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Article

MgO and Au nanoparticle Co-modified g-C₃N₄ photocatalysts for enhanced photoreduction of CO₂ with H₂O

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ABSTRACT

The photoreduction of CO₂ to achieve high-value-added hydrocarbons under simulated sunlight irradiation is advantageous, but challenging. In this study, a series of MgO and Au nanoparticle-co-modified g-C₃N₄ photocatalysts were synthesized and subsequently applied for the photocatalytic reduction of CO₂ with H₂O under simulated solar irradiation. The best photocatalytic performance was demonstrated by the Au and 3% MgO-co-modified g-C₃N₄ photocatalysts with CO, CH₄, CH₃OH, and CH₃CHO yields of 423.9, 83.2, 47.2, and 130.4 μmol/g, respectively, in a 3-h reaction. We investigated the effects of MgO and Au as cocatalysts on photocatalytic behaviors, respectively. The characterizations and experimental results showed that the enhanced photocatalytic activity was due to the synergistic effect among the components of the ternary photocatalyst. The cocatalyst MgO can activate CO₂ (adsorbed at the interface between the MgO and Au particles), and the Mg-N bonds formed in the MgO-CN nanosheets played an important role in the charge transfer. Meanwhile, the Au particles that were modified into MgO/g-C₃N₄ can increase the absorption of visible light via the surface plasmon resonance effect and further reduce the activation energies of the photoreduction of CO₂ using H₂O. This study provided an effective method for the modification of traditional primary photocatalysts with promising performance for photocatalytic CO₂ reduction.

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1. Introduction

Carbon dioxide (CO₂), which is a greenhouse gas that isproduced due to the excessive combustion of fossil fuels, has led to global energy and environmental crises [1–3]. The photocatalytic CO₂ conversion has been considered as a promising

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technology that utilizes solar energy to generate CO, CH₄, CH₃OH, and other high value-added hydrocarbons under mild conditions, such as low temperature and pressure [4–8].

This reaction relies on the development of an active and stable photocatalyst. Among various reported photocatalytic materials, graphitic carbon nitride (g-C₃N₄) is widely applied in the fields of photocatalytic hydrogen production, photoreduction of CO₂, and photodegradation of organic pollutions due to its inexpensiveness, low toxicity, high stability, and narrow band gap [9–11]. However, pure g-C₃N₄ is disadvantageous because of its low light utilization efficiency and high recombination rate of photogenerated electron-holes, resulting in relatively low photocatalytic activity [12–14]. Therefore, to improve the photocatalytic performance, researchers have attempted various methods for g-C₃N₄ modification, such as the doping of foreign elements [15–17], coupling with other compounds [18–22], loading noble metals [23–25], etc.

MgO is an alkaline metal oxide with strong CO₂ adsorption capacity, which can be used to modify semiconductors for the photocatalytic reduction of CO₂ [26–28]. Feng et al. [29] coated an ultrathin MgO overlayer on porous TiO₂ from a metal-organic framework, MIL-125, proving that MgO can significantly increase the surface Ti³⁺ and OH species, and thus contribute to the production of the CO₂ reduction intermediates. Liu et al. [26] adopted porous MgO-TiO₂ microspheres as the photocatalysts and studied the photocatalytic reduction of CO₂ with H₂O vapor for CO production. They found that the adsorption of CO₂ can be improved by incorporating MgO, and that the enhanced desorption of products and intermediates at a higher temperature could be achieved. However, g-C₃N₄ modified by MgO has not been reported for the photocatalytic reduction of CO₂.

On the other hand, co-catalysts, especially the noble metals, have been frequently employed not only to act as electron traps to improve the separation efficiency of photogenerated electron-hole pairs, but also to provide active sites for the reaction [30]. Different noble metals, such as Au, Ag, Pt, and Pd, have been adopted to promote the photocatalytic activity of bare g-C₃N₄ [23,31–33]. Li et al. [34] synthesized a series of Au/g-C₃N₄ nanocomposites using the constant-temperature bath-reduction method and further studied the effect of the Au nanoparticle size on the electron transfer efficiency at the interfaces of the nanocomposite.

Because both MgO and its cocatalyst have shown efficient enhancement in the CO₂ photoreduction, researchers have studied their co-effect by incorporating both of them on semiconductors such as TiO₂. Xie et al. [27] focused on the effects of cocatalysts on the photocatalytic behaviors of TiO₂ for the CO₂ photoreduction in the presence of H₂O. They demonstrated that the addition of MgO and Pt into the TiO₂ catalyst can enhance the selectivity of CH₄. Li et al. [35] revealed that the synergistic effect could be achieved by coupling Ag nanoparticles and MgO on the TiO₂ surface for the improvement of the CO₂ photoreduction in CH₄. Despite these successful demonstrations, limited studies have been conducted to investigate the photocatalytic property of the CO₂ reduction of the MgO and cocatalyst co-modified g-C₃N₄.

In this study, we prepared a series of MgO-modified g-C₃N₄ composites using the calcination method. The Au cocatalyst was then loaded to the composites using the NaBH₄-reduction method. The obtained photocatalysts were then evaluated for the photocatalytic CO₂ reduction in the presence of H₂O under simulated solar light irradiation. The photocatalytic activities of the ternary photocatalysts were found to be enhanced, which was attributed to the synergistic effect between MgO and Au on g-C₃N₄. To the best of our knowledge, this work is the first attempt in demonstrating the MgO and Au co-modification of g-C₃N₄ nanosheets and their synergistic effect on the photocatalytic reduction of CO₂. The results of this study can provide new insights for future technological applications.

2. Experimental

2.1. Materials

All chemicals used were of analytical grade and without further purification. Urea (CH₄N₂O, 99.9%), sodium hydroxide (NaOH), magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, 99.0%), chloroauric acid (HAuCl₄, 99.9%), and sodium borohydride (NaBH₄, 97.0%) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. Carbon dioxide (0.994% CO₂, 99.006% Ar; 99.99% ¹³CO₂) and nitrogen (N₂, 99.99%) were purchased from the Nanjing shangyuan industrial gas plant. H₂¹⁸O (99 atom% ¹⁸O) was purchased from 3A chemicals, Ailan (Shanghai) Chemical Technology Co., Ltd. Deionized water was used throughout the studies.

