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Construction of 2D/2D g-C₃N₄/CeO₂ Heterojunction and its Oxygen Vacancy

Mediated Photocatalytic Activity

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Abstract

CeO₂ sheets (CeO₂-S) through hydrogen treatment (CeO₂-S-H₂) have been coupled with carboxylated g-C₃N₄ (C-g-C₃N₄) to construct 2D/2D C-g-C₃N₄/CeO₂-S-H₂ heterojunction. The ratio of Ce³⁺/Ce⁴⁺ in CeO₂-S was increased from 28.2% to 32.08% in CeO₂-S-H₂. Experiment results demonstrated the highest CO yields in 8 h of 60%C-g-C₃N₄/CeO₂-S-H₂ were 2.41, 6.83 and 1.72 times of that of pure C-g-C₃N₄, CeO₂-S and CeO₂-S-H₂. Heterojunction also exhibited the highest CH₄ yields of 11.997 μmol/g in 8 h. Interestingly, CH₄ yield of CeO₂-S-H₂ was much higher than that of CeO₂-S, verifying oxygen vacancy introduction can effectively enhance CH₄ production. In addition, 60%C-g-C₃N₄/CeO₂-S-H₂ heterojunction demonstrated the best ciprofloxacin degradation performance. It is suggested that the synergistic effects of oxygen vacancy introduction and heterojunction construction promoted charges transfer and separation.

Keywords

Semiconductors; Nanocomposites; g-C₃N₄; CeO₂; Oxygen vacancy

1. Introduction

In recent years, the construction of g-C₃N₄/CeO₂ heterojunction with high redox capability has attracted extensive attention because of their good band matching and the reverse redox characteristics [1-3]. Among different heterostructures, 2D/2D structure has significant advantages of the enhanced light absorption, large contact area and rich active sites [4]. However, photocatalytic performance of 2D/2D g-C₃N₄/CeO₂ heterojunction still faces great limitations mainly due to large size of 2D CeO₂. The modified strategies are quite needed.

It is known that defects inevitably exist for single semiconductor material, which may cause the rearrangement of charges around them and form the localized electronic states in space and corresponding defect state energy level. When surface defects energy levels meet the thermodynamic conditions of catalytic reaction, surface defects have the advantages of providing active sites and improving charges transfer. Thus, it is expected that photocatalytic activity of 2D/2D g-C₃N₄/CeO₂ structure can be significantly improved by introducing defects into CeO₂. Herein, we report the oxygen vacancy mediated method to construct g-C₃N₄/CeO₂ heterostructure through hydrogen treatment on CeO₂. CO₂ reduction and organic pollutants degradation performance were investigated. The inherent catalytic mechanism of heterojunction was also discussed.

2 Experimental

2.1 Synthesis of Photocatalysts

For CeO₂-S preparation, 0.75 mmol of Ce(NO₃)₃·6H₂O, 0.6 mL of acetic acid and 5.25 mmol of hexamethylenetetramine were firstly dissolved in 15 mL of deionized water. Then, the solutions were hydrothermally treated at 140 °C for 9 h to obtain precipitates, which were further annealed in muffle furnace at 500 °C for 2 h. As-obtained CeO₂-S was light yellow. To regulate surface oxygen vacancy, CeO₂-S was further treated in gas mixtures of hydrogen (5%) and argon (95%) at 500 °C for 2 h. The colour of CeO₂-S-H₂ was gray white.

C-g-C₃N₄ was synthesized by refluxing g-C₃N₄ bulks in HNO₃ solution [5]. For C-g-C₃N₄/CeO₂-S-H₂ preparation, a certain amount of C-g-C₃N₄ and CeO₂-S-H₂ with total mass of 0.5 g were firstly mixed. C-g-C₃N₄ content was accounted for 20%, 40%, 60% and 80% respectively. Secondly, solid mixtures were dispersed in 50 mL of methanol solution by ultrasonication and magnetic stirring. Finally, solid powderz were calcined at 150 °C for 4 h. Specific preparation process is shown in Scheme S1. Characterization techniques and photoelectrochemical measurement were shown in supplementary materials.

