

Strain Engineering in Amino-Confined CdS Enables Kinetically Coupled Methanol and Ammonia Oxidation for Photocatalytic Formamide Synthesis

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Article

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Abstract

Photocatalytic synthesis of formamide (FA) through C–N bond construction from carbon and nitrogen-containing small molecules offers a sustainable route for converting solar energy into value-added chemicals. However, selective C–N coupling is often limited by mismatched reaction kinetics between carbon and nitrogen substrates. Here, we develop a CdS–diethylenetriamine (CdS – D) composite with an amino-confined, compressively strained interface for FA synthesis from methanol and ammonia. Local strain promotes methanol C–H activation, while surface amino groups transiently retain methanol-derived species near the interface, improving their temporal overlap with nitrogen-derived intermediates and favoring productive C–N coupling over competing pathways. CdS – D achieves an FA production rate of $8.51 \text{ mmol g}^{-1} \text{ h}^{-1}$ with 84.47% selectivity, 49 times that of pristine CdS, without cocatalysts or external oxidants. This work elucidates how amino confinement and compressive strain mitigate the kinetic disparity between methanol and ammonia oxidation and promote productive interfacial radical conversion, offering a viable strategy for the selective photocatalytic synthesis of value-added amides from simple molecular feedstocks.

Introduction

C–N containing compounds are indispensable building blocks for pharmaceuticals, agrochemicals, polymers and nitrogen containing fine chemicals¹. Formamide (FA), as the simplest amide, is an important synthetic intermediate², but its industrial production still relies mainly on the thermocatalytic reaction of carbon monoxide with ammonia under elevated temperature and pressure, which entails fossil based feedstocks and substantial energy consumption. Photocatalytic FA synthesis from methanol and aqueous ammonia provides a more sustainable alternative^{3,4}, particularly because methanol can be derived from CO₂ valorization or biomass conversion. Nevertheless, this transformation remains challenging because methanol oxidation is highly sensitive to the activation pathway. In conventional thermochemical and strongly oxidative systems, methanol readily undergoes hydroxyl related activation and overoxidation to formaldehyde derived intermediates, which can subsequently participate in condensation and other side reactions with NH₃⁵. Although noble metal cocatalysts have often been introduced to promote methanol activation, their highly active metallic sites can also accelerate nonselective oxidation and hydroxyl hydrogen activation, diverting reactive intermediates into competing pathways and lowering the selectivity toward FA^{6–8}. The central challenge is therefore not simply to accelerate substrate oxidation, but to control the formation and subsequent evolution of short lived carbon and nitrogen derived intermediates, so that productive C–N coupling can outcompete undesired reaction channels^{9–13}.

Cadmium chalcogenides are promising platforms for photocatalytic C–N coupling because their valence-band characteristics favor hole driven substrate oxidation and the generation of reactive intermediates. Among them, cadmium sulfide (CdS) has been the most extensively investigated owing to its effective activation of small molecule substrates and readily regulatable surface structure^{14–16}. In

principle, CdS can oxidatively activate the C–H bond of methanol to form hydroxymethyl radicals ($\bullet\text{CH}_2\text{OH}$)^{17–20}. For instance, Chen and co-workers²¹ showed that hexagonal CdS nanorods promote selective methanol C–H cleavage to generate $\bullet\text{CH}_2\text{OH}$ radicals, enabling C–H methylation of N-heteroarenes with a yield of up to 94% for 2-methylquinoline without additional cocatalysts. Nevertheless, pristine CdS displays clear limitations in the more demanding conversion of methanol and ammonia to FA. This reaction requires methanol C–H activation, ammonia oxidation, radical evolution and product release to proceed within a coordinated interfacial sequence. Bare CdS cannot efficiently reconcile these elementary events, leading to competitive side reactions and mismatched availability windows of the carbon and nitrogen derived reactive species, and consequently to low FA formation efficiency (Fig. 1). Diethylenetriamine (DETA), a flexible polyamine containing multiple nitrogen donor sites, provides a molecular means of tuning the CdS surface without fully blocking its photoactive sites. Through Cd–N coordination, DETA can bind to undercoordinated surface Cd atoms and create localized polar domains. The exposed amino groups can act as hydrogen bond acceptors for the O–H group of methanol and of $\bullet\text{CH}_2\text{OH}$, which retains its hydroxyl group after C–H activation. These N–H $\cdots$ O interactions are expected to increase the local availability of methanol derived species and produce a transiently enriched carbon radical population near the interface^{22–24}. Such regulation could improve the temporal overlap between the slower forming carbon radicals and the more rapidly generated ammonia derived nitrogen species, thereby increasing the probability of productive C–N coupling (Fig. 1).

Inspired by these considerations, we construct CdS–DETA composite photocatalyst (CdS – D) for direct photocatalytic FA synthesis from methanol and aqueous ammonia without cocatalysts or external oxidants. In CdS – D, DETA is coordinatively anchored to surface Cd sites, forming discretely distributed amino-rich domains and simultaneously perturbing the local Cd–S coordination environment to induce lattice contraction and compressive strain. The optimized CdS – D achieves an FA production rate of $8.51 \text{ mmol g}^{-1} \text{ h}^{-1}$ with a selectivity of 84.47%, which is 49 times higher than that of pristine CdS. Structural and photoelectrochemical analyses show that Cd–N anchoring and lattice compression construct a bifunctional interface, in which strain-perturbed CdS surface sites promote photogenerated hole driven substrate activation and hole utilization, while the exposed amino groups provide local adsorption and confinement sites that enhance the interfacial availability of reactive species. Time-dependent spin trapping electron paramagnetic resonance spectroscopy (EPR) identifies the rapid early formation of methanol derived radicals over CdS – D, followed by their accelerated turnover. Femtosecond transient absorption spectroscopy (fs-TAS) further shows that methanol and ammonia mediated hole transfer processes become kinetically coupled at the modified interface, narrowing the disparity between the two substrate oxidation pathways. The earlier evolution of C–N coupling-related intermediates observed by in situ Fourier transform infrared spectroscopy (FTIR) links this kinetic regulation to productive bond formation. Density functional theory (DFT) calculations are used as complementary evidence to show that DETA modification moderates the adsorption of key species. This work highlights radical generation kinetic regulation as a useful perspective for photocatalytic C–N bond formation and provides an amino confined and strain regulated strategy for selective FA synthesis from simple small molecule feedstock^{25,26}.