2.2. Preparation of g-C₃N₄ (CN) nanosheet

The pure CN nanosheet was prepared via a typical thermal-polymerization method, in which urea was applied as the precursor [36]. In detail, 12 g of urea was put into a covered porcelain crucible and sealed with a layer of silver paper. Subsequently, the well-sealed crucible was heated from room temperature to 500 °C with a heating rate of 5 °C/min in a muffle furnace. It was heated at 500 °C for 2 h and then cooled to room temperature. Finally, the resultant yellow biscuit was obtained and ground into powder for further use.

2.3. Preparation of MgO-CN heterojunction

A series of MgO-CN catalysts with different weight percentages of MgO ranging from 1%–10% were synthesized using the facile precipitation and calcination processes. First, 0.3 g of as-prepared CN was dispersed in 40 mL deionized water and sonicated for 10 min. Then, the desired amount of Mg(NO₃)₂·6H₂O was added into the suspension, and the mixture was further stirred for 1 h to ensure that Mg²⁺ was uniformly absorbed on the CN nanosheet. Next, a certain concentration of NaOH solution was slowly added into the above suspension before being stirred for 6 h. Subsequently, the uniform suspension was washed with deionized water for several times and dried at 60 °C overnight under a vacuum oven. Finally, the obtained solid was ground into powder and placed into a cov-

ered porcelain crucible followed by a calcination process at 400 °C for 2 h at a heating rate of 5 °C/min.

The as-prepared sample was denoted as x% MgO-CN, where x represents the weight percentage of MgO compared to that of CN.

2.4. Preparation of Au/MgO-CN photocatalyst

The Au/MgO-CN catalysts were prepared using the NaBH₄-reduction method, in which the HAuCl₄ solution was applied as the precursor [31]. 0.2 g of as-prepared MgO-CN catalysts was dispersed in 40 mL deionized water by sonicating for 15 min. Then, a certain amount of HAuCl₄ solution was added into the above suspension. After constant stirring for 30 min, a certain amount of NaBH₄ solution was quickly added into the mixture. The light-yellow suspension turned into dark purple immediately. Then, the mixture was stirred another 2 h. The obtained solid precipitation was repeatedly washed with deionized water and dried at 60 °C overnight in a vacuum. The nominal weight loadings of the Au in all samples were 1 wt%.

The Ag/MgO-CN, Pt/MgO-CN and Pd/MgO-CN catalysts were prepared followed by the above process; however, the corresponding metal precursor was used instead.

2.5. Characterization methods

The X-ray powder diffraction (XRD) patterns were recorded in ambient atmosphere using a Bruker D8-Discover diffractometer operating with Cu K α radiation ($\lambda = 0.1542$ nm) in the 2θ range from 5° to 80°. To observe the morphology and structure of the samples, scanning electron microscopy (SEM) micrographs were taken on an FEI Inspect F50 instrument with an operating voltage at 15 kV. Transmission electron microscopy (TEM) was performed on an FEI Tecnai G2 F20 with an acceleration voltage of 200 kV. Fourier transform infrared spectroscopy (FT-IR) was conducted on a Thermo Nicolet 5700 spectrometer using KBr pellets. The photoluminescence spectra (PL) were studied on a Horiba Fluoromax-4 fluorescence spectrometer at room temperature with an excitation wavelength of 350 nm. The time-resolved photoluminescence (TRPL) analysis was conducted on a FluoroLog 3-TCSPC spectrometer with an excitation wavelength of 350 nm. The nitrogen adsorption-desorption experiments were performed on a Micromeritics ASAP 2020 HD88 nitrogen adsorption apparatus. The multipoint Brunauer-Emmett-Teller (BET) method based on the adsorption data with relative pressure at 0.05–0.30 was applied to calculate the specific surface area. The ultraviolet visible diffused reflectance spectra (UV-vis DRS) were obtained using a Shimadzu UV-2600 in the wavelength range of 200–800 nm; BaSO₄ was used as the reflectance. The X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Thermo ESCALAB 250XI spectrometer with Al-K α as the radiative source to investigate the electronic structure of the surface elements. The C 1s peak at 284.6 eV was used as the reference to calibrate the binding energies of each element. In-situ diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS) measurements were performed to obtain

the intermediate adsorbed species using a Harrick Scientific HVCDRP reaction chamber equipped with a Praying Mantis DRIFTS accessory. The temperature-programmed desorption of carbon dioxide (CO₂-TPD) was performed with a heating rate of 10 °C/min from room temperature to 600 °C under Ar steam at a flow rate of 30 mL/min. The gas chromatography-mass spectrometer (GC-MS) analyses were performed on the GC 8860 and MS 5977B (Agilent Technologies).

2.6. CO₂ photoreduction experiment

The reaction of the CO₂ photoreduction with H₂O vapor was conducted in a 250-mL micro visual autoclave. The photoreactor was cylindrical and equipped with stainless steel walls. It had a quartz window of thickness 10 mm to allow the light from a Xe lamp operated at 300 W with an accumulated intensity of 84.2 mW/cm² to pass through. A fixed amount of powder catalyst (100 mg) was uniformly dispersed onto the 0.3 g quartz wool, which was inside the inner quartz liner. Before light irradiation, the reactor was purged with N₂ for 30 min to remove the residual air from the reactor. Then, the CO₂ gas was introduced into the reaction system until the pressure reached 1.0 MPa. After 1 mL of deionized water was injected, the reaction system was stirred for 1 h in the dark to establish an adsorption-desorption equilibrium. The photocatalytic activity was recorded after the Xe lamp was turned on.

The gaseous products in the reactor effluent were analyzed at a 30-min interval through a gas valve using an online gas chromatograph (GC-9860-5C) equipped with both a thermal conductivity detector (TCD) and flame ionization detector (FID). All the products were quantified using the external standard curves.

We performed the photocatalytic reduction of CO₂ experiment under the Xe lamp with bandpass filters of 365, 420, 475, and 578 nm. The values of AQE were calculated according to formula:

$$\text{AQE} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\ = \frac{[2 \times M(\text{CO}) + 8 \times M(\text{CH}_4) + 6 \times M(\text{CH}_3\text{OH}) + 10 \times M(\text{CH}_3\text{CHO})] \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where $M(\text{CO})$, $M(\text{CH}_4)$, $M(\text{CH}_3\text{OH})$, $M(\text{CH}_3\text{CHO})$, N_A , h , c , S , P , t , and λ are the quantity of produced CO (mol), quantity of produced CH₄ (mol), quantity of produced CH₃OH (mol), quantity of produced CH₃CHO (mol), Avogadro constant (mol⁻¹), Plank constant (J·s), speed of light (m·s⁻¹), irradiated area (cm⁻²), power of the light source (W·cm⁻²), time of irradiation (s), and wavelength of incident light (m), respectively.