2.2 Photocatalytic Test

CO₂ reduction was carried out in a 120 mL of cylindrical glassware reactor, in which 50 mg of catalyst powders was firstly placed inside. Before reaction, high purity CO₂ (99.99%) gas flushed the reactor. 2 mL of deionized water was injected into the reactor as reducing agent. A 300 W Xe lamp ($\lambda > 400$ nm) was used as light source. Target products were analysed using gas chromatography with FID detector. For ciprofloxacin (CIP) degradation, 50 mg of catalyst was dispersed in 100 mL of CIP aqueous solution (10 mg/L). Typically, suspensions were magnetically stirred in dark for 30 min. Afterwards, it was irradiated by 300 W Xe lamp ($\lambda > 400$ nm). CIP concentration was analysed by UV-visible spectrophotometer (Shimadzu UV-2600, Japan).

3 Results and Discussion

Fig.1 shows the morphologies of photocatalysts. Typical diffraction peaks of both g-C₃N₄ and CeO₂ phases have been observed in patterns of C-g-C₃N₄/CeO₂-S-H₂ (Fig.S1). C-g-C₃N₄ morphology mainly presents nanosheets and nanoparticles (Fig.1a), while CeO₂-S is composed of sheets with diameter of about 200-500 nm (Fig.1b). A layer-to-layer stack-like sandwich structure is observed for 60%C-g-C₃N₄/CeO₂-S-H₂ (Fig.1c). It should be noted that hydrogen treatment has little effect on CeO₂-S morphology. TEM image of 60%C-g-C₃N₄/CeO₂-S-H₂ shows that CeO₂-S-H₂ sheets are evenly

distributed on C-g-C₃N₄ surface, and a 2D/2D stacked layered structure is formed (Fig.1d). High-resolution TEM image displays (Fig.1e) the lattice spacing of CeO₂-S-H₂ is 0.19 nm, which corresponds to (110) crystal plane. These results demonstrate C-g-C₃N₄/CeO₂-S-H₂ was successfully prepared. Elements mapping of 60%C-g-C₃N₄/CeO₂-S-H₂ (Fig.1f-Fig.1j) displays C, N, Ce, and O elements are uniformly distributed, which further ensures that a 2D/2D structure is constructed.