Results and Discussion

Photocatalyst Screening toward FA Synthesis

As depicted in Fig. 2a, CdS – D hybrids were prepared through a one-step microwave assisted route. Initially, a series of representative semiconductor photocatalysts, including TiO_2 , C_3N_4 , CeO_2 , CdSe, and CdS NR, were systematically evaluated for their photocatalytic performance toward FA synthesis. These candidates were selected primarily for their structural stability in the H_2O – CH_3OH – NH_3 mixed solvent system under the employed reaction conditions. The photocatalytic screening experiments were conducted under an argon atmosphere to eliminate potential interference from ambient oxygen, and the corresponding results are summarized in (Fig. 2b and Supplementary Figs. 1–2). In Supplementary Fig. 3, FA was first qualitatively identified by ^1H NMR spectroscopy, with disodium maleate used as the internal standard and its characteristic peak located at approximately 6.0 ppm. The characteristic resonance signal of FA appeared at around 8.1 ppm. Subsequent yield evaluation of FA was mainly performed by high performance liquid chromatography (HPLC), and the corresponding standard curve is presented in Supplementary Fig. 4. Notably, conventional cadmium sulfide nanorods (CdS NR) exhibit intrinsic photocatalytic activity toward FA synthesis. Given that hybrid structures can boost efficient charge separation and transfer^{27,28}, we hybridized CdS with various solvent ligands to further optimize its photocatalytic performance (Fig. 2c and Supplementary Figs. 5–7). The catalytic activities of different composite photocatalysts and pristine CdS reveal a pronounced enhancement upon DETA functionalization, with the activity of CdS – D strongly dependent on the DETA loading concentration (Fig. 2d). In contrast, introducing free DETA into the pristine CdS reaction system affords no appreciable improvement, indicating that the activity enhancement arises from the anchored DETA derived interfacial structure rather than from free DETA in solution²⁹. Specifically, CdS – D achieves a FA production rate of $8510.24 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is approximately 49 times higher than that of pristine CdS ($173.72 \mu\text{mol g}^{-1} \text{h}^{-1}$). This observation is further corroborated by quantitative ^1H NMR analysis (Supplementary Fig. 8). The remarkable enhancement in FA production highlights the unique interfacial regulation achieved by DETA hybridization on CdS, rather than a simple additive effect of organic amine modification. The CdS matrix plays an indispensable role in providing suitable visible light absorption, redox capability and photogenerated holes for initiating methanol and ammonia oxidation, while DETA derived amino groups cooperate with the CdS surface to construct an amino-confined interface. Such an interface promotes methanol derived radical generation and increases the probability of selective coupling with ammonia-derived radicals (Supplementary Fig. 9). Benefiting from this synergistic interfacial regulation, CdS – D achieves a FA selectivity of 84.47%, together with a markedly enhanced FA formation rate. Based on these results, CdS – D was selected as the representative photocatalyst for subsequent mechanistic investigation.

A series of control experiments were then carried out to verify the photocatalytic nature and substrate dependence of FA formation (Fig. 2e,f). No detectable FA was produced in the absence of catalyst, under dark conditions, or when either CH_3OH or NH_3 was removed, confirming that light irradiation,

photocatalyst, methanol and ammonia are all indispensable for the reaction. These results also verify that CH_3OH and NH_3 serve as the carbon and nitrogen sources for FA formation, respectively. Further optimization of the methanol to ammonia molar ratio shows that the FA yield first increases and then decreases with increasing methanol proportion. This volcano type dependence suggests that an appropriate balance between methanol oxidation and ammonia oxidation is crucial for efficient C–N coupling. Excessive methanol may generate an overabundance of $\cdot\text{CH}_2\text{OH}$ species, which favors self-coupling pathways to ethylene glycol and thereby suppresses selective FA formation³⁰. The cycling stability of CdS – D was also evaluated, and approximately 90% of the initial FA production rate was retained after five consecutive reaction cycles totaling 10 h (Fig. 2g), demonstrating its favorable photocatalytic durability.

Structural Characterization

To elucidate the fundamental origin of the superior catalytic activity exhibited by the as synthesized CdS – D, a series of characterizations were performed to decipher its fine structural features. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images demonstrate that CdS – D possesses a sheet like structure with morphology similar to that of pristine CdS (Fig. 3a, b and Supplementary Fig. 10). X-ray diffraction (XRD) patterns show that CdS – D retains the hexagonal wurtzite CdS structure, while the diffraction peaks shift toward higher angles after DETA modification (Supplementary Fig. 11), indicating lattice contraction. High resolution transmission electron microscopy (HRTEM) further confirms this contraction, the (002) lattice spacing decreases from 0.338 nm for pristine CdS to 0.334 nm for CdS – D (Fig. 3c and Supplementary Fig. 12). Geometric phase analysis (GPA) mapping provides additional spatial evidence for local compressive strain (Fig. 3d,e). This compressive strain is attributed to the interaction between DETA derived amino groups and surface Cd sites during hybrid formation, which perturbs the local Cd–S coordination environment and induces lattice contraction near the aminated interface^{31–33}. Ultraviolet visible diffuse reflectance spectroscopy (UV–vis DRS) and Tauc plots reveal a blue shifted absorption edge and widened band gap after DETA modification (Supplementary Figs. 13 and 14), while Mott–Schottky analysis shows that the valence band of CdS – D shifts to a more positive potential (Supplementary Fig. 15). These structural and electronic changes endow CdS – D with enhanced oxidative capability, which is favorable for accelerating the otherwise sluggish methanol oxidation step. Elemental mapping confirms the homogeneous distribution of Cd, S, C, and N in CdS – D (Fig. 3f and Supplementary Fig. 16), supporting the successful construction of the hybrid interface. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) analyses further clarify the chemical nature of the aminated interface. The full survey XPS spectra (Supplementary Fig. 17) confirm the high purity of CdS – D and CdS samples, without the presence of any adventitious or impurity elements. Furthermore, the appearance of N 1s signals in CdS – D (Fig. 4c) and the distinct characteristic peaks of CdS – D observed at 3162 and 3302 cm^{-1} in the FTIR spectrum (Supplementary Fig. 18) confirm the presence of abundant amino groups on its surface, which effectively enhance the surface wettability and hydrophilicity of the

material (Supplementary Fig. 19) thus improving its dispersion stability in aqueous solution. Compared with CdS, the Cd 3d and S 2p peaks of CdS – D shift toward lower binding energies under dark conditions (Fig. 4a,b), indicating increased electron density around CdS after DETA modification. This shift is consistent with electron donation from the lone pair electrons of amino groups to surface Cd sites, suggesting strong interfacial electronic interaction. Under illumination, both Cd 3d and N 1s peaks shift to higher binding energies, revealing photoinduced charge redistribution at the CdS – D interface^{34–36}. Photoelectrochemical measurements, including photocurrent and electrochemical impedance spectroscopy (EIS) responses, further confirm improved charge separation and migration in CdS – D (Supplementary Figs. 20 and 21). X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses confirm that Cd remains predominantly divalent and that the intrinsic Cd–S coordination framework is largely preserved after DETA modification^{37,38} (Fig. 4d – e and Supplementary Figs. 22–23), while quantitative EXAFS fitting identifies an additional Cd–N coordination path in CdS–D³⁹, which appears as a subtle low R scattering feature owing to the low DETA loading and the predominance of the Cd–S coordination environment (Fig. 4f – i and Supplementary Fig. 24). Consistent with this assignment, the fitted Cd–N shell exhibits a coordination number of 1.8 and a bond distance of 2.23 ± 0.01 Å, providing quantitative evidence for the coordination anchoring of DETA at surface Cd sites. Meanwhile, the concomitant shortening of the Cd–S bond from 2.53 ± 0.01 Å in pristine CdS to 2.51 ± 0.01 Å in CdS – D indicates that Cd–N coordination perturbs the local Cd–S framework and induces compressive strain (Supplementary Table 1).