2.7. Photoelectrochemical measurements

The transient photocurrent and electrochemical impedance were measured using a CHI760E electrochemical working station containing a conventional three-electrode system. The prepared samples served as the working electrodes with an active area of ca. 1 cm². A Pt and saturated calomel electrodes (SCE) were applied as the counter and reference electrodes, respectively. The working electrodes were prepared by coating the samples with indium doped tin oxide (ITO) and platinum

carbon electrode (PCE) substrates. Five mg of photocatalyst and 10 μL of Nafion solution (5 wt%) were dispersed in the 400 μL water and isopropanol mixed solvent under ultrasonication to form a homogeneous colloid. Then, the catalyst colloid was deposited on the ITO conductive glass and PCE before being dried in air to form the working electrodes. The measurements were conducted in 0.5 M Na_2SO_4 under the radiation from a 300 W Xe lamp equipped with a 420-nm cutoff filter. Electrochemical impedance spectroscopy (EIS) showed a frequency ranging from 0.1–100 kHz.

3. Results and discussion

3.1. Morphology and composition

The XRD patterns were measured to determine the crystal-line phase structures of the CN, MgO-CN, and Au/MgO-CN catalysts, respectively (Fig. 1). All the samples showed two characteristic diffraction peaks of typical $\text{g-C}_3\text{N}_4$ at $2\theta = 12.9^\circ$ and 27.4° . The peak at 12.9° was attributed to the in-plane structural packing motif of the tri-s-triazine units [37]. The strongest peak at 27.4° was attributed to the (002) peak corresponding to the average interlayer distance of $d = 0.326$ nm. This represented an interlayer stacking of the conjugated aromatic systems [38]. After the addition of the different MgO different proportions, the MgO-CN catalysts still retained the characteristic peak of CN. Moreover, when the content of MgO increased to more than 5%, the characteristic peak of MgO appeared. The characteristic peaks at 42.9° and 62.1° were attributed to the (200) and (220) crystal faces of MgO, respectively, indicating the successful formation of MgO on CN [39]. Compared to that of the MgO-CN catalyst, the Au/MgO-CN composite showed two additional peaks at 37.9° and 44.2° , which were attributed to the (111) and (200) planes of Au, respectively [40].

The SEM and TEM analyses were conducted to investigate the morphology of samples. As shown in Fig. 2(a), the bare CN displayed a typical lamellar structure of the graphitic carbon nitride. Fig. 2(b) shows that Au/3% MgO-CN possessed a similar structure with that of CN, indicating that the loading of MgO and Au would not affect the basic structure of CN. The TEM image of Au/3% MgO-CN is demonstrated in Fig. 2(c), it can be

Fig. 1. XRD patterns of CN, MgO-CN, and Au/MgO-CN. The different shapes indicate crystal surfaces of different materials.

Fig. 2. SEM images of CN (a) and Au/3% MgO-CN (b); TEM (c) and HRTEM (d) image of Au/3% MgO-CN; STEM image (e) and corresponding EDX mappings (f–j) of Au/3% MgO-CN, indicating the particular distributions of Au (f), C (g), Mg (h), N (i), and O (j); (k) EDX pattern of the Au/3% MgO-CN catalyst.

evidently observed that the Au nanoparticles were uniformly located at the CN nanosheet and MgO matrix. Further HRTEM observation (Fig. 2(d)) showed evident lattice fringes with interplanar distances of 0.210 and 0.235 nm, corresponding to the MgO (200) and Au (111) planes, respectively [41]. The results of the HRTEM analysis were also consistent with that of the previous XRD patterns. Moreover, the Au nanoparticles were observed to have been deposited on the surface of MgO. In addition, the STEM (Fig. 2(e)) and EDX analyses (Fig. 2(f)–(k)) of Au/3% MgO-CN were conducted to investigate the elemental distribution of Au/3% MgO-CN. The EDX mappings showed that all elements including C, N, O, Mg, and Au were uniformly distributed in the composite. These results indicated that Au and MgO were uniformly deposited on the CN nanosheet. We also compared the TEM images of the Au/CN and Au/MgO-CN samples in Fig. S1. There was no significant difference for the Au nanoparticles in both the Au/CN and Au/MgO-CN catalysts. The observation indicated that the addition of MgO had little effect on the morphology of the Au nanoparticles. As a result, it can be deduced that the different photocatalytic activity caused by MgO was due to other factors.

In addition, the FTIR spectroscopy (Fig. 3) was further conducted to investigate the chemical structure of the CN, MgO-CN, and Au/MgO-CN samples. All samples demonstrated similar FTIR spectra of the typical molecular skeletal vibration for pure $\text{g-C}_3\text{N}_4$ [42]. The sharp peak at approximately 810 cm^{-1} was

Fig. 3. FTIR of CN, x% MgO-CN, and Au/3% MgO-CN.

attributed to the typical breathing mode of the triazine unit. Several strong bands in the region from 1200 to 1650 cm^{-1} , with characteristic peaks at 1244, 1326, 1407, 1467, 1566, and 1640 cm^{-1} , were typical for the stretching vibrations of the aromatic N=C=N heterocycles in the “melon” framework. Among them, the characteristic absorption peaks at 1244 and 1326 cm^{-1} were attributed to the stretching vibrations of the C–NH–C (partially condensed) and C–N(C)–C (fully condensed) connection units, respectively [33]. Moreover, the broad peak ranging from 2900 to 3500 cm^{-1} was due to the N–H vibration of the surface uncondensed amine groups. Moreover, the O–H vibration was potentially caused by the absorbed water molecules. The insignificant difference in the FTIR spectra was observed after the addition of MgO and Au, indicating that the basic crystal structure of CN did not change.