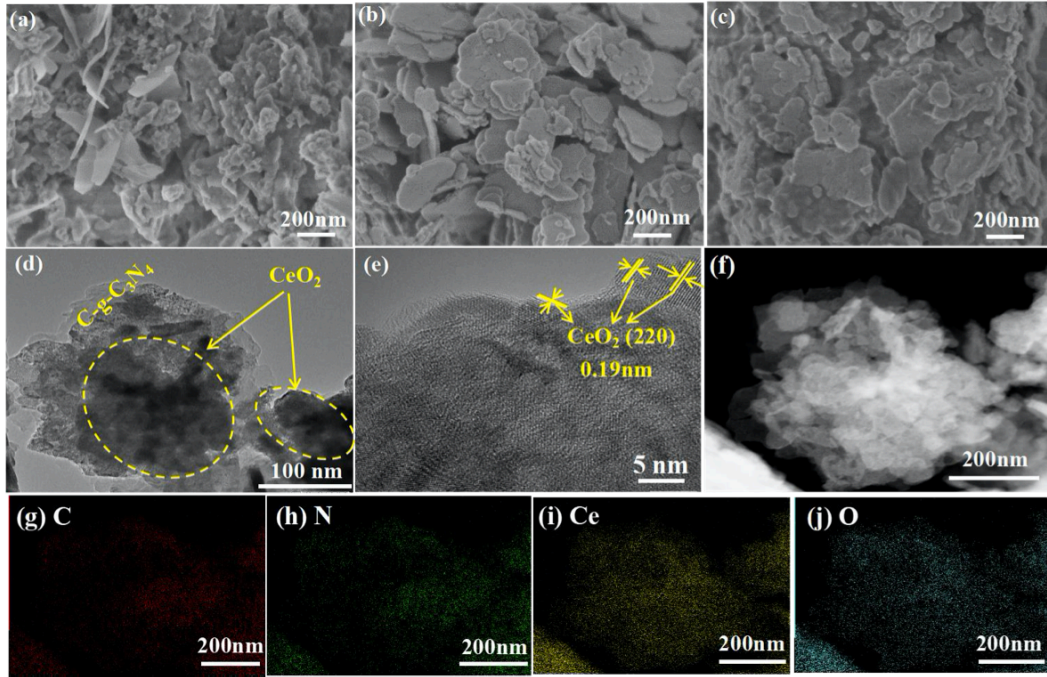
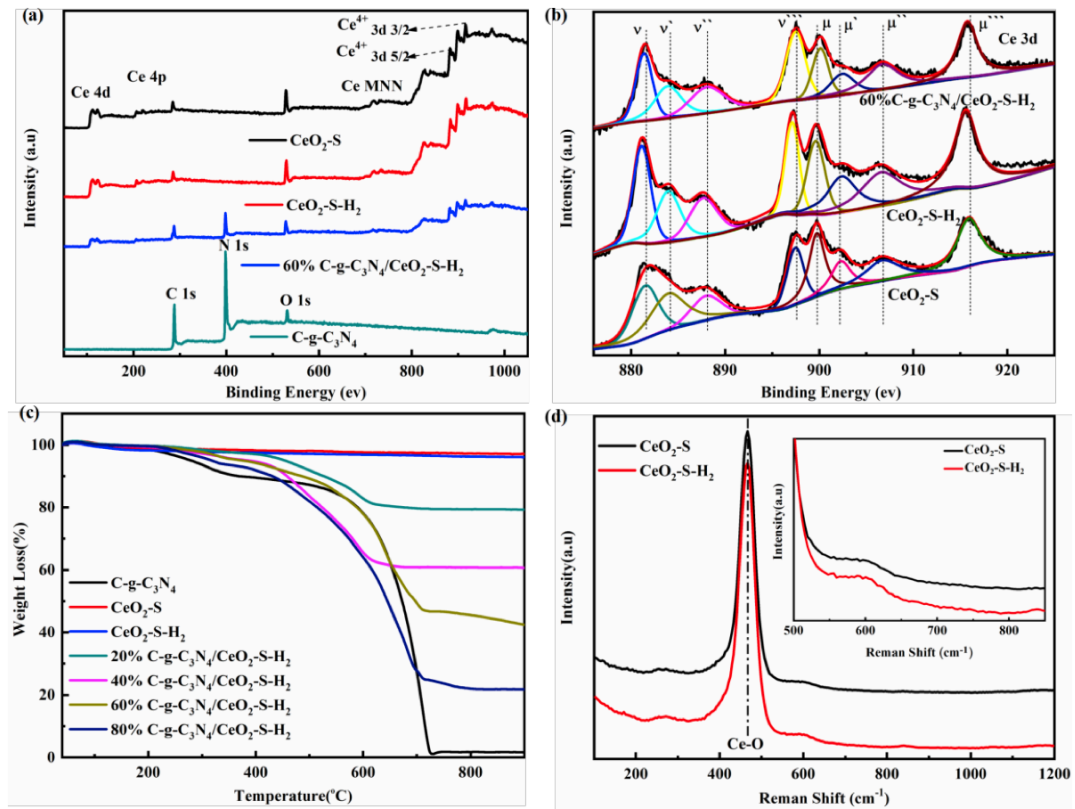


Fig.1 SEM images of C-g-C₃N₄ (a), CeO₂-S (b), and 60%C-g-C₃N₄/CeO₂-S-H₂ (c). TEM images (d, e) and element mapping images of 60%C-g-C₃N₄/CeO₂-S-H₂ (f, g, h, i, j)

To verify the effects of hydrogen treatment on surface defects, XPS spectra, TG analysis and Raman spectra were performed. As indicated in Fig.2a, C, N, O and Ce elements have been observed in the survey scanning spectra. Fig.2b shows high-resolution Ce 3d spectra. Ce 3d orbitals of CeO₂-S can be fitted into 8 peaks. Binding energies centered at 883.93 eV and 902.28 eV are due to Ce³⁺ states, and the other binding energy peaks are characteristics of Ce⁴⁺ states in CeO₂ [6]. The ratio of Ce³⁺ to Ce⁴⁺ in CeO₂-S is 28.2%, while it is 32.08% in CeO₂-S-H₂, which shows that oxygen vacancy content increases after hydrogen treatment. For CeO₂-S-H₂ and 60%C-g-C₃N₄/CeO₂-S-H₂, the position of Ce 3d peak has slightly changed due to the varied chemical environment. The other high-resolution XPS spectra of C1s, N1s and O1s can be found in Fig.S2. In Fig.2c, pristine C-g-C₃N₄ sample has mass loss at about 340 °C due to carboxyl groups decomposition, which is consistent with FTIR results in Fig.S3. Mass loss of CeO₂-S is relatively higher than that of CeO₂-S-H₂ due to oxygen escaping from lattice at