Reaction Mechanism Investigation

To explore the intrinsic photocatalytic mechanism for FA generation over CdS – D, a series of mechanistic experiments and operando characterizations were systematically performed. The roles of photoexcited charge carriers were first identified by scavenger experiments (Fig. 5a). The addition of AgNO₃ as an electron quencher slightly enhanced FA formation, while the hole scavenger Na₂S completely terminated the reaction. These results illustrate that the formation of FA is dominated by a hole driven oxidation pathway. Additionally, FA production was completely suppressed in the presence of 0.1 M 5,5-dimethyl-1-pyrroline N-oxide (DMPO), a widely used radical trapping reagent. This observation indicates that radical species serve as key intermediates in the photocatalytic synthesis of FA^{40–42}.

Control experiments using representative intermediates from conventional thermocatalytic pathways were performed to distinguish the genuine reaction route (Supplementary Table 2). Formaldehyde and formate were employed as alternative carbon sources, while ammonium salts, nitrite, and nitrate were used as alternative nitrogen sources. Although the HCHO/NH₃ system can produce FA under the tested conditions, its substantially lower activity than the CH₃OH/NH₃ system does not support a formaldehyde mediated condensation route as the dominant pathway. No target product was obtained from HCOO[–] or the tested inorganic nitrogen species, while the substrate omission controls confirm that free NH₃ is required as the nitrogen source for FA formation.

To identify the key radical intermediates in the reaction pathway, time-dependent spin-trapping EPR measurements were performed using DMPO as the spin trap in water, methanol, aqueous ammonia, and their mixed systems. In pure water, a characteristic 1:2:2:1 quartet signal was observed (Fig. 5b), which can be assigned to the DMPO-•OH adduct generated via hole-mediated water dissociation. In methanol solution under illumination, strong characteristic signals of DMPO-•R were detected (Fig. 5c). In addition, well resolved signals of DMPO-•R adducts and DMPO-•OH adducts were simultaneously observed for the two catalyst samples in the mixed system, demonstrating that the generation of hydroxyl radicals from water and the oxidation of methanol compete for photoinduced holes (Supplementary Fig. 25). Notably, intense methanol derived radical signals were observed over CdS - D at the initial stage of irradiation, followed by a pronounced attenuation after approximately 5 min. In contrast, the corresponding radical signals over pristine CdS emerged much more slowly and remained clearly detectable upon prolonged irradiation (Supplementary Fig. 26). This distinct rise and decay trend demonstrates that DETA modification accelerates the initial generation and subsequent transformation of methanol derived radicals, revealing that such radicals are transiently enriched within the amino modified interfacial region rather than accumulated persistently in the bulk solution⁴³⁻⁴⁶. Characteristic signals of the amino radical adduct DMPO-•NH₂ with a typical 16 line pattern were clearly observed in aqueous ammonia without catalysts under dark conditions (Figs. 5d and S27), indicating facile and rapid formation of •NH₂. In the ternary CH₃OH-NH₃-H₂O reaction system, the radical signals over CdS - D reached a maximum within 3 - 5 min and then decreased markedly, whereas those over pristine CdS continued to accumulate with prolonged irradiation. Together with the earlier formation of formamide in the CdS - D system, these observations suggest that methanol-derived radicals generated on the CdS - D surface participate more rapidly in subsequent interfacial reactions and are consequently consumed more quickly (Supplementary Fig. 28), further indicating that CdS - D facilitates the efficient conversion of radical intermediates toward the target product, whereas radicals generated on pristine CdS participate less efficiently in the subsequent reaction steps⁴⁷. Furthermore, no other well-resolved characteristic components assignable to DMPO-•NH₂ were observed in the mixed system, suggesting that nitrogen-containing reactive species may undergo rapid consumption, thereby preventing their accumulation to a detectable concentration under the reaction conditions, in agreement with the above results (Fig. 5e). To further verify that the introduction of -NH_x species promotes the selective activation of C-H bonds in methanol to generate •CH₂OH radicals during photocatalysis, Raman spectroscopy was employed to characterize the Raman shifts of chemical bonds for methanol molecules adsorbed on the catalyst surface under different conditions. Distinct vibrational shifts of C-H bonds were clearly resolved, with the symmetric stretching vibration at approximately 2845 cm⁻¹ and the antisymmetric stretching vibration at approximately 2955 cm⁻¹ (Supplementary Fig. 29). Rigorous spectral analysis demonstrated that pure CdS exhibited negligible shifts in the C-H bond peaks at 2845.5 and 2953.6 cm⁻¹ compared with pristine methanol. In contrast, a remarkable red shift of the C-H stretching vibration was observed for methanol adsorbed on amino-modified CdS - D. Furthermore, the peak positions remained unchanged at 2834.4 and 2943.8 cm⁻¹ without further shift after introducing free ammonia into the system. This confirms that methanol C-H bond weakening occurs upon adsorption on CdS - D,

driven by surface amino groups rather than free ammonia. Dissolved ammonia primarily participates in subsequent coupling reactions and does not further alter the methanol bonding environment. These EPR and Raman results demonstrate that CdS – D provides a rich amino interfacial microenvironment for localized methanol C–H activation and radical generation.

The fs-TAS was employed to investigate substrate dependent carrier relaxation and interfacial charge transfer dynamics over CdS – D and pristine CdS^{48,49}. The two dimensional transient absorption maps and delay dependent spectra show that CdS – D exhibits a pronounced ground state bleaching feature at 475 nm in H₂O–CH₃OH, H₂O–NH₃ and H₂O–CH₃OH–NH₃ media (Supplementary Figs. 30–32), whereas pristine CdS displays its dominant bleaching feature at 530 nm under the corresponding reaction conditions (Supplementary Figs. 33–35). The kinetic traces extracted at the respective bleaching maxima were fitted to evaluate the substrate dependent relaxation behavior. For CdS – D, the bleaching recovery is fastest in aqueous NH₃ and slowest in CH₃OH, while the CH₃OH/NH₃ mixed medium exhibits an intermediate decay behavior between those of the two individual substrate systems (Fig. 5f and Supplementary Table 3). The faster recovery in NH₃ reflects more rapid ammonia mediated hole consumption, whereas the slower relaxation in CH₃OH is consistent with the greater kinetic difficulty of methanol C–H activation. The intermediate response in the mixed medium indicates that methanol and ammonia mediated hole transfer processes are both involved and become kinetically coupled at the amino modified CdS – D interface⁵⁰. This interfacial coupling reduces the temporal disparity between rapid ammonia oxidation and comparatively sluggish methanol activation, in line with the rapid generation, transient interfacial enrichment and subsequent conversion of methanol derived radicals observed by EPR. In contrast, although NH₃ also induces faster bleaching recovery than CH₃OH over pristine CdS, the decay profile of the CH₃OH/NH₃ mixed system remains close to that measured in CH₃OH rather than displaying a distinct intermediate response (Supplementary Fig. 36). The mixed reaction over pristine CdS therefore remains predominantly governed by the slower methanol oxidation process, consistent with the delayed formation and prolonged accumulation of methanol derived radicals revealed by EPR. The scavenger experiments, EPR spectra and fs-TAS results collectively support a radical mediated pathway for FA formation over CdS – D (Fig. 5g). Upon irradiation, methanol is oxidatively activated by photoirradiated holes to generate •CH₂OH radicals, while ammonia oxidation provides short lived nitrogen derived reactive species. The amino confined, compressively strained interface promotes methanol C–H activation and improves the temporal overlap between the carbon and nitrogen derived intermediates. Their subsequent interfacial coupling produces an aminomethanol intermediate, which undergoes further dehydrogenation to yield FA.

