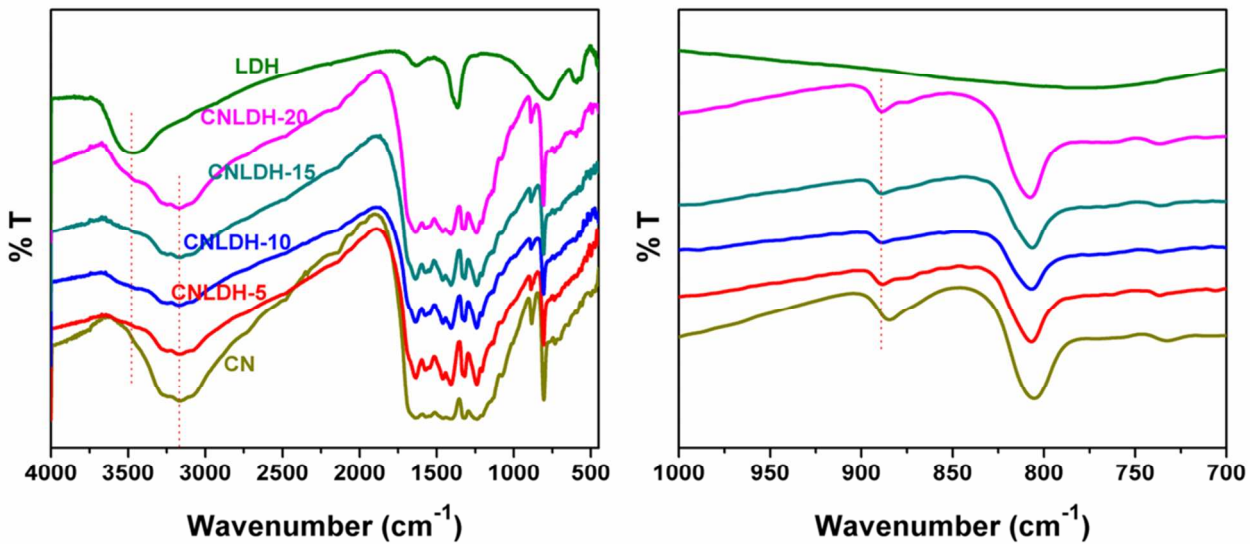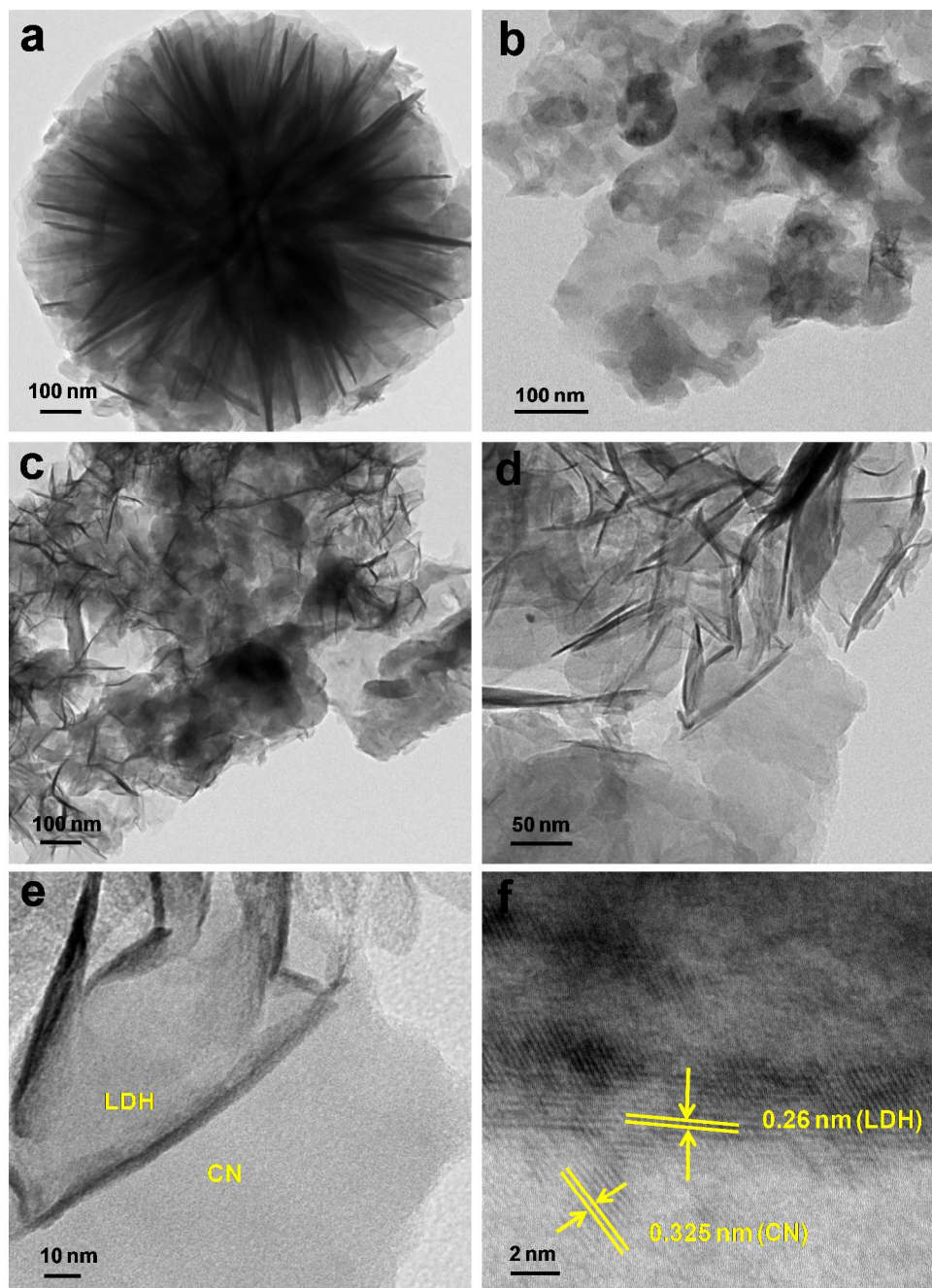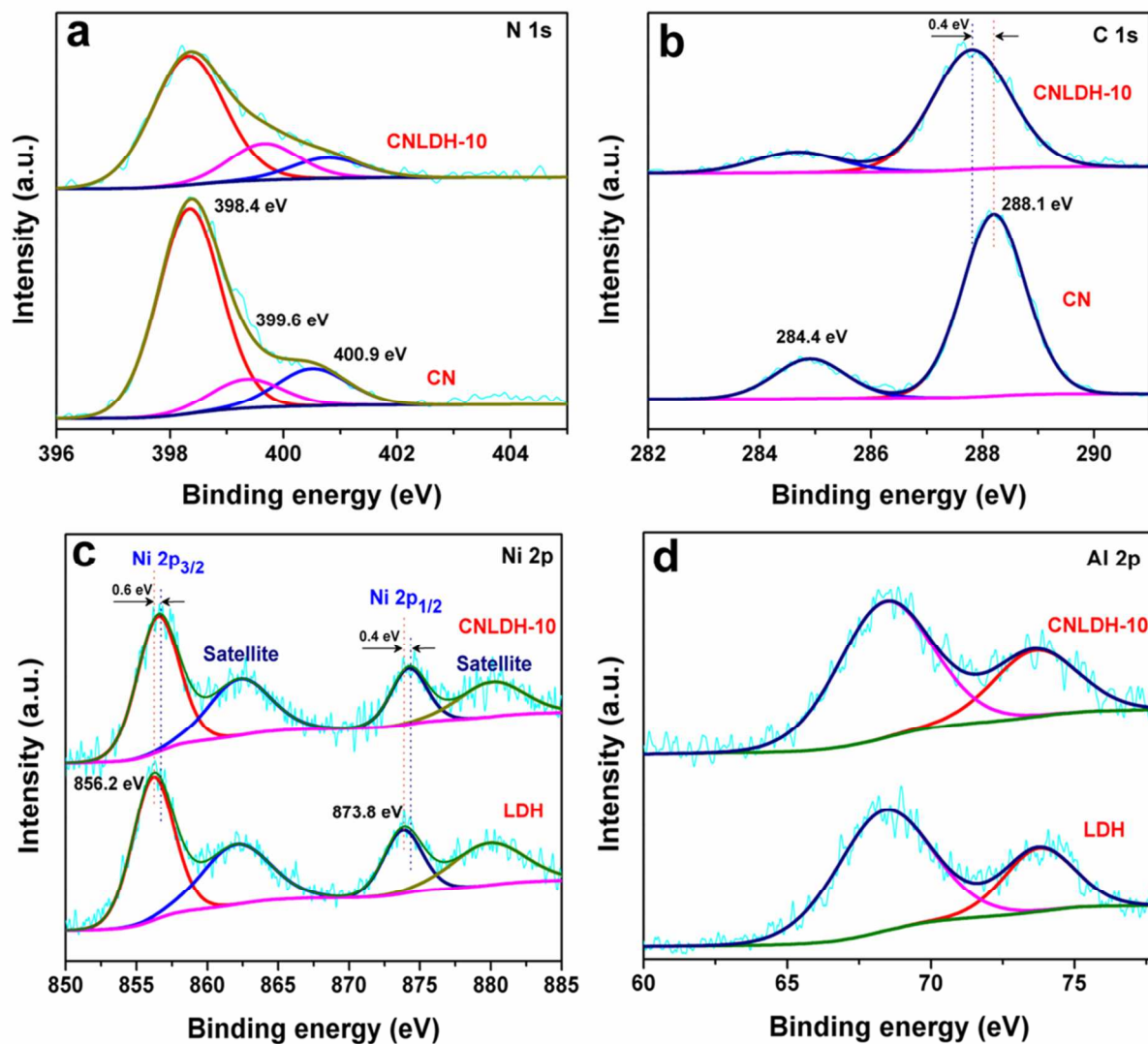