

Integration of CdS Nanoparticles and Molecular Cobalt Catalysts into Metal–Organic Frameworks for Highly Efficient Photocatalytic Amine Oxidation

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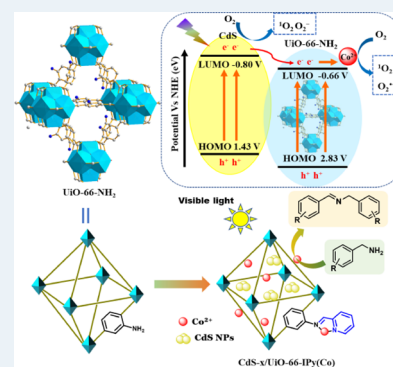
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ABSTRACT: The rational design and construction of metal–organic framework (MOF)-based photocatalytic composites with outstanding visible-light responsiveness, rapid photogenerated charge carrier separation and migration ability, and suitable band gaps for photocatalytic organic transformation have gained enormous attention, yet they are highly challenging. Herein, a series of hybrid materials, CdS- x /UiO-66-IPy(Co) (x represents the theoretical loading amount of CdS into the synthetic system), featuring CdS nanoparticles and molecular cobalt centers, have been constructed by a step-by-step assembly (SSA) strategy. Significantly, the resultant CdS- x /UiO-66-IPy(Co) composites present dramatically improved catalytic activity in the oxidative coupling of amines under ambient air and visible-light irradiation ($\lambda > 400$ nm) as compared with the parent UiO-66 and CdS. Specifically, CdS-20/UiO-66-IPy(Co) can efficiently convert benzylamine derivatives into the target imine products with conversion and selectivity both exceeding 95%, attributed to the formation of a heterostructure between the well-dispersed CdS nanoparticles, molecular Co catalyst, and UiO-66-NH₂, which facilitated an extended range of light absorption, efficient separation and migration of photogenerated charge carriers, and abundant exposed reaction active sites. The recycling experiments confirm the good recyclability and durability of CdS-20/UiO-66-IPy(Co). Furthermore, the underlying catalytic mechanism has been well established by comprehensive experiments involving photocurrent, electrochemical impedance, photoluminescence, transient absorption, and electron paramagnetic resonance spectroscopy measurements.

KEYWORDS: metal–organic frameworks, cadmium sulfide, molecular Co catalyst, photocatalysis, amine oxidation



INTRODUCTION

The synthesis of imines has become a subject of interest in organic chemistry owing to their versatility as building blocks for constructing a wide range of bioactive N-containing compounds, fine chemicals, and pharmaceuticals.^{1–3} Generally, the conventional synthesis route is amine-carbonyl condensation, which usually suffers from stringent conditions, low yields, poor selectivity, and environmental issues. Therefore, it is of great importance to develop efficient and sustainable methodologies for the synthesis of imine compounds.^{4,5}

Recently, photocatalytic oxidative coupling of amines has been proven to be a promising approach for synthesizing diverse imine derivatives under mild reaction conditions due to its effectiveness, sustainability, and eco-friendliness. So far, tremendous endeavors have been devoted to developing various photocatalysts involving, but not limited to, inorganic semiconductors, molecular photocatalysts, organic semiconductors, and hybrid organic–inorganic materials, for facilitating the efficiency and selectivity in the photocatalytic amine oxidation.^{6–14} In this respect, metal–organic frameworks (MOFs),^{15–20} as a type of potential crystalline semiconductor,

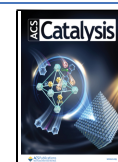
have garnered enormous attention in the field of photocatalytic amine oxidation^{21–24} due to their distinct properties involving functional tunability, structural diversity, and high surface area. The crystalline nature bestows MOFs with the ability to promote the separation and migration of photogenerated charge carriers, while the functional tunability imparts MOFs with great potential to regulate the optical response and photocatalytic activity by introducing photosensitive and photocatalytic centers based on de novo synthesis or postsynthetic modification approaches. Additionally, the high surface area facilitates substrate/product transport and substrate access to the catalytic centers, thus resulting in improved photocatalytic performance. Nevertheless, it remains challenging to develop suitable MOF photocatalysts with

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outstanding optical response, rapid separation, and migration of charge carriers, and highly active catalytic sites, for accomplishing efficient photocatalytic amine oxidation.