In situ FTIR spectroscopy was employed to compare the dynamic evolution of surface intermediates over CdS – D and pristine CdS during photocatalytic C–N coupling^{51,52} (Fig. 6a, Supplementary Fig. 37 and Supplementary Table 4). Upon irradiation, the C–O stretching vibration of adsorbed methanol appeared at 1013 cm^{–1}, together with several progressively evolving bands in the 1000 – 1800 cm^{–1} fingerprint region. Over CdS – D, the bands at 1388 and 1280 cm^{–1}, assigned to the O–H deformation of

*CH₂OH related species and the N–H wagging vibration of adsorbed *NH₂ species, respectively, developed rapidly at the early stage of irradiation⁵³. The C–N stretching band at 1436 cm^{−1} emerged shortly thereafter and increased continuously, accompanied by the growth of the amide C = O vibration of FA at 1640 cm^{−1}. The early onset and rapid increase of these C–N containing species coincide with the initial rise and subsequent attenuation of the methanol derived radical signals observed by time dependent EPR, suggesting that the transiently enriched carbon centered species over CdS – D are rapidly involved in subsequent interfacial conversion. In comparison, pristine CdS exhibited a distinctly delayed and weaker evolution of the C–N and FA related bands, despite the prolonged persistence of methanol derived radical signals, indicating slower conversion of the accumulated radical species into C–N containing intermediates^{54,55}. Moreover, no discernible C = O vibration attributable to molecular formaldehyde was detected in the 1720 – 1750 cm^{−1} region for either catalyst, indicating that aldehydic formaldehyde did not accumulate to a detectable level during the reaction.

To deeply explore the intrinsic mechanism of the enhanced photocatalytic FA synthesis via methanol/ammonia co-oxidation over CdS – D, DFT calculations were performed. Comprehensive comparisons between pristine CdS and CdS – D were conducted from the perspectives of interfacial electron transfer, reactant adsorption behavior, charge distribution of key intermediates, energy barriers of elementary reactions, and the nature of C–N bond formation^{56–59}. Bader charge analysis shows that the electron transfer amount of CH₃OH on CdS – D is 0.105 e, which is much higher than that on pristine CdS⁶⁰ (Supplementary Fig. 38). This indicates that DETA modification effectively promotes the activation and oxidation of methanol on the catalyst surface. Similarly, NH₃ exhibits an identical enhanced electron transfer trend on the CdS – D surface (Supplementary Fig. 39). Adsorption energy calculations reveal that pristine CdS possesses excessively strong adsorption toward CH₃OH and NH₃, with adsorption energies of − 2.36 and − 3.22 eV, respectively. The reactants can spontaneously form stable and rigid adsorption configurations on pristine CdS. Nevertheless, such over strong adsorption hinders the continuous progression of catalytic reactions, restricts intermediate transformation and product desorption, occupies active sites, and impedes reaction kinetics, thereby inhibiting the stable and efficient production of FA. After DETA modification, the adsorption energies of CH₃OH and NH₃ on CdS – D are appropriately tuned to − 0.38 and − 0.53 eV, respectively (Supplementary Fig. 40). While maintaining stable reactant adsorption, the optimized adsorption strength provides favorable interfacial and kinetic conditions for subsequent dehydrogenation, radical coupling, and FA desorption^{61–63}. In addition, the pristine CdS system exhibits two high energy barriers, the energy barrier for methanol dehydrogenation to •CH₂OH is 2.19 eV, and that for ammonia dehydrogenation to •NH₂ reaches 2.60 eV, which severely limits the overall reaction efficiency. Amino functionalization significantly optimizes the reaction energy barriers. The methanol dehydrogenation barrier decreases to 1.80 eV, while the ammonia dehydrogenation barrier is sharply reduced to 1.32 eV. The prominently lowered energy barriers facilitate the conversion of adsorbed reactants into key active radical intermediates, providing superior kinetic advantages for subsequent radical coupling, C–N bond construction, and FA generation (Fig. 6b). The electronic origin of directional C–N coupling was further explored by analyzing the charge distribution of

•CH₂OH and •NH₂ intermediates. On pristine CdS, the C atom of •CH₂OH carries a positive charge of + 0.63 e, whereas the N atom of •NH₂ possesses a negative charge of – 0.67 e. Such charge polarization is further strengthened on CdS – D, where the C center becomes more electron deficient (+ 0.73 e) and the N center becomes more electron rich (– 0.78 e)⁶⁴ (Supplementary Fig. 41). The improved electrophilic nucleophilic matching promotes highly selective C–N coupling at the strained amino functionalized interface. Integrated crystal orbital Hamilton population (ICOHP) analysis was employed to quantify the C–N bonding strength. A larger –ICOHP value corresponds to stronger orbital interaction and more stable bonding. The CdS – D system delivers a higher –ICOHP value for the newly formed C–N bond compared with pristine CdS, demonstrating stronger orbital coupling and more stable bond configuration (Supplementary Fig. 42). Consistent with the Bader charge results, DETA modification strengthens the charge polarization of radical intermediates before coupling and reinforces orbital interaction after C–N bond formation.

Conclusion

In summary, an amino confined, compressively strained CdS – D photocatalyst was developed for the direct synthesis of FA from methanol and aqueous ammonia without cocatalysts or external oxidants. Cd–N coordination simultaneously creates localized amino-rich domains and perturbs the Cd–S framework, enabling CdS – D to achieve an FA production rate of 8.51 mmol g^{–1} h^{–1} with a selectivity of 84.47%, corresponding to a 49-fold enhancement over pristine CdS. Mechanistic investigations reveal that the enhanced activity does not originate from prolonged accumulation of detectable radicals. Instead, compressive strain facilitates the early activation of methanol C–H bonds, while amino confinement increases the transient interfacial availability of methanol derived carbon radicals and promotes their timely conversion with nitrogen derived reactive species. The combined EPR, fs-TAS, and in situ FTIR results associate this regulated formation consumption behavior with improved kinetic coupling of the two substrate oxidation pathways and earlier interfacial C–N bond formation. These findings reveal that selective photocatalytic C–N coupling is governed not merely by radical generation, but by the coordinated regulation of intermediate formation, transient interfacial availability, and subsequent conversion. The mechanistic insights into amino confinement, strain assisted substrate activation, and intermediate regulation provide a useful basis for developing selective solar driven routes to high value nitrogen containing chemicals from simple molecular feedstocks.

Methods

Chemicals.

Unless otherwise stated, all reagents were of analytical grade and were used as received without further purification.

Catalyst preparation

CdS – D. A mixture of 24 mL diethylenetriamine (DETA) and 12 mL ultrapure water was prepared, followed by the addition of 0.164 g $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and 0.128 g sublimed sulfur. After stirring for 2 h, the suspension was heated in a microwave reactor at 80°C for 30 min. The product was washed three times with absolute ethanol and ultrapure water, collected by centrifugation and freeze-dried.

CdS. Pristine hexagonal CdS was obtained by hydrothermal removal of the amine groups from CdS – D. CdS – D (50 mg) was dispersed in 50 mL water and treated in a 100 mL Teflon-lined stainless steel autoclave at 120°C for 12 h. After cooling, the product was collected by centrifugation, washed with water and ethanol, and freeze-dried overnight.