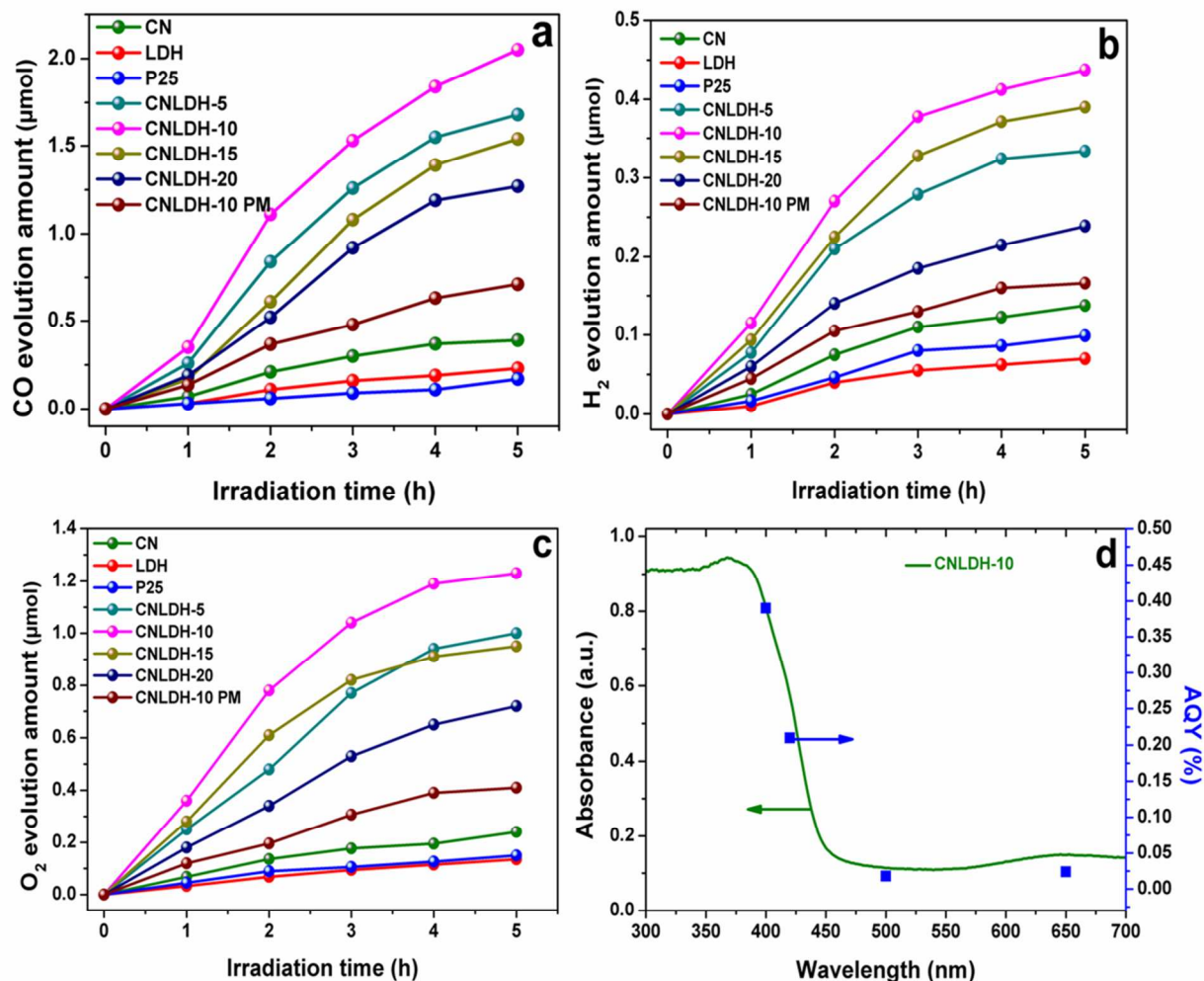**Scheme 1.** Schematic illustration of the synthesis process of g-C$_3$N$_4$/NiAl-LDH hybrid heterojunctions.

