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Article

Improved charge transfer by size-dependent plasmonic Au on C₃N₄ for efficient photocatalytic oxidation of RhB and CO₂ reduction

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ABSTRACT

A series of Au/g-C₃N₄ (Au/CN) nanocomposites were successfully prepared, where g-C₃N₄ nanosheets (CN NSs) served as a substrate for the growth of different sized Au nanoparticles (Au NPs) using the constant temperature bath-reduction method. The effect of Au NP size on electron transfer efficiency between the interfaces of the nanocomposite was studied. The three-dimensional finite-difference time-domain results revealed that larger Au NPs showed increased strength of the localized surface plasmon resonance effect. An increased number of high-energy electrons were available for transfer from Au NPs to CN under the visible light irradiation, inhibiting electron transfer from CN to Au NPs. Photoelectrochemical performance analysis showed that smaller Au NPs exhibited higher separation efficiency of the electron-hole pairs photo-generated with reasonable distribution density. These results are favorable for the improvement of photocatalytic performance. Compared to other nanocomposites, the 3-Au/CN sample (prepared using 3 mL HAuCl₄ solution) with reasonable distribution density and small Au NPs exhibited the best photodegradation activity (92.66%) of RhB in 30 min under the visible light irradiation and photoreduction performance of CO₂ to CO and CH₄ with yields of 77.5 and 38.5 μmol/g, respectively, in 8 h under UV light irradiation. Considering the experimental results in the context of the literature, a corresponding size-dependent photocatalytic mechanism was proposed.

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1. Introduction

Photocatalysis has been applied for environmental contaminant treatment and energy conversion and has attracted significant attention in recent several decades [1–4]. The discovery of the photocatalytic process using semiconductors under solar irradiation in 1972 opened up a promising method for

water pollution treatment [5]. After decades of scientific research, the technology for photocatalytic degradation of water pollutants has flourished. Zhang et al. [6] reported a P25-graphene photocatalyst synthesized using the water bath reduction method, which exhibited excellent photodegradation performance of methylene blue under the UV light irradiation. In addition, Jiang et al. [7] reported that the boron nitride mod-

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ified graphene-phase nitride exhibited good degradation performance for tetracycline under the visible light irradiation. Khalil et al. [8] showed that the environmental pollutant Cr(VI) in water could be photoreduced using a semiconductor as a photocatalyst. The photocatalytic technique has shown good performance for organic dye degradation, antibiotic degradation, and heavy metal ion reduction.

Similarly, a number of recent studies have shown that the photocatalytic reduction of carbon dioxide (CO₂) is a promising solution for the reducing CO₂ in the atmosphere forming hydrocarbon fuel to alleviate the energy shortage [9–14]. Pan et al. [15] prepared indium-oxide (In₂O₃) nanobelts coated with carbon for photoreducing CO₂ to CO (126.6 μmol/h) and CH₄ (27.9 μmol/h) under Xe-lamp irradiation. Jiang et al. [16] prepared α-Fe₂O₃/g-C₃N₄ heterojunctions that provided a superior photoreduction of CO₂ to CO with a CO yield of 27.2 μmol/(g·h), which was >2.2 times higher than that of g-C₃N₄ (10.3 μmol/(g·h)). The development of photocatalytic techniques has mainly focused on the evolution and innovation of photocatalysts. The analysis and construction of a good photocatalyst are crucial for photocatalytic performance. Therefore, it is necessary to fabricate clean and efficient photocatalysts. Generally, the main factors affecting photocatalytic activity of semiconductor materials include their band gap [17], optical absorption range [18], adsorption performance [19], and oxidation-reduction potential [20].

g-C₃N₄ (CN) has attracted significant attention and been widely researched in the field of photocatalysis due to its suitable band gap (2.7 eV), easy synthesis, non-toxicity, low cost, non-metallic semiconductor properties, and favorable chemical stability [21–27]. In particular, the conduction band (CB) edge of CN is –1.13 eV vs. NHE, which is sufficiently negative to provide strong redox reaction ability [20]. Therefore, CN is an ideal catalyst for pollutant degradation and CO₂ reduction. Various morphologies of CN photocatalysts have been reported, including CN microrods [28], CN quantum dots [29], and CN nanosheets [21]. Of these CN catalysts, two-dimensional g-C₃N₄ nanosheets (2D CN NSs) have attracted significant interest because of their large specific surface area, strong adsorption ability, and unique photoelectric properties [30]. However, the practical applications of pure CN for photocatalysis are severely limited by its poor photoelectron transport performance and high photogenerated charge recombination rate. Thus, improving the separation efficiency of photogenerated carriers of CN is essential. CN complexation with other materials is an effective method to solve the above problems, and compounds such as metal oxide/CN [31], metal sulfide/CN [32], carbon material/CN [33], and noble metal/CN [34] have been developed.