Fig. 4 demonstrates the N_2 adsorption-desorption isotherms and corresponding pore size distribution curves of the CN, 3% MgO-CN, and Au/3% MgO-CN samples. Evidently, as shown in Fig. 4(a), all samples exhibited type IV isotherms with H3 hysteresis loops, suggesting the presence of mesopores and generation of slit-shaped pores due to the aggregates of the sheet-like particles [43]. As shown from the pore size distribution curves (Fig. 4(b)), the pore sizes of all the samples were mainly in the range 1.5–5 nm, and a broad peak at approximately 40 nm was also observed, indicating the formation of the mesoporous and macroporous structures. The specific surface area, pore size, and pore volume of the different photo-

Table 1

Specific surface area, pore size, and pore volume of the different photocatalysts.

Catalyst	S_{BET} (m^2/g)	D_{pore} (nm)	V_{pore} (cm^3/g)
CN	66.790	3.837	0.7645
MgO-CN	67.618	3.455	0.8787
Au/MgO-CN	61.963	3.821	0.9051

catalysts are summarized in Table 1. As shown, the specific surface areas of CN and 3% MgO-CN were similar, while that of Au/3% MgO-CN was smaller due to the addition of Au, which caused the blocking of the fine capillaries of the parent CN surface. Furthermore, the similar pore volumes and average pore diameters of the all samples further suggested that the loading of the MgO and Au nanoparticles had negligible effect on the microstructure of g- C_3N_4 . Therefore, the difference in the photocatalytic performance among these samples was mainly attributed to the different CO_2 adsorption abilities, which will be discussed later.

To investigate the surface chemical composition and valence states of Au/3% MgO-CN, XPS measurements were conducted. The survey XPS spectrum (Fig. 5(a)) indicated that the main elements on the surface of the catalyst were C, N, O, Mg, and Au. The C 1s spectrum (Fig. 5(b)) was fitted to the three peaks at 284.6, 285.9, and 287.9 eV, which corresponded to the sp^2 C–C bonds, C– NH_2 species, and sp^2 -bonded carbon in N-containing aromatic rings (N=C–N), respectively [44]. The four peaks in the N 1s spectrum (Fig. 5(c)) at approximately 398.5, 399.3, 400.8, and 403.8 eV were derived from the sp^2 -hybridized nitrogen (C=N=C), sp^3 -hybridized nitrogen (N– C_3), amino functional groups (C–N–H), and excitation of π bond, respectively [45]. Specifically, compared to that of the bare CN, a new peak appeared at approximately 398.0 eV, corresponding to the Mg–N bonds [46]. In addition, the O 1s spectrum (Fig. 5(d)) was fitted to the two peaks at 531.6 and 533.2 eV, which were attributed to the lattice oxygen in the Mg–O and O–H groups, respectively [47]. The Mg 1s XPS spectrum (Fig. 5(e)) was deconvoluted into two peaks at approximately 1303.9 and 1305.0 eV, which was attributed to the Mg–O and Mg–N bonds, respectively [48]. The binding energies of Au 4f at 83.0 and 86.4 eV (Fig. 5(f)) were attributed to Au 4f $_{7/2}$ and 4f $_{5/2}$, respectively, indicating that the Au nanoparticles occurred in their metallic state [49].

Fig. 4. N_2 adsorption-desorption isotherms (a) and pore size distribution curves (b) of CN, 3% MgO-CN, and Au/3% MgO-CN.

Fig. 5. XPS spectra of Au/3% MgO-CN. (a) Survey spectrum; (b) C 1s; (c) N 1s; (d) O 1s; (e) Mg 1s; (f) Au 4f.

3.2. Optical properties

To investigate the optical absorption of the samples, the UV-vis DRS analysis were conducted (Fig. 6(a)). Compared to that of the pure CN sample, the MgO-CN samples showed a slight red shift and increased intensity of light absorbance, which can be attributed to the doping of Mg into CN, resulting in the formation of Mg-N bonds. The presence of the Mg-N bonds in the MgO-CN nanosheets facilitated the charge transfer from CN to MgO [50]. After loading with Au, the adsorption edge shifted to a longer wavelength at approximately 480 nm, whereas that of the pure CN was at approximately 450 nm. Basically, the Au nanoparticles in the Au/MgO-CN sample can cause the hot electron transfer and near-field enhancement effect, which can result in the slight change in the absorption edge of CN and increased absorption at the spectra tail [51]. The enhanced light absorption indicated that more visible light can be utilized to produce photogenerated charge carriers, which could efficiently promote the photocatalytic reaction. Meanwhile, it can be observed that the Au/MgO-CN sample showed a broad absorption peak at approximately 580 nm, which can be attributed to the surface plasmon resonance (SPR) effect of the Au nanoparticles. To further investigate the role of Au deposition, we also measured the UV-vis DRS spectra of the Au/3% MgO-CN samples with different Au amounts. As shown in Fig. S2, the intensity of the characteristic band in the visible light range gradually increased with increasing Au content, indicating a strong Au-content-dependent SPR effect.

To determine the bandgaps of CN and MgO, the Tauc plots using the Kubelka-Munk function were generated. As shown in Fig. 6(b), the bandgap of CN was estimated to be 2.66 eV, while that of MgO was approximately 5.32 eV, both of which we consistent with the values in previous reports [50,52]. Based on the results of the XPS valance band spectra in Fig. 6(c), the valance band potentials of CN and MgO was estimated to be 1.51 and 4.27 eV, respectively. According to the values of the bandgaps and valance band potentials, the conduction band potentials of CN and MgO was -1.15 and -1.05 eV, respectively.

3.3. Separation of photogenerated charge carriers

The addition of MgO and Au to the bare CN can not only make a noticeable effect on the light absorption, but also influence the separation and transfer of the photogenerated charge carriers, which can be investigated using the PL spectroscopy measurements [53]. Fig. 6(d) demonstrated the PL emission spectra under an excitation wavelength of 380 nm, and the pure g-C₃N₄ sample showed an intense peak at approximately 445 nm. When MgO was loaded on CN, the PL peak gradually decreased in intensity for all MgO-CN samples. It was observed that the 3% MgO-CN sample exhibited the lowest peak intensity among all the MgO-CN samples. After depositing Au on 3% MgO-CN, the PL peak decreased and became the lowest among those for all the samples, suggesting that the formation of the Au/MgO-CN ternary junction promoted the separation of the photogenerated charge carriers, which is important in enhancing the photocatalytic activity [54]. This could have been due to

Fig. 6. (a) UV-vis absorption spectra of CN, MgO-CN, and Au/MgO-CN; The transformed diffuse reflectance (b) and XPS valence band spectra (c) of CN and MgO; (d) PL spectra of CN, MgO-CN, and Au/MgO-CN.

the efficient separation of the photogenerated charge carriers, which led to more charge carriers being utilized for the photocatalytic reduction of CO_2 . Moreover, the effect of the different Au amounts on the PL spectra of Au/3% MgO-CN samples was also investigated in Fig. S3. Evidently, Au/3% MgO-CN catalyst showed the lowest PL intensity, suggesting that an excellent efficiency of charge separation was achieved. On the other hand, an excessively high Au loading would induce additional recombination centers for the photogenerated charge carriers, resulting in the increased PL intensity.