1 high temperature. Compared with pure C-g-C₃N₄, the introduction of CeO₂-S-H₂ has resulted in
 2 decomposition temperature decrease for C-g-C₃N₄/CeO₂-S-H₂ heterojunction. Fig.2d shows Raman
 3 spectra of CeO₂-S and CeO₂-S-H₂. The sharp characteristic peak at 460 cm⁻¹ corresponds to F2g
 4 vibration mode (Ce-O), while the weak peak at 600 cm⁻¹ is caused by oxygen vacancy [7]. The peak
 5 intensity of CeO₂-S-H₂ at 600 cm⁻¹ is higher than that of CeO₂-S, which further proves that hydrogen
 6 treatment has led to the increase of oxygen vacancy in CeO₂ lattice.
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13 Fig.2 Survey scanning spectra (a) and high-resolution Ce 3d spectra (b) of CeO₂-S, CeO₂-S-H₂, and
 14 60% C-g-C₃N₄/CeO₂-S-H₂. TG curves of C-g-C₃N₄, CeO₂-S, CeO₂-S-H₂ and C-g-C₃N₄/CeO₂-S-H₂
 15 heterojunctions (c) and Raman spectra of CeO₂-S and CeO₂-S-H₂ samples (d)
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43 Fig.3a shows CIP degradation curves. CIP degradation efficiency of 60% C-g-C₃N₄/CeO₂-S-H₂
 44 reaches 78.5% within 120 min, which are 3 times, 7.48 times and 2.34 times of that of pristine
 45 C-g-C₃N₄ (26.1%), CeO₂-S (10.5%) and CeO₂-S-H₂ (33.5%). Degradation rate constant of
 46 60% C-g-C₃N₄/CeO₂-S-H₂ is 5.027, 15.347 and 3.916 times of that of C-g-C₃N₄, CeO₂-S and CeO₂-S-
 47 H₂ (Fig.3b). Fig.3c and 3d show CO and CH₄ yields on different photocatalysts. CO yields on
 48 C-g-C₃N₄, CeO₂-S, CeO₂-S-H₂ and 60% C-g-C₃N₄/CeO₂-S-H₂ are 7.904 μmol/g, 2.785 μmol/g, 11.040
 49 μmol/g and 19.032 μmol/g, while CH₄ yields are 0.261 μmol/g, 5.139 μmol/g, 11.211 μmol/g and
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11.997 $\mu\text{mol/g}$. Especially, CO_2 reduction on $\text{CeO}_2\text{-S-H}_2$ is much better than $\text{CeO}_2\text{-S}$, which may be related to the increase of oxygen vacancy content. Interestingly, CH_4 yields on $\text{C-g-C}_3\text{N}_4$ is negligible. However, 60% $\text{C-g-C}_3\text{N}_4/\text{CeO}_2\text{-S-H}_2$ exhibits the highest CH_4 yields in 8 h, demonstrating heterojunction has advantages of both single components.