Noble metal nanoparticles (M NPs), such as Au NPs or Ag NPs, are suitable for preparing heterogeneous catalysts due to their extraordinary electrical conductivity and localized surface plasmon resonance (LSPR), playing important roles as both electron acceptor and photosensitizer in photocatalytic systems [34–38]. Wang et al. [39] prepared a Fe₃O₄@SiO₂@ZnO-Au photocatalyst with great photodegradation performance owing to the presence of Au and the large

specific surface area that improved the separation efficiency of photo-generated carriers and overall photocatalytic performance. Because of the LSPR effect, M NPs on wide band gap semiconductor surfaces are useful for broadening their visible light absorption and enhancing the separation efficiency of photo-generated carriers by the nanocomposite catalyst. Hayashido et al. [40] reported the preparation of Ag/AgBr/TiO₂ and showed that the enhanced photocatalytic ability of this catalyst was caused by the enhancement of the local electric field. Wang et al. [41] reported that the plasmonic excitation of Au nanoparticles on the surface of ZnO catalysts resulted in significant heating, accelerating the conversion rate of CO₂ and H₂ reactants to form CO and CH₄. Nevertheless, the LSPR effect is quite complicated due to the additional effects that occur simultaneously. In addition to the enhancement effect of the local electric field and localized heating mentioned above, the LSPR sensitization effect has a significant impact on the photocatalytic process [34]. When the M NPs are excited by photons of a certain energy, the electrons in the excited state can be injected from the surface of the M NPs to the CB of the semiconductor. This process affects the electron transmission process in the composite [40,41]. It is well known that the LSPR effect of the M NPs depends on the particle size. With increasing size of the M NPs, the induced electric field around the NPs significantly increases. Moreover, the surface effect of the particles is another important factor affecting photocatalytic performance, especially for M NPs [40,41].

Based on their extraordinary electrical conductivity, LSPR effect, superior corrosion resistance, and chemical stability, Au NPs were selected as electron acceptors contacted with 2-D CN NSs to form an Au/CN nanocomposite photocatalyst [42]. The effect of Au NP size on interfacial electron transport and the photocatalytic properties of the related composite materials was studied. Although many recent reports of the Au/CN heterojunction have been published, the effect of Au NPs with different sizes in the composite system on the photodegradation performance and CO₂ photoreduction ability is rarely mentioned along with the related size-dependent photocatalytic mechanisms.

2. Experimental

2.1. Preparation of the samples

2.1.1. Preparation of the CN NSs

All chemical reagents used herein were analytically pure and applied without further treatment. Fig. 1 shows the typical preparation of CN NSs. First, 10 g of urea as a raw material was placed into an aluminum oxide crucible, sealed with tin foil, and calcined at 550 °C for 4 h in air (5 °C/min). Subsequently, the as-prepared sample was magnetically stirred in an HNO₃ aqueous solution (pH = 1) at 80 °C for 8 h. Next, the obtained sample was washed with deionized water and ethanol several times until a neutral pH was obtained. Afterwards, the as-prepared samples were calcined in air for the second time at 500 °C for 2 h (5 °C/min). Finally, the color of the sample changed from yellow to light yellow or even white, indicating

Fig. 1. The synthesis process of the as-prepared samples.

that few-layer 2D CN NSs were obtained.

2.1.2. Preparation of the Au/CN NSs

The Au/CN NSs nanocomposites were prepared via constant temperature bath-reduction with the CN NSs as a substrate. For this process, 0.1 g of the as-prepared CN NSs in 50 mL of deionized water was transferred to an ultrasonic bath for 30 min to separate the nanosheets. Subsequently, 1, 3, 5, or 10 mL of HAuCl₄ aqueous solution (0.025 mol/L) was dropped into the CN NSs turbid liquid at 80 °C. After 0.5 h, 10 mL of KBH₄ (0.1 mol/L) aqueous solution was added to the mixture, and the system was maintained under the same experimental conditions for 2 h. Finally, the nanocomposites were obtained through repeated washing with deionized water and ethanol and drying under vacuum conditions. For simplicity, the as-prepared Au/CN NSs nanocomposites are referred to as 1-Au/CN, 3-Au/CN, 5-Au/CN, and 10-Au/CN according to the different contents of HAuCl₄ used in the preparation process. For detailed characterization and photocatalytic testing methods, please refer to the Supporting Information.