In order to gain an in-depth understanding of the effects of MgO and Au, time-resolved photoluminescence (TRPL) studies were conducted to investigate the dynamics of the photogenerated charge carriers as shown in Fig. S4. A tri-exponential fitting was performed for the luminescence decay curves using the following equation [55]:

$$y(t) = y_0 + B_1 \exp\left(-\frac{t}{\tau_1}\right) + B_2 \exp\left(-\frac{t}{\tau_2}\right) + B_3 \exp\left(-\frac{t}{\tau_3}\right)$$

where y_0 is the baseline correction; B_1 , B_2 and B_3 are pre-exponential factors; and τ_1 , τ_2 and τ_3 are the three decay time constants: the radiative (τ_1), non-radiative process (τ_2), and energy transfer processes (τ_3). The average lifetimes (τ) were calculated using the following equation:

$$\tau = \frac{B_1\tau_1^2 + B_2\tau_2^2 + B_3\tau_3^2}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3}$$

The fitting results of the TRPL spectroscopy of CN, 3% MgO-CN, and Au/3% MgO-CN photocatalysts for a 350-nm excitation wavelength are shown in Table S1. The τ of bare CN

was 1.29 ns; however, it became 1.80 ns after the addition of MgO. The Au/MgO-CN sample demonstrated the longest decay time of 3.18 ns. This was attributed to the formation of the intimate interfaces in the Au/MgO-CN photocatalyst, which prolongs the lifetime of charge carriers, thereby improving the photocatalytic activity [56].

It was determined that the photoelectrochemical measurements were sufficient to prove the electron-hole pair separation and transfer in the photocatalysts. As shown in Fig. 7, the photoelectrochemical properties of the as-prepared catalysts were investigated using the photocurrent response and EIS. Fig. 7(a) shows the transient photocurrent responses for the CN, 3% MgO-CN, and Au/3% MgO-CN samples under several on and off cycles of irradiation. When the light was turned on, the photocurrent rapidly achieved its peak value before being stable. However, the photocurrent decreased to the background level when the light was turned off. All the samples showed similar photocurrent responses during several on and off cycles of irradiation. Among all the samples, the Au/3% MgO-CN catalyst demonstrated the highest photocurrent. Moreover, the photocurrent of 3% MgO-CN was higher than that of the bare CN. These observations indicated that the heterojunction between MgO and CN, and the addition of the Au nanoparticles, can promote the efficiency of the photogenerated electron-hole separation and transfer, resulting in an enhanced photocatalytic activity [57].

EIS was performed to determine the charge transfer capability of the prepared samples [58]. The EIS Nyquist plots of CN,

Fig. 7. Photocurrent response density (a) and electrochemical impedance spectra (b) of CN, 3% MgO-CN, and 1% Au/3% MgO-CN.

3% MgO-CN, and Au/3% MgO-CN (Fig. 7(b)) were represented by semicircles whose diameters corresponded to the charge transfer resistance at the contact interface between the sample and electrolyte solution. A smaller semicircle diameter means that the charge transfer resistance is lower, which indicates an easy charge transfer. The diameter of the semicircle decreased in the order of CN, 3% MgO-CN, and Au/3% MgO-CN. Among all the samples in Fig. S5(b), the Au/3% MgO-CN sample exhibited the smallest diameter in the EIS plot, indicating the best charge separation property. The result was consistent with the observation of the photocurrent response in Fig. S5(a).

Therefore, the results of the characterizations including the PL spectra, TRPL analysis, and photoelectrochemical measurements demonstrated the synergetic effect of the MgO and Au on the significantly promoted charge separation and transfer behavior.

3.4. Photocatalytic performance of CO₂ reduction

The as-prepared catalysts were applied to the photocatalytic reduction of CO₂ in the presence of H₂O vapor to determine the photocatalytic performance of the catalysts. In order to determine the interaction between the various components of the catalyst, we conducted several control experiments (Fig. 8(a)) to study the photocatalytic activities of the Au/3% MgO-CN, Au/CN, 3% MgO-CN, and CN catalysts after 3 h of simulated sunlight exposure. It can be seen from Fig. 8(a) that pure CN possessed the lowest photocatalytic activity, which could only produce the trace amounts of CO. As shown in Table S2, the photocatalytic activity of CO on the Au/CN and 3% MgO-CN catalysts was 6.2 and 13.2 times higher than that of the pure CN, respectively. Moreover, the performance of the CO production on the Au/MgO-CN ternary catalyst was 29 times higher than that of the bare CN. This superiority confirmed that the co-modification of MgO and Au significantly enhanced the photocatalytic activity of CN, which was due to the excellent synergetic effect among CN, MgO, and Au.

A series of control experiments were performed: (a) in the absence of photocatalysts, (b) without light irradiation, (c) using pure Ar in the presence of H₂O, and (d) using pure Ar with CO₂. The results indicated that neither CO nor hydrocarbon

products can be detected, verifying the generation of the products from both CO₂ and H₂O on the photocatalysts under light irradiation. To further verify the origin of the carbon products, isotopic ¹³CO₂ was used as the reactant to perform the photocatalytic reaction under identical conditions. The gases produced were analyzed using gas chromatography-mass spectrometry (GC-MS). The result shown in Fig. S6 confirmed that the generated CO originated from the reactant CO₂ as opposed to the possible decompositions of the catalyst. It was noted that the detectors used in this study were more sensitive to CO than that of the hydrocarbon products. As a result, the amount of generated hydrocarbon products may have been underestimated. In addition, the oxygen source of O₂ can be proved by the isotopic experiments using CO₂ and H₂¹⁸O under identical photocatalytic conditions. As shown in Fig. S7, ¹⁸O¹⁶O (*m/z* = 34), and ¹⁸O₂ (*m/z* = 36) were simultaneously detected, suggesting that the product O₂ was derived from the oxidation of H₂O.