Photocatalytic formamide synthesis and product analysis

Photocatalytic formamide synthesis was carried out in a custom quartz tube. Photocatalyst (5 mg) was ultrasonically dispersed in 20 mL of a $\text{CH}_3\text{OH}/\text{NH}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}$ mixture with a volume ratio of 1:2:37. The reactor was purged with Ar 20 times using a PLAMAC1005 multi-gas controller and irradiated with a 300 W xenon lamp (Microsolar 300, Beijing Perfectlight Technology Co. Ltd) at an intensity of 3.17 W cm^{-2} . The reaction temperature was maintained at 20°C using circulating cooling water, and the standard irradiation time was 2 h.

Gas products were analyzed using a Shimadzu GC-2014C gas chromatograph equipped with a 5 Å molecular-sieve column and a thermal-conductivity detector, with N_2 as the carrier gas. Liquid organic products were qualitatively identified by ^1H NMR spectroscopy, and formamide was quantified by HPLC using a calibration curve constructed from standard solutions in the range of 5-100 mg L^{-1} . The calculation procedures for the formamide production rate and carbon selectivity are provided in the Supplementary Information.

In situ ATR–FTIR spectroscopy

In situ liquid attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy was performed using an INVENIO R Fourier Transform Infrared Spectrometer (Bruker) equipped with an MCT detector. CdS – D (10 mg) was dispersed in 1 mL deionized water containing 50 μL Nafion, and 50 μL of the suspension was drop-cast onto a silicon crystal and dried at room temperature. A 2 mL reaction solution containing CH_3OH , NH_3 and H_2O at a volume ratio of 1:2:37 was introduced into the ATR cell under an air atmosphere. After adsorption–desorption equilibrium, the system was irradiated with a 300 W Xe lamp, and time-dependent spectra were collected over 1000 – 4000 cm^{-1} .

Femtosecond transient absorption spectroscopy

Femtosecond transient absorption spectroscopy (fs-TAS) was performed in transmission mode using a HELIOS transient absorption spectrometer (Ultrafast Systems, s.r.o.). Samples were excited with a 400

nm pulse generated by an Apollo-T optical parametric amplifier pumped by a Solstice ACE laser source (pulse width < 100 fs). A white-light continuum probe covering 420 – 800 nm was used, with a temporal resolution of approximately 150 fs. For each measurement, 20 mg of CdS – D or CdS was dispersed in 20 mL of H₂O–CH₃OH–NH₃ (0.5 mL CH₃OH, 1.0 mL NH₃·H₂O and 18.5 mL H₂O), H₂O–CH₃OH (0.5 mL CH₃OH and 19.5 mL H₂O), or H₂O–NH₃ (1.0 mL NH₃·H₂O and 19.0 mL H₂O). The suspensions were transferred to sealed optical cells and purged with Ar before measurement. Kinetic traces were extracted at 475 nm for CdS – D and 530 nm for pristine CdS.

Data availability

The data supporting the findings of this study are available within the Article and its Supplementary Information. Source data are provided with this paper.

Declarations

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Figures

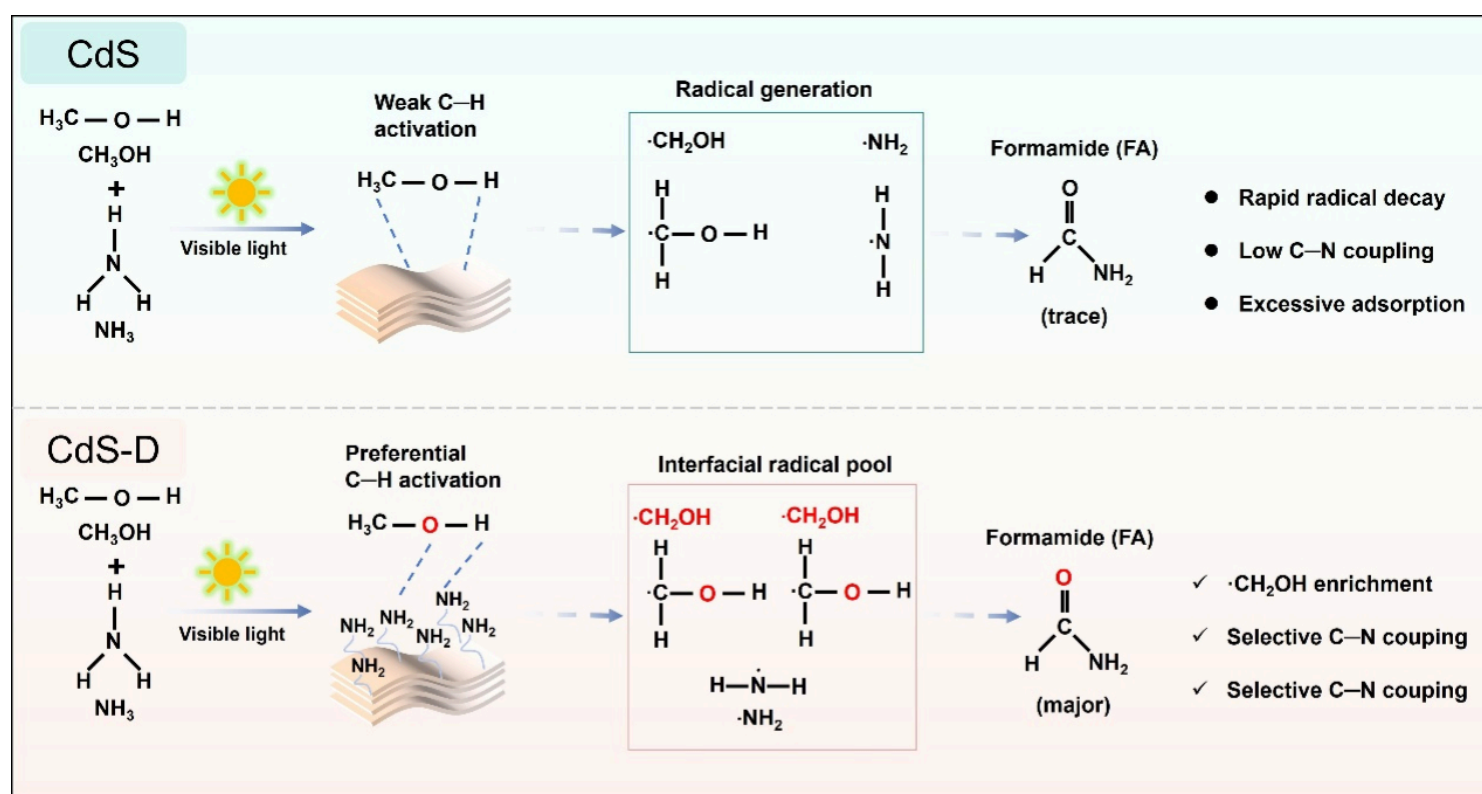


Figure 1

Conceptual illustration of oxidation-kinetic mismatch and its interfacial regulation. Proposed reaction processes for methanol and ammonia conversion over pristine CdS and CdS-D, illustrating the kinetic disparity between methanol-derived carbon species and ammonia-derived nitrogen species and its mitigation at the amino confined, strained CdS-D interface.