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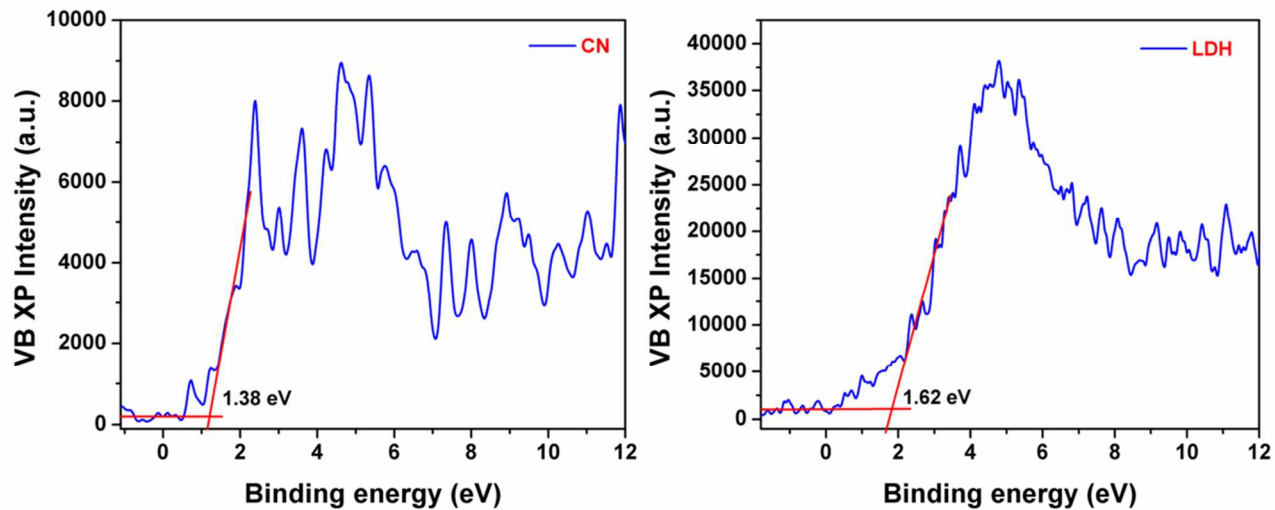
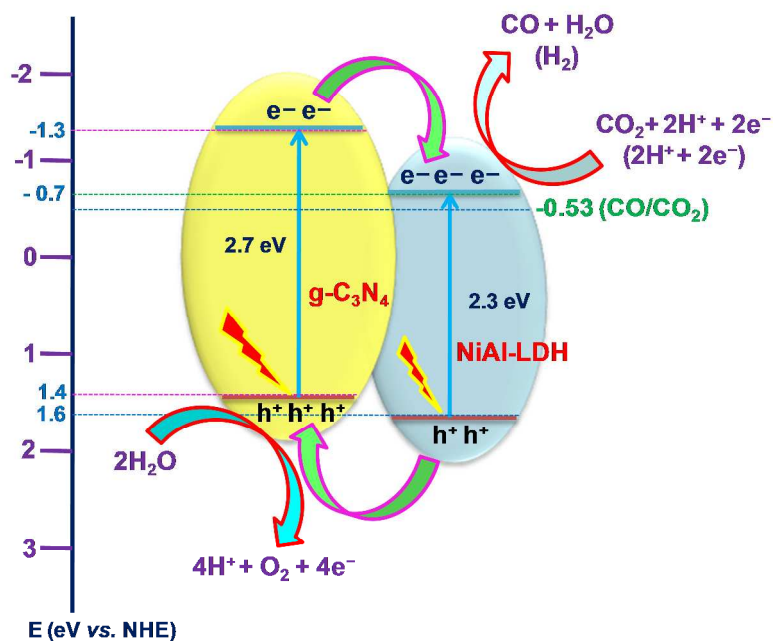**Figure 9.