To determine the role of MgO in the photocatalytic reduction of CO₂, a series of MgO-CN catalysts with different weight percentages of MgO ranging from 1%–10% were synthesized. Fig. 8(b) shows the effect of different amounts of MgO on the photocatalytic activity of the MgO-CN composites under simulated sunlight for 3 h. The effect of the MgO content on the composite catalyst was evident. As the MgO content increased, the photocatalytic activity initially increased before decreasing. When the content of MgO was 3%, the photocatalytic activity was at its highest. This may have been due to the excess MgO, which affected the light absorption capacity of the catalysts. To investigate the effect of MgO on CO₂ adsorption, the CO₂ adsorption curves of CN and MgO-CN with different amounts of MgO are displayed in Fig. S8. It can be observed that the MgO-CN samples absorbed more CO₂ molecules than that of the bare CN, and the adsorption capacity of the MgO-CN samples increased with higher MgO content. Moreover, MgO increased the chemisorption of CO₂ due to its alkalinity, which will be proved by the CO₂-TPD analysis in the later section.

Fig. 8(c) demonstrates the effect of the different amounts of Au nanoparticles on the photocatalytic activity of the Au/3% MgO-CN composites. It can be observed that the highest photocatalytic activity was achieved in the 1% Au/3% MgO-CN

Fig. 8. Photocatalytic performance of CO₂ photoreduction with H₂O vapor at 3 h under simulated solar irradiation. (a) Comparison of photocatalytic activities on 1% Au/3% MgO-CN, 1% Au/CN, 3% MgO-CN, and CN; The effect of amounts of MgO (b) and Au (c) nanoparticles, and metal cocatalysts (d).

catalyst, with the yields of CO, CH₄, CH₃OH, and CH₃CHO of 423.9, 83.2, 47.2, and 130.4 $\mu\text{mol/g}$, respectively. To determine the effect of the different noble metal cocatalysts on the photocatalytic activity, we loaded 3% MgO-CN with different noble metals including Au, Ag, Pt, and Pd. The content of the noble metal cocatalysts in each sample was uniform. As shown in Fig. 8(d), the loading of the noble metal cocatalysts enhanced the photocatalytic performance of the CO₂ reduction. The result can be attributed to their roles of acting as electron traps, which could significantly improve the separation efficiency of the electron-hole pairs. Moreover, the different cocatalysts can have different distributions of final products, indicating the different electron capture abilities of the metal architectures. Fig. 8(d) shows that the occurrence of Au, Pt, or Pd can help generate CH₃OH, which cannot be produced in the presence of Ag. Specifically, the product selectivity of the photocatalytic CO₂ reduction was dependent on the occurrence of the noble metal cocatalyst.

Among these different noble metals containing composite catalysts, Au/3% MgO-CN demonstrated the highest photocatalytic activity, which may have been due to the strong SPR effect of the Au nanoparticles. In the Au/MgO-CN system, the Au nanoparticles played two roles in the photocatalytic system. On the one hand, the Au nanoparticles acted as cocatalysts to capture electrons, allowing the spatial separation of the charge

carriers. The efficient separation of charge carriers was evidence by the PL spectra, TRPL spectra, and photoelectrochemical measurements including the photocurrent response and EIS analyses. On the other hand, the Au nanoparticles can increase the absorption of visible light through the SPR effect and further reduce the activation energies of the photoreduction of CO₂ in the presence of H₂O. This SPR behavior with enhanced visible light absorption on the Au nanoparticles can be demonstrated using the UV-vis spectra.

Table S2 reveals the selectivity of CO, CH₄, and CH₃CHO for the photocatalytic CO₂ reduction of the CN, 3% MgO-CN, 1% Au/CN, and 1% Au/3% MgO-CN catalysts. Compared to that of CN, the selectivity of CO and CH₄ on the MgO-CN catalyst decreased, while the selectivity of CH₃CHO increased from 36.6% to 56.0%. Similarly, compared to that of Au/CN, the selectivity of CH₃CHO on the Au/MgO-CN catalyst increased from 36.8% to 42.1%. These results indicated that the presence of MgO can improve the selectivity of CH₃CHO. It was noted that the oxidation reaction of H₂O was critical during the reaction of the CO₂ photoreduction. As shown in Table S2, the yield of O₂ on the Au/MgO-CN catalyst was the highest. To sustain the charge balance of the whole reaction system, the photogenerated electrons consumed during the transformation from CO₂ to all the reduction products should be equal to the photogenerated holes consumed by water oxidation. As expected, the yields of

O₂ stoichiometrically matched that of the reduction products.

The control experiments in the photocatalytic activities under different wavelengths are important to determine the relationship between the solar energy conversion efficiency and light response ability. Table S3 shows the photocatalytic activities of the Au/3% MgO-CN catalyst and its corresponding AQEs under different wavelengths. The highest AQE of 4.96% was obtained at 365 nm. The AQE decreased with increasing wavelength, implying that the yields of the products on the Au/MgO-CN catalyst was dependent on the wavelength of the incident light. By comparing it with previous reports of photocatalytic CO₂ reduction on g-C₃N₄-based heterostructures in Table S4, the synthesized Au/MgO-CN catalyst in our work presented a considerable photocatalytic activity and selectivity of CO₂ reduction. This comparison suggested the significant role of the synergetic effect between MgO and Au toward the improved photocatalytic activity for CO₂ reduction.

To investigate the stability of the catalyst, we therefore performed a five-time cycling photocatalytic test on the Au/MgO-CN catalyst under identical reaction conditions as shown in Fig. S9. The evolution rate of the products exhibited minimal fluctuations during the whole measurement, indicating a good photostability of the Au/MgO-CN catalyst. The catalyst after the cycling tests was also investigated using TEM, SEM, and XPS (Figs. S10 and S11). No evident changes in the

structures and chemical states of the catalysts was observed. Hence, the Au/MgO-CN catalyst should be stable enough for CO₂ photoreduction.