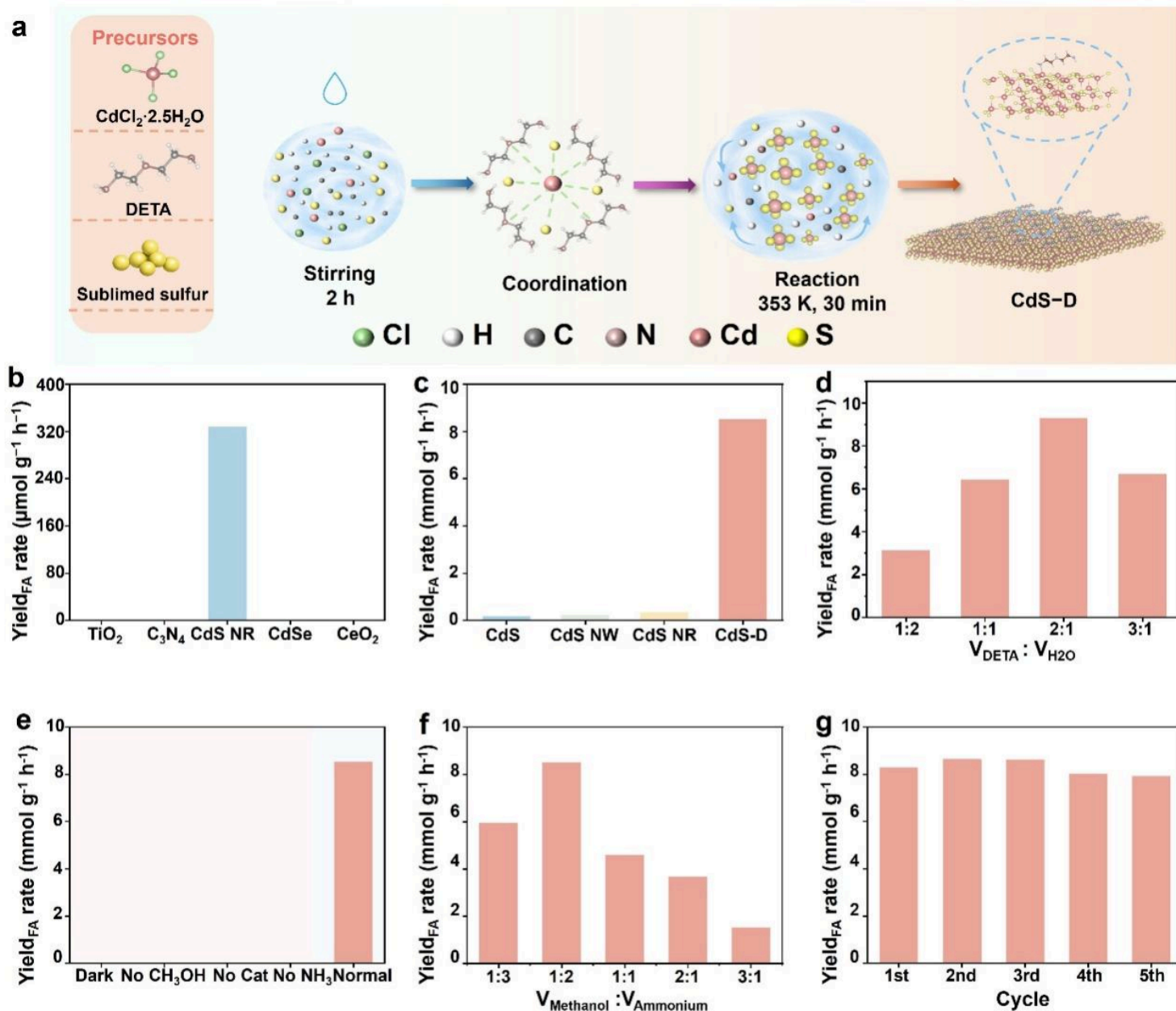


Figure 2

Photocatalytic performance and reaction condition evaluation of CdS-D for formamide synthesis. a, Schematic representation of the synthesis of CdS-D. b, FA production rates over representative photocatalysts. c, Photocatalytic FA synthesis over ligand modified CdS samples. d, Effect of the DETA loading on FA production over CdS-D. e, Blank control experiments for FA synthesis in the absence of NH₃, CH₃OH or light. f, Effect of the CHOH₃/NH₃ ratio on FA production over CdS-D. g, Cycling stability of CdS-D.