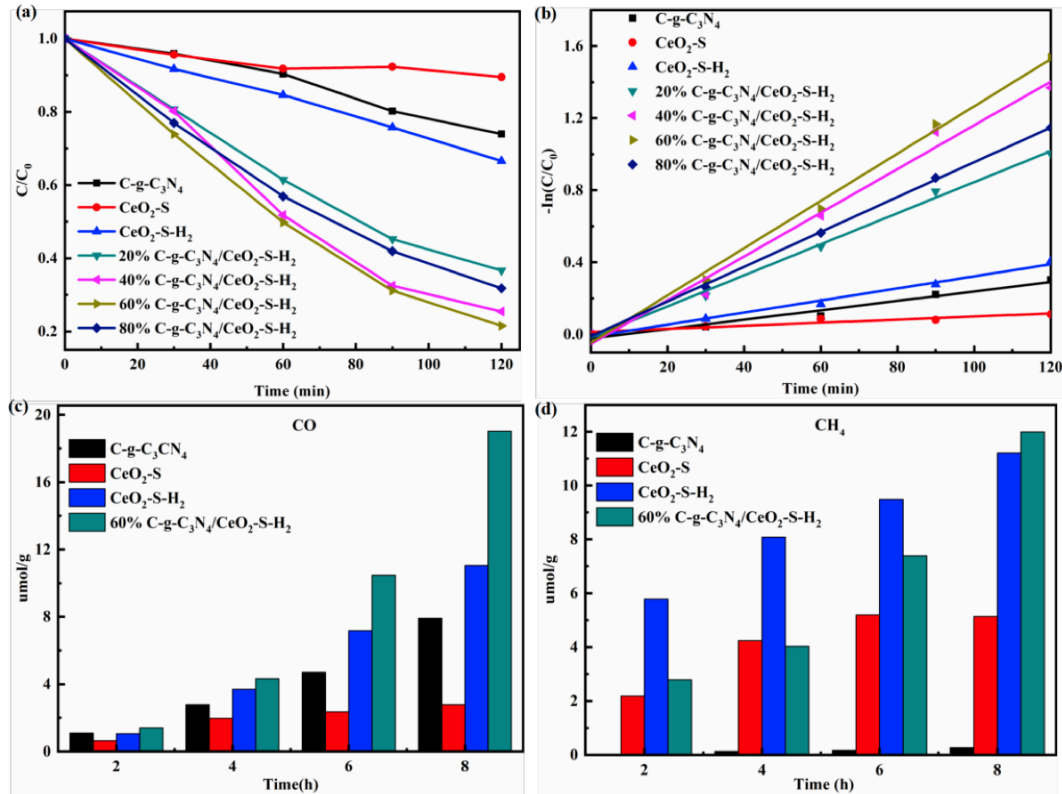


Fig.3 CIP degradation curves (a), first-order reaction kinetics curves (b), CO yields (c) and CH_4 yields (d) using $\text{C-g-C}_3\text{N}_4$, $\text{CeO}_2\text{-S}$, $\text{CeO}_2\text{-S-H}_2$ and $\text{C-g-C}_3\text{N}_4/\text{CeO}_2\text{-S-H}_2$ samples

Charges transfer and separation is of significance for photocatalytic activity enhancement. In Fig.4a, 60% $\text{C-g-C}_3\text{N}_4/\text{CeO}_2\text{-S-H}_2$ heterojunction displays the strongest photocurrent response. Accordingly, its semicircular diameter of Nyquist curve is the smallest as depicted in Fig.S4. Similarly, it shows the lowest photoluminescence intensity (Fig.4b). The corresponding transient PL was also depicted in Fig.S5. All these results demonstrate that heterojunction has enhanced charges separation efficiency. More charges will participate in the reaction. In Fig.4c, trapping experiments were carried out using 60% $\text{C-g-C}_3\text{N}_4/\text{CeO}_2\text{-S-H}_2$ as photocatalyst for CIP degradation. 1 mmol potassium iodide (KI), 1 mmol isopropanol (IPA) and nitrogen (N_2) were used as h^+ , $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ scavengers. It can be observed that $\bullet\text{OH}$ is the most important active species involved in CIP degradation. h^+ is one of the major active species, which can seriously suppress heterojunction activity. However, $\bullet\text{O}_2^-$ is not a major

active species.