2.2. Photocatalysis

2.2.1. Photodegradation

The photocatalytic performance of the as-prepared samples was studied via photodegradation of a rhodamine B (RhB) aqueous solution under visible light irradiation. The source of the visible light was provided by a Xe lamp (CEL-HXUV300 300 W) purchased from Beijing Zhongjiao Jinyuan Technology Co., Ltd. The intensity of the Xe lamp was 5 W/cm² with a 420 nm cutoff filter. For each photocatalytic process, 30 mg of the photocatalyst was added to the reactor with 100 mL of RhB aqueous solution (7 mg/L). Prior to irradiation, the system was mechanically stirred for 30 min in the dark to allow for adsorption-desorption equilibrium to be reached between the photocatalyst and RhB molecules. Before and after fixed irradiation intervals, the absorbance of RhB was measured using a UV-vis spectrophotometer (UV-5800PC, Shanghai Metash Instruments Co., Ltd). The control photodegradation experiment was performed without addition of the catalyst for comparison under the same conditions.

2.2.2. CO₂ photoreduction

The CO₂ photoreduction ability of the as-prepared samples was evaluated using a closed photochemical reactor (300 mL volume) under irradiation by an 8 W Hg lamp. In this process, 30 mg of the photocatalyst was added to the photochemical reactor containing 100 mL of a NaOH (0.1 mol/L) solution and

a certain amount of triethanolamine (TEOA). CO₂ (99.999%) gas was bubbled into the suspension for 30 min to remove gaseous impurities. Subsequently, the system was maintained at 1.4×10^5 Pa and the gas products were detected via gas chromatography (GC-7920, China, FID-II detector) every 2 h. The specific structure of the photocatalytic CO₂ reduction system is shown in Fig. S1.

3. Results and discussion

3.1. Analysis of crystal structure

The XRD patterns of the as-prepared samples are shown in Fig. 2. Two distinct peaks were observed at 13.1° and 27.2° for all photocatalysts, corresponding to the peaks of CN (JCPDS 87-1526) as in previous reports [30,42]. The diffraction peaks at approximately 38.2° and 44.4° in the patterns of (1, 3, 5, and 10) Au-CN were attributed to the (1 1 1) and (2 0 0) diffraction faces of the Au species [40,45], respectively. It is clear that the intensities of the two diffractive peaks increase with increasing gold content. In addition, no impurity-related peaks were detected, indicating that the prepared catalyst was a complex of Au and CN.

3.2. Microstructure and elemental distribution

TEM was used to study the micro-morphologies of the as-prepared samples. As shown in Fig. S2a, the bulk $g\text{-C}_3\text{N}_4$ (BCN) was thick and lacked a regular morphological structure. After acid treatment and secondary calcination, few-layer 2D-CN NSs were obtained (Fig. S2b). With increasing addition of the HAuCl₄ aqueous solution, as shown in Fig. S2c–f, the sizes

Fig. 2. XRD patterns of the as-prepared samples.

of the Au NPs in the nanocomposites increased and the distribution density of the Au NPs in the nanocomposites increased. Fig. S3a and S3b show typical atomic force microscopy (AFM) images of the CN NSs and corresponding thickness profile corresponding to the red line in (a). The thickness of the pure CN NSs was approximately 3.3 nm. Fig. 3a–3d show the high-magnification TEM images of the four prepared samples. With increasing volume of the HAuCl₄ aqueous solution, the Au NP size gradually grew. The distribution density of the Au NPs in 3-Au/CN increased significantly compared with that of the 1-Au/CN sample. However, this phenomenon was not significant for the other samples in the nanocomposite material system. The size distributions of the Au NPs in the samples were statistically analyzed by analyzing 100 nanoparticles from each sample under low and high magnification. The particle sizes of the samples were mainly concentrated in the following range, as shown in Fig. 3a1–3d1 (size distribution histogram): 73% 2–4 nm (1-Au/CN), 56% 4–6 nm (3-Au/CN), 34% 6–8 nm, 37% 8–10 nm (5-Au/CN), and 38% 10–12 nm (10-Au/CN). In this system, the distribution density of the Au NPs on the sample surfaces increased with the amount of Au added. When the amount of HAuCl₄ aqueous solution added was 5 mL, the Au NPs began to agglomerate. When the volume of added HAuCl₄ solution was 10 mL, the agglomeration of the Au NPs was most significant and the largest Au particles were observed at approximately 15–20 nm. The high Au ion concentration allows the gold nanoparticles to stack and bond together. Fig. 3b3–3b5 show the EELS elemental mapping images of N, C, and Au for the 3-Au/CN sample, indicating that the distributions of N and

C were uniform. The distribution of Au was similar to that of the Au NPs in Fig. 3b2. The insert of Fig. 3b2 shows the HRTEM of 3-Au/CN, with the distance between adjacent lattice facets of 0.235 nm, consistent with the (111) plane of Au [46]. This observation indicates that the surface of CN was successfully coated with Au NPs.