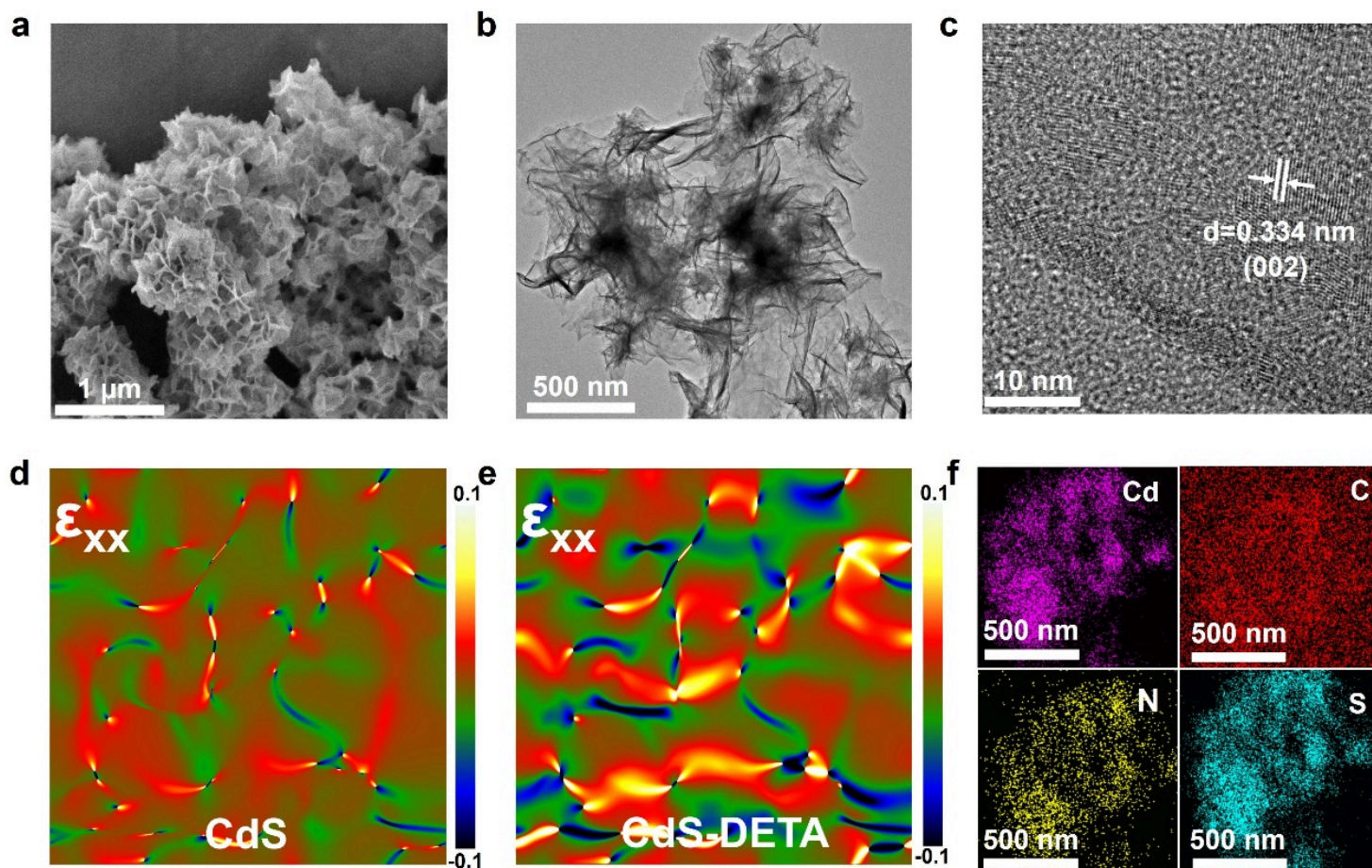


Figure 3

Morphological characteristics and compressive strain features of CdS-D. a,b, SEM and TEM images of CdS-D, respectively. c, High resolution TEM image of CdS-D. d,e, Selected lattice regions and corresponding geometric phase analysis (GPA) strain maps of pristine CdS and CdS-D, respectively. f, Elemental mapping of CdS-D.

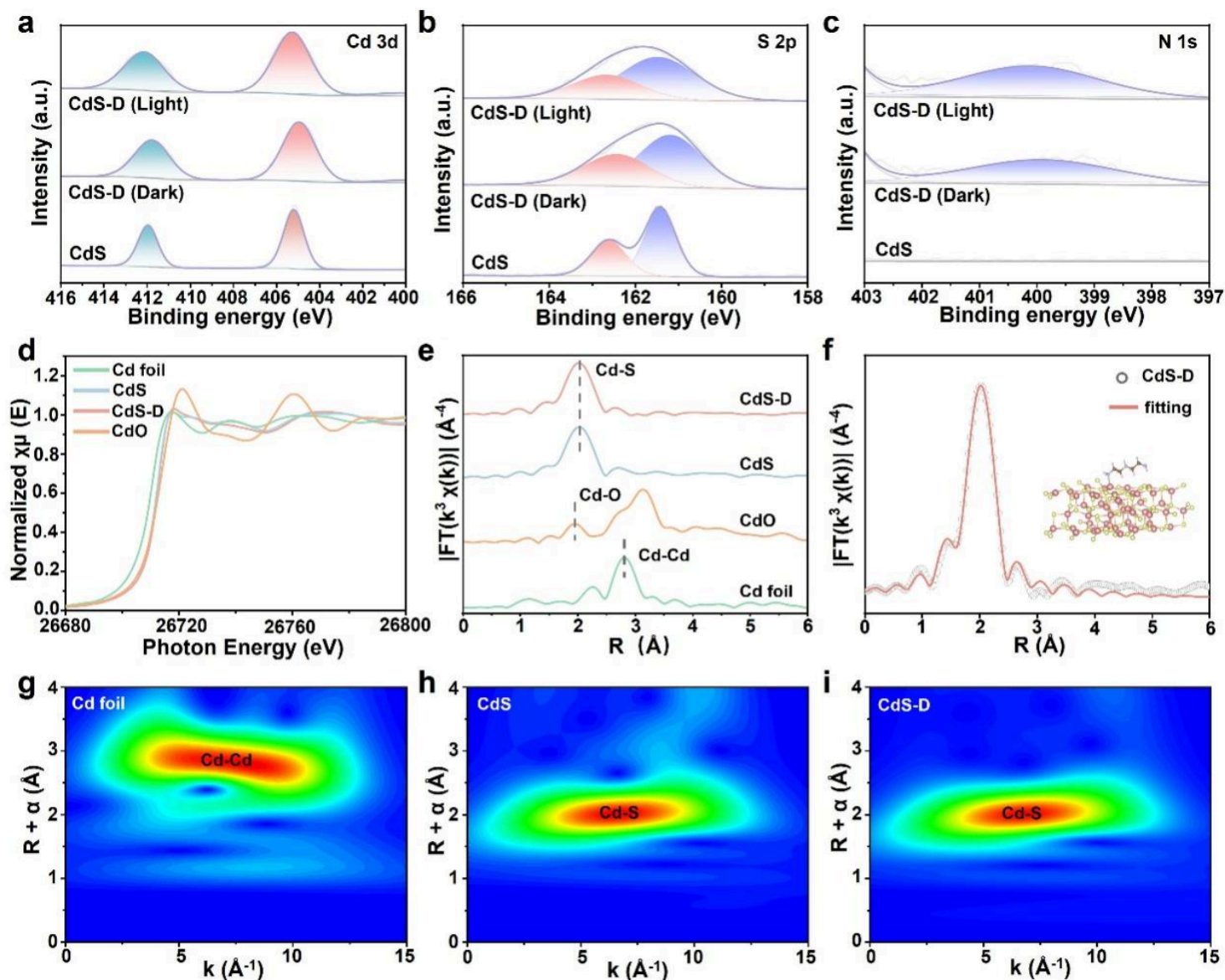


Figure 4

Interfacial electronic structure and local coordination environment of CdS-D. **a–c**, In situ irradiated X-ray photoelectron spectroscopy (ISI-XPS) spectra of Cd 3d, S 2p and N 1s, respectively, for CdS-D under dark and illuminated conditions. **d**, Normalized Cd L₃-edge X-ray absorption near edge structure (XANES) spectra of the reference samples and CdS-D. **e**, k^2 -weighted Fourier transformed Cd L₃-edge extended X-ray absorption fine structure (EXAFS) spectra in R space for Cd foil, CdS-D, CdS and CdO. **f**, Experimental and fitted Cd L₃-edge EXAFS spectra of CdS-D in R space. **g–i**, Wavelet transform analysis of the k^2 -weighted Cd L₃-edge EXAFS spectra of Cd foil, CdS and CdS-D, respectively.