** Valence band XP spectra of g-C$_3$N$_4$ and NiAl-LDH samples.

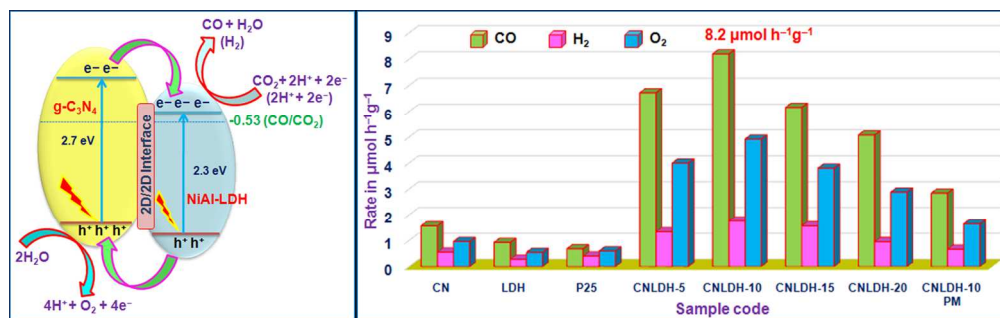**Figure 10.** Schematic illustration of the proposed mechanism for CO_2 photoreduction in the g-C_3N_4/NiAl-LDH heterojunctions.

322x100mm (300 x 300 DPI)