3.3. XPS analysis and FT-IR spectroscopy

Fig. 4a shows the XPS data of the prepared CN NSs and 3Au-CN nanocomposite. It is clear that the XPS patterns were almost identical, except that the peaks of Au appear in the 3-Au/CN spectrum. In Fig. 4b, the binding energy of C 1s could be divided into three peaks at energies of 283.1 eV (C–C), 283.8 eV (C–O), and 286.4 eV (N–C=N) [47]. The spectrum of N 1s shown in Fig. 4c can be divided into four peaks located at 397.1 eV (N–H), 398.3 eV (N–(C)₃), 399.4 eV (C–N=C), and 402.6 eV (π -excitations) [48]. Two characteristic peaks at 82.2 and 86.2 eV were observed in Fig. 4d, originating from Au 4f_{5/2} and Au 4f_{7/2}, respectively [9,46,48]. The O 1s peak at approximately 530.3 eV in Fig. 4e was attributed to the absorbed CO₂ or H₂O and other oxygen-containing intermediates produced via pyrolysis of urea. The above results indicate that the Au NPs were successfully loaded onto the CN NSs, which is consistent with the XRD and TEM analyses [4,40].

The bonding structures of the as-prepared samples were characterized by FT-IR. As shown in Fig. S4, a clear characteristic peak located at approximately 810 cm^{−1} was observed in each sample, which could be attributed to the characteristic

Fig. 3. (a–d) TEM images; (a1–d1) Size distribution histograms of 1-Au/CN, 3-Au/CN, 5-Au/CN, and 10-Au/CN, respectively; (b2) Select area of 3-Au/CN, HRTEM images inset; (b3–b5) EELS elemental mapping images of 3-Au/CN.

Fig. 4. Typical XPS spectra of CN NSs and 3-Au/CN. (a) Whole-range spectrum of these samples; (b)–(f) Contents of the sample.

breathing mode of the tri-s-triazine units. In addition, the chemical band at 1200–1640 cm^{-1} was attributed to the skeletal vibrations of aromatic CN heterocycles and no other characteristic peaks were observed. These results confirm the presence of CN in the as-prepared nanocomposite samples [26].

3.4. UV-vis diffuse reflectance spectroscopy and photoluminescence analysis

The optical absorption properties of the as-prepared samples were studied by UV-vis DRS. The spectra in Fig. 5 show an absorption edge of pure CN NSs at approximately 450 nm, which corresponds to the typical CN absorption peaks reported in the literature [49]. The light absorption intensity of the samples from CN NSs to 10-Au/CN was greatly improved with increasing gold content in the visible light region. Significant absorption bands at approximately 540 nm originated from the LSPR effect, as observed in a previous report [50]. The inset in Fig. 5 shows that the band gaps (E_g) of the prepared samples decreased with increasing the size and amount of Au NPs. The E_g was calculated using plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$. The α , h , and

ν terms mentioned above are the absorption coefficient, Planck's constant, and incident light frequency, respectively. The E_g of pure CN is approximately 2.82 eV and the band gaps of the as-prepared nanocomposite samples were 2.78, 2.76, 2.74, and 2.73 eV. In general, decreased band gap in the semiconductor materials improves photocatalytic performance

Fig. 5. UV-vis DRS of the prepared samples.

[51].

The photoluminescence (PL) emission spectra of the as-prepared samples were measured and the results are shown Fig. S5. The PL emission of each composite sample was lower than that of pure CN, indicating that the loading of Au NPs in the composites was beneficial for the separation of photo-generated electron-hole pairs and inhibited their recombination [49]. The inset in Fig. S5 shows the macroscopic images of all as-prepared samples. It is clear that the sample color changes from light yellow to dark purple with increasing Au NP size and loading.

3.5. Analysis of electric field intensity

The three-dimensional finite-difference time-domain (FDTD) method with perfectly matched layer boundary conditions was applied to further study the relationship between the strength of the LSPR effect and Au NP size in the nanocomposite system. The corresponding FDTD simulation diagrams of the different nanocomposites are shown in Fig. 6. In the FDTD computational domain, the mesh size was set to 0.2 nm. According to the size distribution histogram in Fig. 3, the Au NP sizes on each nanocomposite sample were 3, 5, 8, and 12 nm, respectively. In each FDTD simulation, the induced electric fields near the Au NPs were calculated under plane-wave source irradiation. The local field enhancement around the Au NPs was indicated by the electric field intensity of each sample, and the relative enhancement of the electric field intensity is represented by colors with different depths. As the Au NP size increased from 3 to 12 nm, the local electric field around the Au NP gradually increased, indicating that the LSPR effect was

gradually enhanced and an increasing amount of electrons with high energy were generated [40].