Cadmium sulfide nanoparticles (CdS NPs) have been widely utilized in photocatalysis due to their excellent optical response, suitable band gap, and affordability.^{25–27} However, the rapid recombination of photogenerated electron–hole (e^-h^+) pairs and photocorrosion severely hamper their application in photocatalysis, which spurs us to develop more efficient strategies to handle the above issues to enhance the photocatalytic performance. Among these, the construction of a heterojunction photocatalytic system through the integration of MOFs with CdS NPs represents a promising approach to achieve efficient photocatalytic performance, like the degradation of pollutants,^{28–30} hydrogen evolution,^{31–33} CO₂ conversion,^{34–36} and organic transformation,^{37–39} attributed to their good visible-light absorption, charge carrier separation, and migration ability. However, it is still unsatisfactory for CdS/MOF composites to achieve high photocatalytic performance, ascribed to the lack of catalytic centers. Additionally, the uncertain location of CdS in the MOF matrix poses a great challenge in elucidating the underlying catalytic mechanism at a molecular level.

As a class of potential alternatives to noble metal molecular catalysts (Ru and Ir-based complexes), nonprecious metal catalysts like Fe, Co, and Ni complexes have been widely used in organic catalysis,^{40–43} such as C–C and C–N bond-forming reactions, due to their good catalytic activity, low cost, abundance, and facile synthesis. Among these, cobalt (Co)-based molecular catalysts have become prominent in homogeneous photocatalytic reactions due to their redox properties, resulting in the efficient generation of superoxide radicals ($O_2^{\bullet-}$) and singlet oxygen (1O_2) under light excitation and high photothermal chemical stability. However, the homogeneous properties and poor optical response of Co-based catalysts limit their catalytic performance and concurrently increase the difficulty in separation and recovery. It has been reported that anchoring molecular catalysts into the MOF matrix represents an efficient approach to surmount the above points.^{44–46} Considering the features of CdS/MOF composites, we envision that the immobilization of a Co-based molecular catalyst into the CdS/MOF composite may provide a promising protocol for achieving efficient and selective photocatalytic amine oxidation.

Based on the aforementioned considerations, we reported a series of composites, termed CdS-*x*/UiO-66-IPy(Co) (*x* represents the theoretical loading amount of CdS into the synthetic system), bearing CdS NPs and molecular cobalt centers, by a step-by-step assembly (SSA) strategy. This strategy involves the postsynthetic modification of UiO-66-NH₂ with pyridine-2-carboxaldehyde (PA) through a Schiff base condensation reaction, the incorporation of Cd ions and subsequent transformation to CdS, and the immobilization of a molecular Co-catalyst for visible-light-driven amine oxidation. UiO-66-NH₂ is chosen as the prototypical MOF to implement the following SSA strategy due to its simple synthetic protocol, good physicochemical stability, easily tunable functions, good optical response, and high specific surface area. PA is selected to postsynthetically covalently modify UiO-66-NH₂ via a Schiff-base reaction to form UiO-66-IPy with potential metal-chelating sites that can preanchor Cd ions for the subsequent synthesis of CdS NPs on UiO-66-IPy (CdS-*x*/UiO-66-IPy) with precise placement. After immobilizing Co ions into CdS-

x/UiO-66-IPy, a series of CdS-*x*/UiO-66-IPy(Co) composites are constructed, in which CdS-20/UiO-66-IPy(Co) is screened out to showcase dramatically improved photocatalytic performance for the conversion of amine to various imine derivatives, with both the yield and selectivity exceeding 95% under ambient air and visible-light irradiation ($\lambda > 400$ nm) than its parent UiO-66-NH₂ and CdS NP counterparts. This is due to the excellent optical response, suitable band gap, efficient separation and migration of photogenerated charge carriers, and abundant reaction active sites. Notably, the efficient integration of UiO-66-NH₂, CdS NPs, and molecular Co catalysts takes full advantage of their merits while avoiding their drawbacks, which not only promotes the efficient amine conversion to imine but also significantly improves recyclability and durability, as corroborated by the cycling experiments. Moreover, the catalytic mechanism is well-detangled by comprehensive experiments involving photocurrent, electrochemical impedance, photoluminescence, transient absorption, and electron paramagnetic resonance spectroscopy measurements.