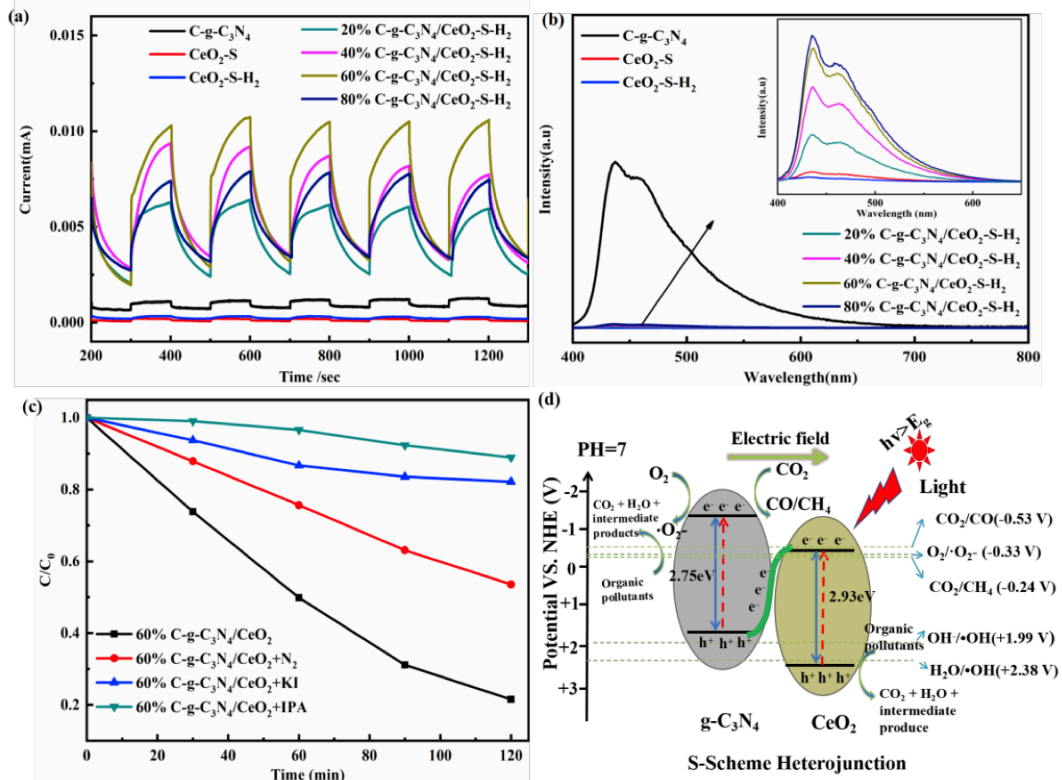


Fig.4 Transient photocurrent responses (a) and PL spectra of C-g-C₃N₄, CeO₂-S, CeO₂-S-H₂,

C-g-C₃N₄/CeO₂-S-H₂ heterojunction. Trapping experiments of CIP degradation by

60% C-g-C₃N₄/CeO₂-S-H₂ heterojunction (c) and proposed photocatalytic mechanism

Band gaps of C-g-C₃N₄ and CeO₂-S-H₂ have been calculated as 2.75 eV and 2.93 eV from UV-Vis DRS spectra (shown in Fig.S6). According to the Mulliken's electronegativity theory formula [8], VB and CB positions of C-g-C₃N₄ and CeO₂-S-H₂ are +1.615 eV, -1.135 eV and +2.535 eV, -0.395 eV. As O₂/•O₂⁻ reduction potential is -0.33 V (NHE, pH=7), C-g-C₃N₄ is more favorable for •O₂⁻ radicals formation due to its more negative CB potential. On the other hand, VB potential of CeO₂-S-H₂ is more positive than H₂O/•OH (+2.38 V vs. NHE) and OH/•OH (+1.99 V vs. NHE). Therefore, the photogenerated h⁺ can react with H₂O molecules or OH⁻ to produce •OH radicals. In contrast, C-g-C₃N₄ cannot generate •OH radicals under the same conditions. Thus, an S-scheme photocatalytic mechanism is proposed in Fig.4d [2, 9]. For CO₂ reduction, CB potential of C-g-C₃N₄ is more negative than the potential required for CO/CO₂ (-0.53 V) and CH₄/CO₂ (-0.24 V) conversions. Therefore, it is easy to reduce CO₂ to CO or CH₄. In CO₂ reduction process, H₂O is firstly oxidized to H⁺ and O₂ by holes. Meanwhile, CO₂ molecules are reduced to CO and CH₄ with the aid of H⁺ and electrons. It should be

1 noted that oxygen vacancy in CeO₂-S-H₂ can be used as electrons capture centers. As a result, electrons
2 enrichment improves the kinetic conditions of CO₂ reduction, especially for CH₄ production. At the
3 same time, oxygen vacancy can adsorb and activate CO₂ molecules, thus 2D/2D C-g-C₃N₄/CeO₂-S-H₂
4 heterojunction exhibits high CO and CH₄ yields in contrast to single components. In addition, Ce⁴⁺ in
5 CeO₂-S-H₂ can enhance electrons capture to form Ce³⁺, so as to promote charges separation and
6 significantly improve photocatalytic activity.
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10 **4 Conclusions**

11 In conclusion, C-g-C₃N₄ have been compounded with hydrogen treated flaky CeO₂-S-H₂ to
12 construct 2D/2D C-g-C₃N₄/CeO₂-S-H₂ heterojunction. In contrast to pure components,
13 60%C-g-C₃N₄/CeO₂-S-H₂ exhibited the highest activity for CIP degradation and CO₂ reduction.
14 Radicals trapping experiments showed •OH and h⁺ were the two major active species in CIP
15 degradation. The introduction of oxygen vacancy in CeO₂-S-H₂ has greatly enhanced CH₄ yields as it
16 can be used as electron capture centers and promoted charges separation efficiency. Possible S-scheme
17 mechanism of C-g-C₃N₄/CeO₂-S-H₂ was proposed.
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