3.6. Photoelectrochemical performance

The photoelectrochemical (PEC) performance of catalysts is important in the study of photocatalytic process [41,52]. Thus, electrochemical impedance spectroscopy (EIS) and photocurrent response measurements were used to investigate the performance of the as-prepared samples. Fig. 7a clearly shows that the arc radii of all nanocomposites were smaller than that of pure CN, indicating that the Au NP loading is effective for reducing the impedance during electron transmission and increasing the rate of photogenerated electron transfer between material interfaces [9]. The arc radius of 3-Au/CN was the smallest of all samples, and it is well known that impedance in the process of photo-generated charge transfer is correlated with the semicircle in the high frequency region. A small semicircle radius indicates a smaller impedance in the process [52]. Therefore, the results show that the impedance of 3-Au/CN was the smallest of all samples, which is beneficial for the separation and transmission of photo-generated charges on the Au NP and CN surfaces. The impedances of the samples increase in the order 3-Au/CN < 5-Au/CN < 1-Au/CN < 10-Au/CN < CN NSs.

To further investigate the generation and transfer performance of photogenerated carriers, the transient photocurrent responses of the samples were measured during light on-off cycles under visible light irradiation, and the curves of photocurrent as a function of time are shown in Fig. 7b. The photocurrent sharply increased and saturated under light irradiation

Fig. 6. Simulation of the electric field intensity under a plane-wave source incident on 3-Au/CN in the x-y plane. The Au NP sizes acquired by TEM measurements (3, 5, 8, and 12 nm) were used for the simulations.

Fig. 7. (a) EIS and (b) photocurrent responses of the as-prepared samples.

(the “on” state). The photocurrent immediately dropped to the initial value when the light was switched off. This was caused by the transmission of the electrons photogenerated when the photogenerated holes are caught by hole acceptors in the electrolyte [53]. The photocurrent density of each nanocomposite was higher than that of pure CN, which is likely due to the excellent electrical conductivity of the Au NPs. The photocurrent density of 3-Au/CN was approximately 3.5 times higher than that of pure CN. The photocurrent density of the as-prepared samples decreased in the order 3-Au/CN > 5-Au/CN > 1-Au/CN > 10-Au/CN > CN NSs, which is similar to the EIS results. This phenomenon was attributed to the reasonable contact area between the Au NPs and CN and the effective separation of the photogenerated electron-hole pairs on the interface area caused by the electron acceptor Au NPs [39,44,54,55]. Inter-

estingly, except for 1-Au/CN with a low distribution density, both EIS and photocurrent changed regularly with Au NP size.

3.7. Photocatalytic analysis

3.7.1. Photodegradation and stability

The photodegradation activities of the as-prepared samples were measured using the photocatalytic process of RhB aqueous solution under visible light illumination. The broken line graphs of photodegradation activities as a function of light exposure time of each sample are shown in Fig. 8a. The control experiment was performed under the same conditions. The photodegradation rate of the photocatalyst was defined as $(1 - C_t/C_0)$, where C_t and C_0 represent the residual and initial concentrations of RhB, respectively. After 30 min, the photodegra-

Fig. 8. (a) Degradation efficiency of RhB; (b) $-\ln(C_t/C_0)$ versus irradiation time for the prepared photocatalysts; (c) Time-dependent absorption spectra of the RhB aqueous solution in the presence of 3-Au/CN; (d) Recycling experiments for the degradation of RhB using the 3-Au/CN photocatalyst.

degradation efficiency of each experiment was 12.2%, 52.93%, 83.21%, 92.66%, 85.59%, and 69.38% for the blank, CN, 1-Au/CN, 3-Au/CN, 5-Au/CN, and 10-Au/CN, respectively. These results indicate that the photodegradation efficiency of 3-Au/CN was optimal. As shown in Fig. 8b, the first-order rate constant of the photocatalytic reaction, $K = -\ln(C_t/C_0)$, was used to evaluate the photodegradation efficiency of the sample. Here, K is the apparent first-order rate constant, and C_t and C_0 are the same as defined above [56,57]. The value of K for 3-Au/CN was 0.0792 min^{-1} for the photodegradation of RhB aqueous solution after 30 min, which was the highest rate constant of all prepared samples. The reaction rate was improved by approximately 300% compared to that of the CN NSs (0.0257 min^{-1}). The photocatalytic performance of 3-Au/CN as a function of irradiation time is shown in Fig. 8c. The typical absorption peak at approximately 520–555 nm decreased rapidly when the light was on and disappeared completely after 30 min. Photodegradation stability is another important indicator to measure catalyst performance. Thus, cyclic photodegradation experiments were performed for 4 cycles. Fig. 8d shows that the photodegradation efficiency of 3-Au/CN was largely unchanged after the 4 cyclic experiments, confirming that this sample exhibited great catalytic stability.