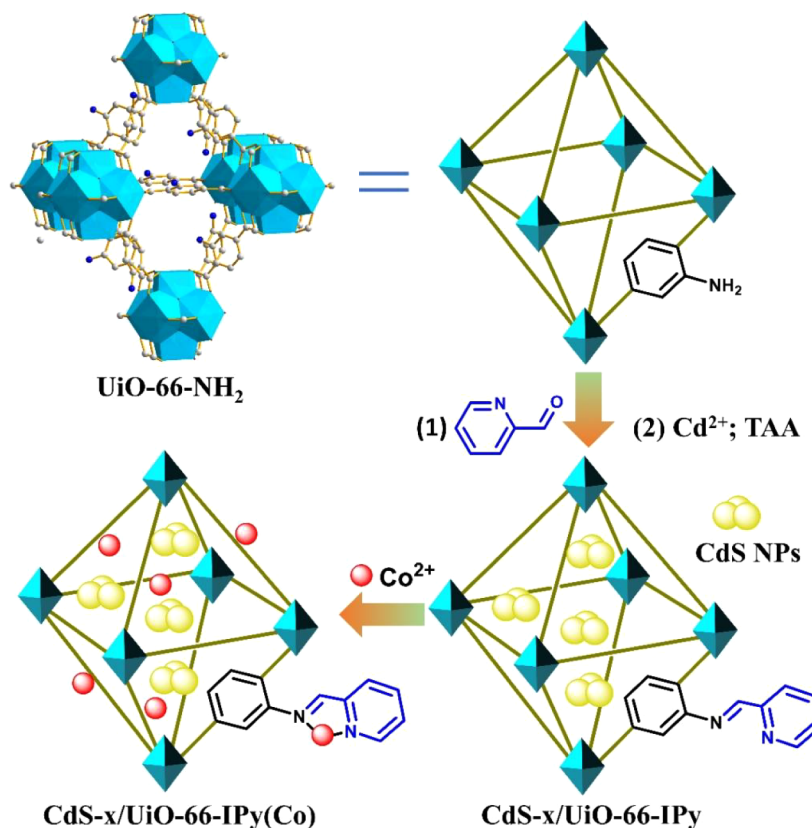
EXPERIMENTAL SECTION

Methods and Materials. All of the reagents were obtained from commercial sources and used directly without further purification unless noted. 2-Aminoterephthalic acid (BDC-NH₂), pyridine-2-carboxaldehyde (PA), thioacetamide (TAA), benzylamine, ZrCl₄, Cd(CH₃COO)₂·2H₂O, and Co(NO₃)₂·6H₂O were purchased from Energy Chemical. *N,N'*-Dimethylformamide (DMF, 99.9%), ethanol (99.7%), and acetonitrile (99.7%) were purchased from Shanghai Adamas.

Catalyst Preparation. *Synthesis of UiO-66-NH₂.* ZrCl₄ (0.48 g, 2.10 mmol) and BDC-NH₂ (0.35 g, 2.10 mmol) were dissolved in 60 mL of DMF solvent under ultrasonication, respectively. Thereafter, the two solutions were mixed, followed by the addition of 100 μ L of deionized water, which was then transferred to a Teflon-lined stainless-steel autoclave and reacted in an oven at 120 °C for 24 h. After cooling to room temperature, the precipitate was collected by centrifugation and washed with DMF and acetone three times. The obtained product was immersed in acetone for 3 days, during which fresh acetone was replenished twice a day. Finally, the solid was dried under vacuum at 120 °C overnight prior to further use.