3.5. Possible photocatalytic mechanism

To further reveal the conversion pathways and reaction mechanism, the in-situ DRIFTS of the photocatalytic CO₂ reduction under irradiation were subsequently conducted. It is known that the adsorbed reaction intermediates and products on the photocatalyst surface can be monitored with the time course. Figs. 9(a)–(c) show the DRIFTS spectra of the adsorption species of CO₂ and H₂O adsorbed on the surface of the Au/3% MgO-CN catalyst in the dark for 30 min and subsequently under simulated solar light for 15, 30, 120, and 180 min. As shown in Fig. 9(a), the bands at approximately 3730, 3706, and 3632 cm⁻¹ were attributed to the OH on the surface of the MgO, and the isolate OH was due to the absorbed H₂O [59]. As the illumination time increased, the bands of all the adsorption species significantly decreased. Fig. 9(b) presents the CO₂ adsorption in the wavenumber range of 2200–2500 cm⁻¹. The bands at 2336 and 2360 cm⁻¹ was assigned to the asymmetric stretching of CO₂ in the gas phase, which indicated a dramatic reduction [60]. The decrease in both the CO₂ and H₂O adsorption species indicated that the CO₂ and H₂O vapors

Fig. 9. In situ DRIFTS spectra of the OH groups on the catalysts (3000–3800 cm⁻¹) (a), CO₂ adsorption (2200–2500 cm⁻¹) (b), CO₂ interaction (1300–1800 cm⁻¹) with Au/3% MgO-CN under irradiation (c), and CO₂-TPD profiles of CN, 3% MgO-CN, and Au/3% MgO-CN (d).

were converted to other species during the irradiation time.

Fig. 9(c) shows several adsorption species generated under the irradiation due to the CO_2 interaction with the photocatalyst in the region of 1300–1800 cm^{-1} . The bands at 1507, 1324, and 1404 cm^{-1} can be attributed to the adsorption of CO_2 in the forms of monodentate carbonate (m-CO_3^{2-}), bidentate carbonate (b-CO_3^{2-}), and bicarbonate (HCO_3^-), respectively [61–63]. The peaks displayed a slight enhancement with increasing irradiation time. In addition, the bending vibration of H_2O at 1654 cm^{-1} was derived from the surface adsorption of the catalyst. The band at 1698 cm^{-1} was attributed to the formation of $\bullet\text{CO}_2^-$, which requires the existence of a metal ionic site and surface OH [59]. As the irradiation time progressively increased, the peak of the $\bullet\text{CO}_2^-$ species gradually increased and maintained after 2 h. Therefore, the $\bullet\text{CO}_2^-$ species was considered a key intermediate in the photoreduction of CO_2 . CO can be produced if a C–O bond in $\bullet\text{CO}_2^-$ were cleaved to form C–Mg bonds. It was noted that the strong band at 1711 cm^{-1} indicated the bending vibration of C=O, which was due to the accumulation of CO. The peak of the methyl radicals ($\bullet\text{CH}_3$) was at 1450 cm^{-1} , suggesting the production of CH_4 and potentially of CH_3OH and CH_3CHO [64].

Furthermore, the CO_2 -TPD analysis (Fig. 9(d)) was conducted to determine the active sites of the CO_2 absorption. Generally, there are several different modes of CO_2 adsorption including molecularly adsorbed CO_2 and carbonates formation, which are the main forms of CO_2 adsorption [65]. The monodentate carbonates (m-CO_3^{2-}) will be generated when a CO_2 molecule bonds directly with an oxygen atom, while the bidentate carbonates (b-CO_3^{2-}) will be generated when a CO_2 molecule bonds with both oxygen and metal atoms. As for the bicarbonate (HCO_3^-), the combination of the CO_2 molecule with surface hydroxyl leads to the formation of HCO_3^- . It was observed that the bare CN showed a characteristic peak at around 100 $^\circ\text{C}$, which can be attributed to the decomposition of the molecularly adsorbed CO_2 (75–180 $^\circ\text{C}$). After loading with MgO, the characteristic peak of the molecularly adsorbed CO_2 increased, and an additional peak was observed at approximately 510 $^\circ\text{C}$, which was attributed to b-CO_3^{2-} (380–570 $^\circ\text{C}$), indicating that MgO could greatly enhance the CO_2 adsorption because of its basicity. Moreover, the addition of Au resulted in a new peak that was attributed to HCO_3^- (180–380 $^\circ\text{C}$), indicating a new base position and increased active sites for the reaction of the Au nanoparticles. Particularly, compared to that of MgO-CN, the peak in the range of b-CO_3^{2-} of Au/MgO-CN shifted from 510 to 470 $^\circ\text{C}$, suggesting a more favorable activation process over Au/MgO-CN. The shift can be attributed to the CO_2 adsorption at the interface between MgO and Au, where the reduction of the adsorbed CO_2 occurred. The synergistic effect among CN, MgO, and Au was thus further confirmed. Therefore, it can be concluded that the CO_2 adsorption was the key factor in determining the different photocatalytic performances of the above catalysts. Moreover, it further reduced the activation energies of the photoreduction of CO_2 with H_2O .

Based on the above characterization results, we proposed a possible mechanism for the Au/MgO-CN catalyst for photocatalytic reduction of CO_2 as shown in Fig. 10. Under irradiation,

Fig. 10. Schematic illustration of the mechanism for the photocatalytic reaction of the Au/MgO-CN catalyst.

tion, the free electrons and holes can be generated at the conduction and valence bands of CN, respectively. These electrons on the conduction band of CN subsequently transferred to MgO through the Mg–N bond at the interface of MgO and CN and were further captured by the Au nanoparticles to reduce the activated CO_2 . This yielded CO, CH_4 , CH_3OH , and CH_3CHO . It was noted that the hot electrons generated by the SPR effect of the Au nanoparticles can also be injected back to the interface of MgO and CN to react with CO_2 therein [34,66]. For the holes, they were left on the valence band of CN and could oxidize H_2O to O_2 . The synergistic effect created by CN, MgO, and Au in our hybrid photocatalysts was thus clearly illustrated.

To further verify the charge separation path, we conducted an in-situ experiment using the photoreduction of the Pt precursor for the Pt deposition under identical photocatalytic conditions. After approximately 30 min, the Pt precursor was reduced into zero-valent Pt nanoparticles using the photogenerated electrons on the surface. Therefore, the position of the Pt deposition can be regarded as active sites for photoreduction. Under HRTEM, these sites can be resolved. As shown in Fig. S12, the small Pt nanoparticles were deposited on the surface of Au, which indicated that the reactive sites were mainly on the Au nanoparticles in the Au/MgO-CN catalyst.