3.7.2. ESR behavior of 3-Au/CN active species analysis

As previous reports have discussed [4,49,58], the free radical content ($\cdot\text{O}_2^-$ and $\cdot\text{OH}$) during photodegradation is important to estimate photocatalytic activity. These active species significantly impact the photodegradation process. Based on the above analyses, ESR was used to further characterize the $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radical contents in the 3-Au/CN photocatalytic process under visible light irradiation, and the related results are shown in Fig. 9. For comparison, the same experiment was performed using the pure CN. No peaks were observed in Fig. 9a or 9b before the light was turned on. Upon light irradiation, the characteristic peaks of DMPO- $\cdot\text{O}_2^-$ quickly appeared in the spectra of both 3-Au/CN and CN NSs (Fig. 9a). This indicates that the photogenerated electrons reacted with oxygen to form $\cdot\text{O}_2^-$ radicals during the photodegradation process [17,39]. In addition, DMPO- $\cdot\text{OH}$ radical detection of these samples was confirmed (Fig. 9b). However, the VB positions (E_{VB}) of CN and 3-Au/CN are 1.52 and 1.60 eV, respectively, as calculated from

the XPS analysis (Fig. S6). These values are too negative to oxidize H_2O to $\cdot\text{OH}$ (+2.4 eV, vs. NHE, pH = 7) or $-\text{OH}$ to $\cdot\text{OH}$ (+2.7 eV, vs. NHE, pH = 7) [49,53]. Thus, $\cdot\text{OH}$ radicals must be obtained by the further reaction of $\cdot\text{O}_2^-$ radicals with photogenerated electrons and H^+ , which originate from the ionization of H_2O and dye molecules [53]. After loading the Au NPs, the peak intensities of these two free radicals were significantly enhanced. This directly explains why the photodegradation performance of 3-Au/CN was better than that of pure CN.

3.7.3. Photoreduction of CO_2

The yields of CO and CH_4 over the 2D Au/CN nanocomposite catalysts under UV irradiation for 8 h are shown in Fig. 10a and 10b, respectively. The CO and CH_4 yields with each composite catalyst are higher than that of the CN catalyst, indicating that the Au NPs on the surface of the 2D-CN NSs significantly affected the conversion of CO and CH_4 [59]. When the 3-Au/CN sample with uniform distribution density of Au NPs was used as the catalyst, the yield of CO reached a maximum of $77.5 \text{ } \mu\text{mol/g}$, which is approximately 6 times greater than that of pure CN ($13.0 \text{ } \mu\text{mol/g}$). The yield of CH_4 ($38.5 \text{ } \mu\text{mol/g}$) was also the largest of 3-Au/CN at nearly 10 times higher than that of pure CN ($4.1 \text{ } \mu\text{mol/g}$). After 8 h, the yields of CO and CH_4 for each catalyst were determined, as shown in Table 1.

These results indicate that the CO_2 photoreduction ability of 3-Au/CN was the best of all prepared samples and the photoreduction ability followed the order 3-Au/CN > 5-Au/CN > 1-Au/CN > 10-Au/CN > CN NSs. The photoreduction evolution rates of CO and CH_4 under UV irradiation were calculated to be 9.69 and $4.813 \text{ } \mu\text{mol}/(\text{g}\cdot\text{h})$, respectively. The electron utilization rates over the different catalysts were calculated as $R(\text{electron}) = 2r(\text{CO}) + 8r(\text{CH}_4)$ [60]. In this equation, $R(\text{electron})$ is the utilization rate of electrons, 2 and 8 are the number of electrons required for generating one CO and one CH_4 , respectively, and $r(\text{CO})$ and $r(\text{CH}_4)$ are the formation rates of CO and CH_4 in the photoreduction process of CO_2 , respectively. $R(\text{electron})$ of 3-Au/CN with the smallest Au NPs size was $57.83 \text{ } \mu\text{mol}/(\text{g}\cdot\text{h})$, which is largest of all prepared samples and approximately 8 times higher than that of pure CN ($7.36 \text{ } \mu\text{mol}/(\text{g}\cdot\text{h})$). It is clear that loading the appropriate amount of Au NPs with smaller size greatly improves the $R(\text{electron})$ of the CN. Except for 1-Au/CN with the lowest distribution densi-

Fig. 9. DMPO spin-trapping ESR spectra of CN NSs and 3-Au/CN in (a) aqueous dispersion and (b) methanol dispersion.

Fig. 10. (a) Time courses of the photocatalytic CO evolutions; (b) Time courses of the photocatalytic CH₄ evolutions; (c) rates of electron consumption over different catalysts; (d) Recycling experiments for the photoreduction of CO₂ with 3-Au/CN after 8 h under UV light irradiation.

ty, $R(\text{electron})$ decreased with increasing Au NP size. The electron utilization rates varied for the Au-CN catalysts, indicating that the Au NP size has important effects on the light energy utilization in the photoreduction of CO₂. With increasing Au NP size, the utilization of light energy increased [61]. Fig. 10d shows the results of the recycling experiments for the CO₂ photoreduction with 3-Au/CN. After 4 recycling experiments, no significant decrease in photocatalytic activity of 3-Au/CN was observed, indicating excellent photostability.