Synthesis of UiO-66-IPy. The activated UiO-66-NH₂ samples (1.00 g) were suspended in ethanol (100 mL), to which 5 mL of PA was added. The mixture was sonicated for 10 min and heated at 80 °C for 20 h under an N₂ atmosphere. After cooling to room temperature, the solid was collected by centrifugation and washed with ethanol three times. The obtained powder, named UiO-66-IPy, was dried under vacuum at room temperature for further use.

*Synthesis of CdS-*x*/UiO-66-IPy.* CdS-*x*/UiO-66-IPy (*x* = 0, 5, 10, 15, 20, and 30 wt %, representing the theoretical loading amount of CdS) was prepared according to the following procedure. Taking 10 wt % as an example: Cd(CH₃COO)₂·2H₂O (0.095 g, 0.36 mmol) was dissolved in 100 mL of ethanol, to which UiO-66-IPy (0.40 g) was added, and the mixture was sonicated for 20 min. After that, the suspension was heated at 80 °C for 30 min before the slow addition of 100 mL of thioacetamide (TAA, 0.032 g, 0.43 mmol) aqueous solution with intense agitation. The obtained mixture was heated at 80 °C for another 30 min. The precipitates were centrifuged and rinsed with H₂O and ethanol several times.

Scheme 1. Schematic Diagram of the Synthesis Route of CdS- x /UiO-66-IPy(Co)

Finally, the product was dried at 60 °C under vacuum for 12 h. When $x = 0$, UiO-66-IPy was directly used in the next step.

Synthesis of CdS- x /UiO-66-IPy(Co). CdS- x /UiO-66-IPy (0.2 g) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.05 g) were added to 30 mL of acetonitrile and sonicated for 10 min. Then, the suspension was heated at 80 °C for 20 h under an N_2 atmosphere. After cooling to room temperature, the solid was collected by centrifugation, washed with acetonitrile, and dried at 60 °C under vacuum for 12 h to obtain the final composite, termed CdS- x /UiO-66-IPy(Co).

Photocatalytic Oxidative Coupling of Amines. Typically, the catalyst (10 mg), benzylamine (0.20 mmol), and acetonitrile (1.5 mL) were mixed in a 25 mL reaction tube and sealed with a rubber stopper under an air atmosphere. The suspension was irradiated with a 300 W Xe lamp (Beijing Perfectlight) equipped with a UV cutoff filter ($\lambda > 400$ nm). After the reaction, the reaction mixture was filtered through a porous membrane before being injected into a gas chromatograph (Fu Li GC9790) with an FID detector to determine the conversion and selectivity.

For the recycling study, the catalyst was collected through centrifugation after the reaction, washed with acetonitrile (3×5 mL), and dried in an oven at 80 °C overnight for use in the next run. For the trapping experiment, only different scavengers were added to the reaction system while maintaining the standard experimental conditions.

RESULTS AND DISCUSSION

Design and Synthesis of the Composites. The synthetic route of CdS- x /UiO-66-IPy(Co) is represented in Scheme 1. UiO-66- NH_2 was first prepared through the solvothermal reaction of $\text{NH}_2\text{-BDC}$ and ZrCl_4 in DMF/

H_2O solvents at 120 °C for 24 h. UiO-66-IPy was synthesized by a postsynthetic covalent modification method, in which UiO-66- NH_2 reacted with PA via a Schiff-base reaction in ethanol at 80 °C for 20 h to afford the target product. Notably, UiO-66-IPy features iminopyridine units as potential metal-chelating sites that can preanchor Cd ions, beneficial for the following synthesis of CdS NPs on UiO-66-IPy with precise placement. CdS- x /UiO-66-IPy (x represents the theoretical loading amount of CdS into the synthetic system) was synthesized by first treating UiO-66-IPy with $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in ethanol at 80 °C for 0.5 h, followed by the addition of thioacetamide (TAA) aqueous solution. Finally, the CdS- x /UiO-66-IPy(Co) composites were afforded by the reaction of CdS- x /UiO-66-IPy with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile under an N_2 atmosphere at 80 °C for 20 h.