Accordingly, a possible reaction pathway was illustrated as shown in Fig. S13, which clearly showed the transfer of the photo-generated electrons on the Au nanoparticles and CO_2 activated on the surface of Au/MgO-CN catalyst under simulated sunlight irradiation. Specifically, the CO_2 molecules were adsorbed at the interface between the MgO and Au nanoparticles to become activated CO_2 . The activated CO_2 molecules can combine with the photogenerated electrons on the Au nanoparticles to form $\bullet\text{CO}_2^-$ radicals, thereby further generating $\bullet\text{CH}_3$ radicals. Subsequently, a part of $\bullet\text{CO}$ was desorbed from the catalyst surface to form CO. The others can continue to combine with the photogenerated electrons to form $\bullet\text{CHO}$, while $\bullet\text{CH}_3$ radicals can be combined with $\bullet\text{CHO}$ and the photogenerated electrons to produce CH_3CHO and CH_4 , respectively. Simultaneously, the H_2O molecules reacted with the photo-generated holes to generate $\bullet\text{OH}$ radicals, which can combine with $\bullet\text{CH}_3$ radicals to form CH_3OH .

4. Conclusions

In summary, this study demonstrated the photocatalytic property on the CO₂ reduction in the presence of H₂O vapor over the g-C₃N₄ nanosheet can be enhanced using the simultaneous modification of MgO and Au. The best photocatalytic performance was achieved using the 1% Au and 3% MgO co-modified g-C₃N₄ photocatalysts under simulated solar light irradiation, with CO, CH₄, CH₃OH, and CH₃CHO yields of 423.9, 83.2, 47.2, and 130.4 μmol/g, respectively, in a 3 h reaction. Notably, the performance of CO production in the 1% Au/3% MgO-CN ternary catalyst was 29 times higher than that of the bare CN. All the characterizations above showed that the enhanced photocatalytic activities can be attributed to the synergistic effect between MgO and Au on g-C₃N₄. Particularly, the cocatalyst MgO can activate CO₂ (adsorbed at the interface between the MgO and Au particles) and the Mg–N bonds formed in the MgO-CN nanosheets play an important role in the charge transfer. Meanwhile, the Au particles can not only act as a cocatalyst for capturing electrons, but they can also increase the absorption of visible light through the SPR effect. Moreover, they could further reduce the activation energies of the photo-reduction of CO₂ with H₂O.

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Graphical Abstract

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MgO and Au nanoparticle Co-modified g-C₃N₄ photocatalysts for enhanced photoreduction of CO₂ with H₂O

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A series of MgO and Au co-modified g-C₃N₄ photocatalysts were prepared via a facile route, which exhibited a remarkably high activity for the photocatalytic reduction of CO₂ to CO, CH₄, CH₃OH, and CH₃CHO.

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MgO和Au纳米颗粒共修饰g-C₃N₄光催化剂增强CO₂-H₂O光催化反应过程

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摘要: 光催化CO₂还原制备太阳燃料被广泛关注并逐渐形成研究热点, 该过程利用可再生清洁能源太阳能, 在低温低压的温和条件下驱动CO₂还原制备CO、CH₄、CH₃OH等燃料气体或者高附加值的碳氢化合物。半导体光催化剂能够将清洁的太阳能有效地转化为化学能, 其中, g-C₃N₄由于其成本低、毒性低、稳定性高和带隙窄等优点, 被广泛应用于光催化领域。然而, 纯g-C₃N₄具有光利用效率低和光生电子-空穴复合率高的缺点, 导致光催化活性相对较低。因此, 需要对g-C₃N₄进行修饰改性来提高其光催化性能。一方面, MgO具有强大的CO₂吸附能力, 可用于修饰半导体以提高光催化还原CO₂的反应活

性。另一方面,助催化剂尤其是贵金属,不仅能够捕获电子以提高光生电子-空穴对的分离效率,而且还能提供反应的活性位点。本文通过沉淀和煅烧法制备了不同复合量的MgO-g-C₃N₄催化剂,同时负载贵金属Au作为助催化剂,用于光催化CO₂和H₂O反应,考察MgO含量和不同贵金属助催化剂对光催化活性的影响。发现Au和3% MgO共改性的g-C₃N₄光催化剂上表现出最佳的光催化性能,3 h后CO, CH₄, CH₃OH和CH₃CHO的产量分别高达423.9、83.2、47.2和130.4 μmol/g。

本文分别研究了MgO和贵金属Au作为助催化剂对光催化行为的影响。XPS结果表明, Au/MgO-g-C₃N₄纳米片中形成了Mg-N键; UV-vis漫反射光谱表明Au/MgO-g-C₃N₄复合催化剂能够大大地增强紫外和可见光的吸收,且Au纳米颗粒具有表面等离子体共振(SPR)效应; PL光谱、TRPL光谱和光电化学测试都显示了MgO和Au的加入可以有效地提高光生电荷载流子的分离效率,这是由于Mg-N键的存在以及Au纳米颗粒对电子的捕获作用。CO₂吸附曲线证明了MgO的存在能够增强对CO₂的吸附; CO₂-TPD测试则表明CO₂的有效吸附主要发生在MgO和Au纳米颗粒的界面处,而该界面正是光生电子和活化吸附后的CO₂反应的活性位点。值得注意的是,在Au/3% MgO-g-C₃N₄三元催化剂上CO的产量是纯g-C₃N₄的29倍。实验和表征结果均表明, MgO和Au的共修饰显著提高了纯g-C₃N₄的光催化活性,这是由于三元光催化剂各组分之间的协同作用所致。助催化剂MgO可以激活CO₂(吸附在MgO和Au颗粒之间的界面),并且MgO-g-C₃N₄纳米片中形成的Mg-N键在电荷转移中起着重要作用。同时, Au颗粒修饰的MgO-g-C₃N₄可以通过SPR效应增加可见光的吸收,并进一步降低H₂O对CO₂的光还原活化能;且Au纳米颗粒能够捕获电子,从而促进光生载流子的分离。本研究通过MgO和Au纳米颗粒共修饰的方法改性传统的光催化剂,具有光催化还原CO₂的应用前景。

关键词: CO₂光还原; MgO; Au; g-C₃N₄; 光催化; 协同效应; 助催化剂

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