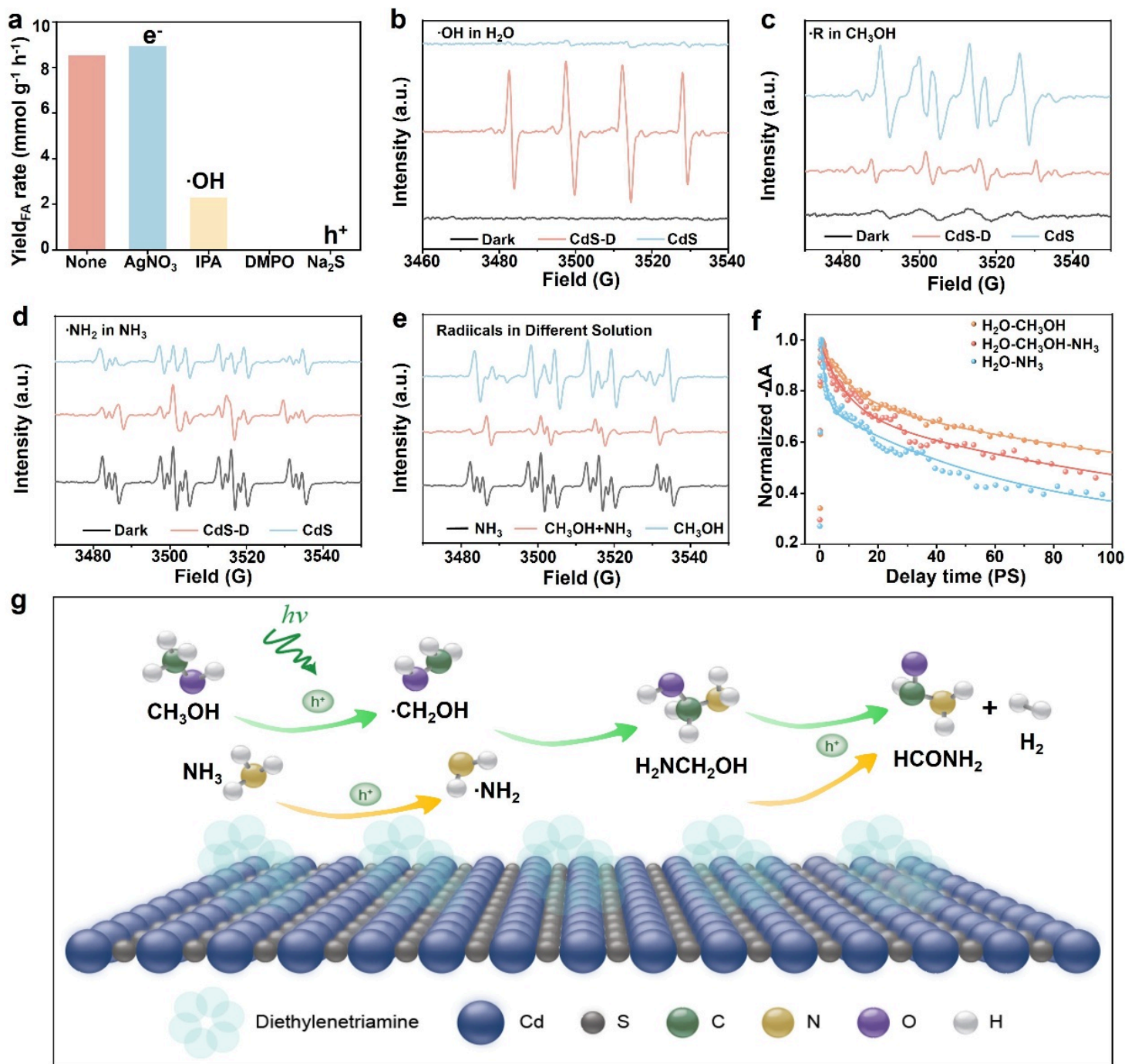


Figure 5

Identification of radical intermediates and substrate dependent interfacial charge dynamics. a, Effects of charge-carrier and radical scavengers on FA production over CdS-D. b–e, Time-dependent spin trapping EPR spectra of CdS and CdS-D under different reaction conditions: b, H₂O; c, CH₃OH/H₂O; d, NH₃/H₂O; and e, Time-dependent spin trapping EPR spectra of CdS-D under CH₃OH/NH₃/H₂O. f, Femtosecond transient absorption spectroscopy (fs-TAS) kinetic traces showing substrate dependent bleaching recovery behavior over CdS-D and pristine CdS. g, Proposed radical-mediated pathway for photocatalytic FA formation over CdS-D.

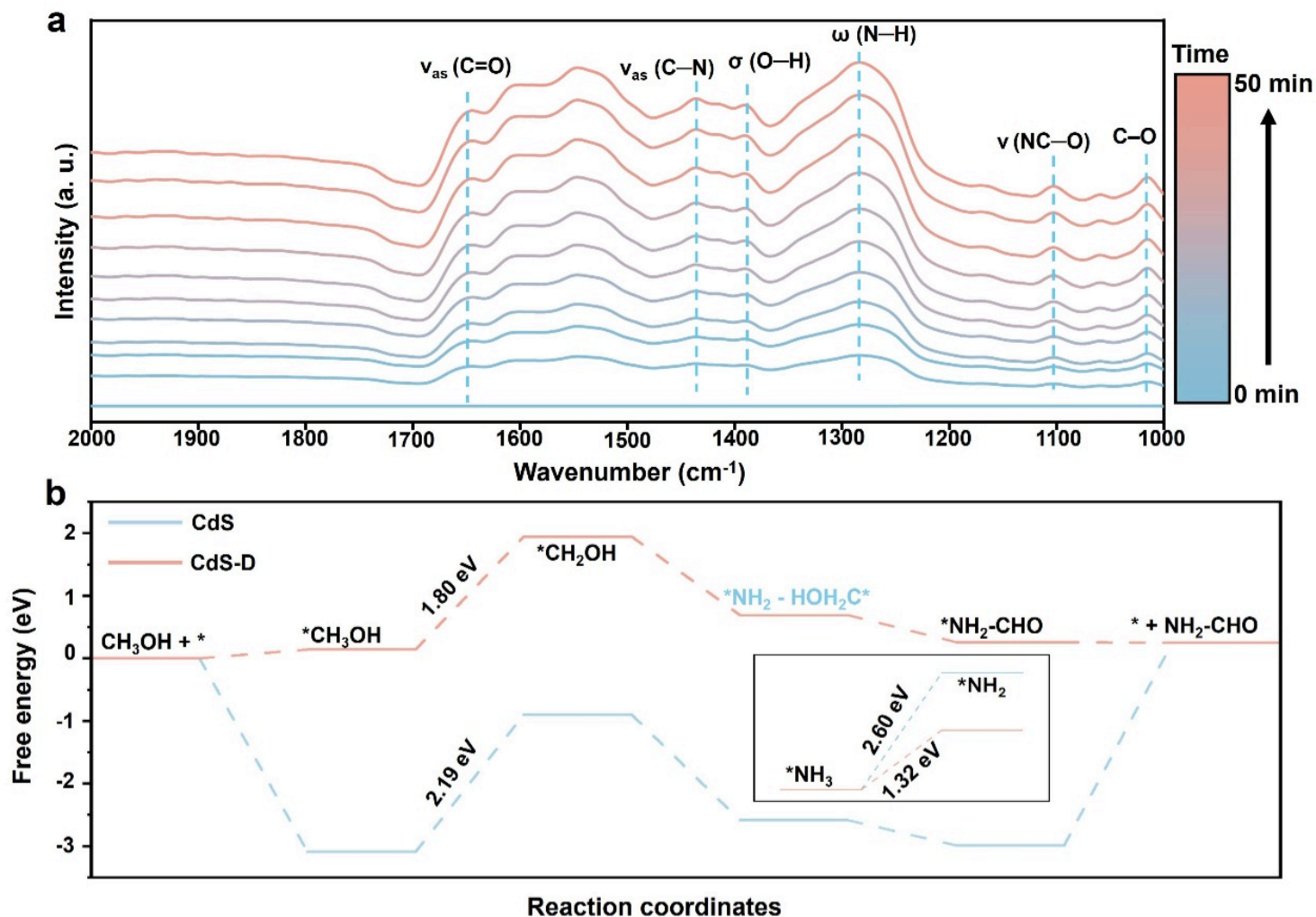


Figure 6

Tracking interfacial C–N bond formation and reaction energetics. a, Time-dependent in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra during photocatalytic conversion of methanol and ammonia over CdS–D, revealing the evolution of methanol derived, nitrogen containing and C–N coupling related surface intermediates. b, Calculated free energy profiles for FA formation over pristine CdS and CdS–D.

Supplementary Files

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