The phase purity of UiO-66- NH_2 and UiO-66-IPy was confirmed by the powder X-ray diffraction (PXRD) patterns (Figures S1 and S2). Compared with UiO-66- NH_2 , the weakening of the characteristic -NH vibration at 3400–3600 cm^{-1} in the FT-IR spectra (Figure S3) and the emergence of a new vibration at 1621 cm^{-1} belonging to the typical stretching vibration of -C=N suggest the successful synthesis of UiO-66-IPy, which was further confirmed by ^{13}C CP/MAS NMR (Figure S4). Additionally, the ^1H NMR spectra for the digested UiO-66-IPy were performed to assess the content of iminopyridine units, which revealed that approximately 23.8% of the amino groups converted to iminopyridine units (Figure S5 and Table S1). For CdS- x /UiO-66-IPy(Co), the PXRD patterns match well with those of UiO-66- NH_2 and CdS NPs, in which the diffraction peaks with the 2θ values of 26.6, 44.0, and 52.1° represent the (111), (220), and (311) lattice planes of the hawleyite CdS phase

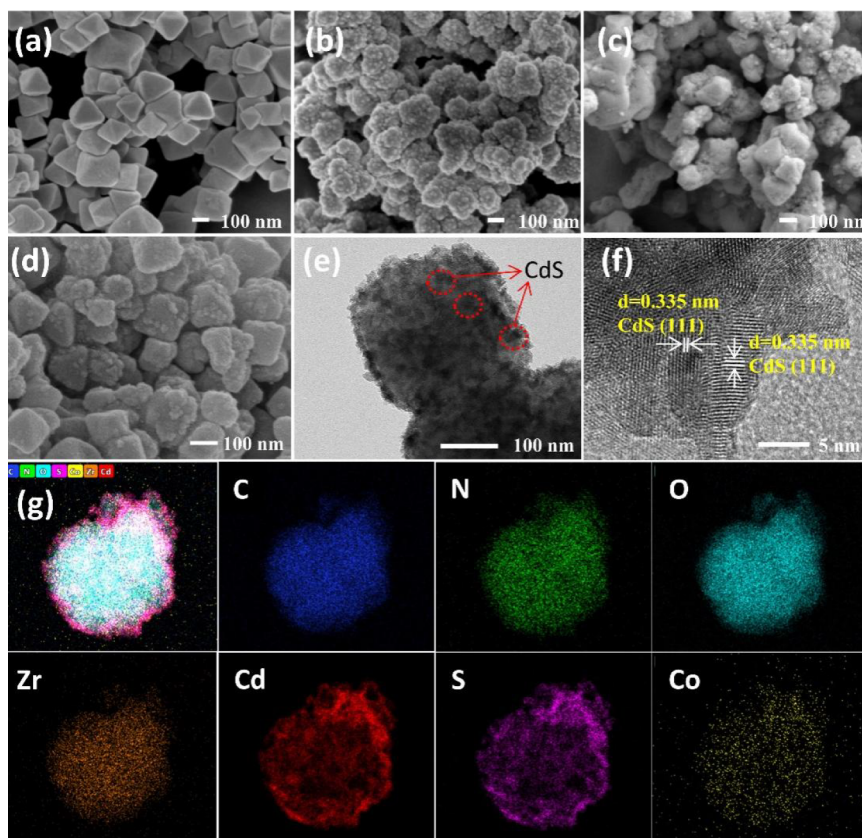


Figure 1. SEM images of UiO-66-NH₂ (a), CdS (b), CdS-20/UiO-66-IPy (c), and CdS-20/UiO-66-IPy(Co) (d); TEM (e), HRTEM (f), and elemental mapping images (g) of CdS-20/UiO-66-IPy(Co).

(JCPDS No. 10–0454), indicating the formation of a heterojunction structure between CdS NPs and UiO-66-IPy(Co), as further confirmed by high-resolution transmission electron microscopy (HR-TEM) images (Figure 1e). The contents of Cd in CdS-*x*/UiO-66-IPy(Co) were determined by ICP-OES measurements (Table S2). Notably, the gradually increasing Cd content in CdS-*x*/UiO-66-IPy(Co) resulted in a gradually decreasing Co content, implying that partial iminopyridine chelating sites were occupied by CdS NPs (Table S2). The gradual increase of Cd ion loading amount during the synthetic process of CdS/UiO-66-IPy has not resulted in the obvious enhancement of CdS peak intensity, which might be attributed to the low and broadened diffraction peaks of CdS NPs (Figure S2).