3.8. Photocatalytic mechanism analysis

According to the above investigation and literature analyses [62–64], possible photocatalytic mechanisms of the Au/CN nanocomposite for photodegradation and photoreduction are illustrated in Fig. 11. The position of the 3-Au/CN CB was -1.16 eV, as calculated by $E_{\text{VB}} - E_{\text{g}}$ [49]. More generally, the photoexcited CN NSs can generate holes and electrons in the VB and CB, respectively. For the Au/CN nanocomposite system, Au NPs serve as an electron acceptor to facilitate the transport and separation of electrons photogenerated between the interfaces of the composite materials. Simultaneously, high-energy electrons obtained by the LSPR effect could be transmitted back from the Au NPs to CN NSs across the barrier [44,65]. Based on

the trapping experiments in Fig. S7, the photocatalytic mechanism was proposed. The photogenerated electrons could react with the O₂ in the water to form $\cdot\text{O}_2^-$ and further react with photogenerated electrons and H⁺ to form $\cdot\text{OH}$ radicals. These radical can photo-degrade any organic molecules present in the solution with relatively high efficiency [48]. In addition, the holes photogenerated in the VB of CN can directly oxidize the organic molecules to form inorganic small molecules. For photoreduction, the photogenerated electrons can photoreduce CO₂ to CO and CH₄ through a well characterized process [15]. Meanwhile, TEOA acts as a sacrificial agent and electron donor source to inhibit electron-hole recombination on CN and provide more electrons to participate in photoreduction [66–69].

For photodegradation and photoreduction, it is essential to improve the separation, transmission efficiency, and concentration of photogenerated electrons. The results of the photocatalytic experiments show that 3-Au/CN exhibited the greatest photodegradation and CO₂ photoreduction abilities of all prepared catalysts and the reasons underlying this phenomenon are as follows.

It is well known that the work function is the minimum energy required to remove an electron from the Fermi level to the surface of the object. The work function of CN is $\Phi_{\text{CN}} = 4.3$ eV [70], significantly lower than that of Au ($\Phi_{\text{Au}} = 5.3$ eV) [71]. In Au/CN nanocomposites, the rectifying effect of Schottky contacts will be active at the interface between the Au NPs and CN. The Fermi level will shift to a more negative level until equilibrium is reached between Au and CN under light irradiation. The Fermi energy shifts to a more negative position for smaller NPs, leading to a decreased potential difference between the CB of CN and Fermi level of the Au NPs [64]. In our study, except for 1-Au/CN with a low distribution density of Au NPs, the Fermi level of the Au NPs in 3-Au/CN was closest to the CB position of

Table 1

The yields of CO and CH₄ (8 h) for each catalyst.

Photocatalyst	Yield of CO (μmol/g)	Yield of CH ₄ (μmol/g)
CN	13	4.1
1-Au/CN	32.6	9.7
3-Au/CN	77.5	38.5
5-Au/CN	50.9	25.2
10-Au/CN	28.6	6.1

Fig. 11. Proposed photocatalytic mechanism of the 3-Au/CN photocatalyst (a) for photodegradation under visible light irradiation and (b) for photoreduction of CO₂ under UV light irradiation.

CN and the surface area of Au NPs was the largest of all samples, which is beneficial for transfer of the photogenerated electrons from CN to the Au NPs [64]. Smaller Au NPs contain more unsaturated dangling bonds on their surfaces, which increase the activity by the surface effect and greatly improve the distribution density of defects and separation efficiency of photogenerated electron-hole pairs. These factors are beneficial for improved photo-degradability and are essential for CO₂ photoreduction [59,72]. The PEC results of the Au/CN nanocomposites were superior to those of pure CN, with 3-Au/CN exhibiting the highest photocurrent density and lowest charge transfer impedance of all prepared samples. This indicates that the electron separation and transmission efficiency were the highest at the interface between the Au NPs and CN in 3-Au/CN compared with the other samples. The variation of EIS and photocurrent results are consistent with the Au NP size on the surface of CN and the catalytic performance of the samples, which is also consistent with our literature analysis [42,44].

Furthermore, the LSPR sensitization effect of the Au NPs on the Au/CN nanocomposite surfaces is another important reason for the increased photodegradation efficiency with Au NP size [42,43,72]. With increasing Au NP size, the local electric field rapidly improved. High-energy electron transfer from the Au NPs to CN will also be facilitated. The space charge separation from CN to Au NPs at the interface of the Au/CN nanocomposite is inhibited by this electron transmission process, resulting in a gradually decreased photocatalytic activity. Therefore, 3-Au/CN with a minimum NP size and a reasonable distribution density was least affected by LSPR sensitization among all composite samples (except 1-Au/CN with a low distribution density). Therefore, the photodegradation ability of 3-Au/CN was the greatest of all samples under visible light irradiation. From the above analysis and discussion, it is clear that the Au NP size on the surface of CN significantly affects photocatalytic performance.