The morphology of all the structures was characterized by scanning electron microscopy (SEM), in which UiO-66-NH₂ presents the typical octahedral morphology with a smooth surface, with sizes ranging from 150 to 250 nm (Figure 1a), while CdS NPs show irregular morphology with a rough surface and a tendency to aggregate together, with an average size of approximately 150 nm (Figure 1b). Compared with the pure CdS NPs and UiO-66-NH₂, CdS-20/UiO-66-IPy presents an octahedral morphology with a rough surface due to the uniform distribution of small-sized CdS NPs (Figure 1c). After the immobilization of Co ions, the resultant CdS-20/UiO-66-IPy(Co) presents an octahedral morphology similar to that of CdS-20/UiO-66-IPy (Figure 1d). Transmission electron microscopy (TEM) images also reveal that CdS NPs are well-dispersed on the surface of UiO-66-IPy(Co), consistent with the SEM results (Figure 1e). The morphology of the CdS nanoparticles is elongated, with lengths ranging

from 20 to 30 nm (Figure S6). The high-resolution TEM (HR-TEM) images were obtained to reveal a lattice spacing of approximately 0.335 nm (Figure 1f), corresponding to the (111) plane of hawleyite CdS, which is consistent with the PXRD results. The images of element mapping for the CdS-20/UiO-66-IPy(Co) composite show that C, N, O, Zr, Cd, S, and Co are uniformly distributed throughout the entire material (Figure 1g), further confirming the successful integration of UiO-66-NH₂ with CdS NPs and the molecular Co catalyst.

N₂ adsorption experiments at 77 K were carried out to assess the porosity of UiO-66-NH₂, CdS NPs, and CdS-20/UiO-66-IPy(Co). As shown in Figure S7, both UiO-66-NH₂ and CdS-20/UiO-66-IPy(Co) present the microporous type I adsorption isotherm characteristic, while CdS NPs present a nonporous structure characteristic. The Brunauer–Emmett–Teller (BET) surface area of UiO-66-NH₂ is calculated to be 952 m² g^{−1}, while that for CdS NPs is 27 m² g^{−1}. After decorating CdS NPs on the surface of UiO-66-IPy and anchoring Co ions into CdS-20/UiO-66-IPy, the resultant CdS-20/UiO-66-IPy(Co) shows a decreased BET surface area with the value of 667 m² g^{−1} resulting from the dispersion of the nonporous CdS NPs and the introduction of molecular Co catalysts. The pore size distributions for UiO-66-NH₂ are estimated to be 0.64 and 1.22 nm by the DFT method, while that for CdS-20/UiO-66-IPy(Co) is 0.68 nm, attributed to the introduction of a molecular Co catalyst (Figure S8). Additionally, the preservation of porosity for CdS-20/UiO-66-IPy(Co) signifies that the CdS NPs are mainly dispersed on the surface of UiO-66-IPy.

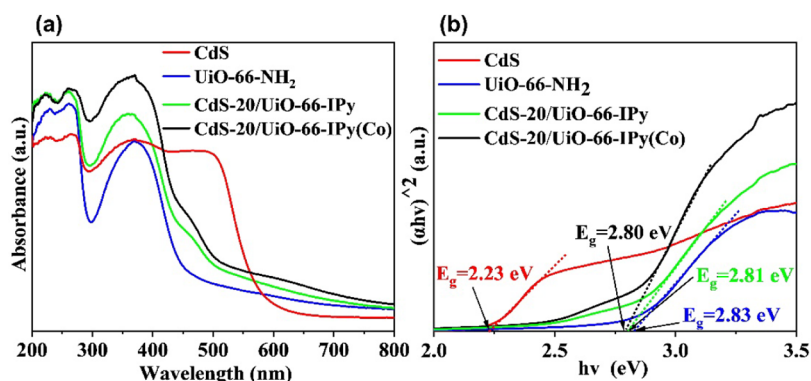


Figure 2. (a) UV–visible diffuse reflectance spectra of CdS, UiO-66-NH₂, CdS-20/UiO-66-IPy, and CdS-20/UiO-66-IPy(Co); (b) the band gaps of CdS, UiO-66-NH₂, CdS-20/UiO-66-IPy, and CdS-20/UiO-66-IPy(Co).