4. Conclusions

A series of Au/CN nanocomposites with different Au NP siz-

es were successfully prepared by changing precursor concentration. The photocatalytic performance of the prepared nanocomposites was enhanced by effective electronic interfacial transmission between the Au and CN in the catalyst. Smaller Au NPs reduced the distance between its Fermi level and that of the CN substrate, with an increased number of unsaturated dangling bonds on the surface. These factors are beneficial for the effective separation and transmission of photogenerated electrons at the interface between Au NPs and CN. With increasing Au NP size, high-energy electrons back transferred from Au NP to CB of CN became more frequent, inhibiting the separation of photogenerated electron-hole pairs in the CN NSs with gradually decreasing photodegradation activity. Thus, 3-Au/CN with a reasonable distribution density and the smallest NP size exhibited the best photodegradation and reduction abilities of all prepared samples. The 3-Au/CN sample exhibited the highest photodegradation activity of 92.66% after 30 min and great photocatalytic stability during the degradation of RhB under visible light irradiation. For photoreduction, the CO yield of 77.5 $\mu\text{mol/g}$ was approximately 6 times higher than that of pure CN (13.0 $\mu\text{mol/g}$) and the CH₄ yield of 38.5 $\mu\text{mol/g}$ was nearly 10 times higher than that of pure CN (4.1 $\mu\text{mol/g}$) under UV light irradiation for 8 h.

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Graphical Abstract

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Improved charge transfer by size-dependent plasmonic Au on C_3N_4 for efficient photocatalytic oxidation of RhB and CO_2 reduction

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The Au NP size on the surface of Au/CN was controlled to improve photogenerated charge transfer, and the photocatalytic performance of Au/CN could be improved for photodegradation and photoreduction.

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二维g-C₃N₄表面Au粒子尺寸调节的界面电子传输行为及光催化性能

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摘要: 目前, 环境污染与能源危机是直接影响着人类生存与发展的两大难题. 以半导体材料作为催化剂、太阳能作为驱动力的光催化技术由于具有成本低廉、清洁环保、反应条件温和等优点被认为是解决上述问题最具开发价值的理想方法, 并得到科研工作者的广泛研究与关注. 近几十年的研究表明, 该技术在有机污水处理及光催化还原CO₂转化成高能燃料领域均有良好表现. 本文采用高温热聚合及酸处理剥离技术, 以尿素作为原料, 成功制备出薄层二维g-C₃N₄(CN)纳米片材料, 并以该材料作为载体及催化主体, 通过恒温水浴还原技术在其表面负载不同尺寸的Au纳米粒子, 成功制备出一系列Au/CN复合光催化材料.

运用系统的表征及测试手段, 对所制备的二维光催化材料的晶相结构、化学组分、形貌和表面特征及光电化学特性进行了详细表征与研究, 并针对该二维材料表面Au纳米粒子的尺寸效应、表面效应和等离子体共振效应(LSPR)等特性研究了复合材料界面间电子的传输效率与迁移机制. 尺寸较小的Au纳米粒子的费米能级到CN导带底端的距离较短, 其表面原子比例及缺陷含量较高, 有利于Au纳米粒子对光生电子的捕获并抑制电子空穴对的复合. 由于LSPR效应, 可见光下Au表面可产生大量高能热电子并注入到CN表面, 从而抑制光生电子从CN导带到Au表面的传输. 三维时域有限差分法(FDTD)模拟结果显示, Au纳米颗粒的尺寸越大, 拥有的LSPR效应越强, 其表面热电子含量越高, 光电子传输抑制现象越强烈. 光电化学性能分析(PEC)结果显示, 在颗粒分布密度合理的情况下, 具有较小尺寸Au纳米颗粒的复合材料内部光生电子空穴对的分离效率越高.

光催化实验表明, 在Au纳米粒子分布合理的情况下, 拥有最小Au纳米颗粒尺寸的3-Au/CN样品表现出最好的光催化活性. 在可见光条件下照射30 min, 该样品对罗丹明B水溶液(RhB, 10 mg/L)的光降解效率高达92.66%; 紫外光条件下照射8 h, 该样品光催化还原CO₂转化成CO和CH₄的产率分别为77.5和38.5 μmol/g, 约是纯CN还原性能的6倍和10倍. 结合文献报道及上述实验结果, 我们提出了一个尺寸影响的光催化作用机制.

关键词: Au/g-C₃N₄; 纳米片; 尺寸影响; 光催化还原CO₂; 光催化剂

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