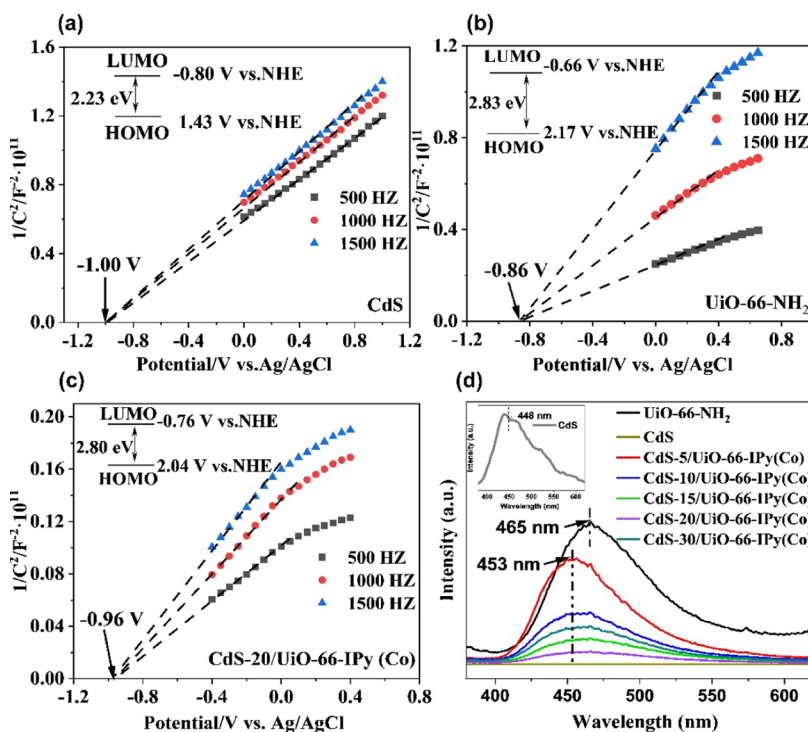


Figure 3. (a–c) The Mott–Schottky plots of CdS, UiO-66-NH₂, and CdS-20/UiO-66-IPy(Co); (d) the photoluminescence (PL) spectra of UiO-66-NH₂, CdS, and CdS-*x*/UiO-IPy(Co) under 350 nm excitation.

To elucidate the surface chemical states of CdS-20/UiO-66-IPy(Co), X-ray photoelectron spectroscopy (XPS) was meticulously performed. As depicted in Figure S9, the survey spectra reveal the presence of Zr, Cd, S, Co, N, C, and O in the CdS-20/UiO-66-IPy(Co) composite. Specifically, the Zr 3d XPS spectra of CdS-20/UiO-66-IPy(Co) (182.6 eV for Zr 3d_{5/2} and 185.0 eV for Zr 3d_{3/2}) shift to lower binding energies compared with the parent UiO-66-NH₂ (183.1 eV for Zr 3d_{5/2} and 185.4 eV for Zr 3d_{3/2}), suggesting a change in the local coordination environment of Zr. Similarly, the C 1s XPS spectra of CdS-20/UiO-66-IPy(Co) (284.8 eV for C=C, 286.3 eV for C–N, and 288.5 eV for C=O) also exhibit lower binding energies than those of UiO-66-NH₂ (284.9 eV for C=C, 286.5 eV for C–N, and 288.9 eV for C=O). The N 1s spectra for CdS-20/UiO-66-IPy(Co) displayed binding energies of 399.6 and 401.2 eV, assigned to –NH₂ and –C=N units, respectively (Figure S10). However, compared with the parent CdS NPs, the binding energies of Cd 3d and S 2p for

CdS-20/UiO-66-IPy(Co) increased by 0.1 eV. The slight yet different change for Zr 3d, C 1s, Cd 3d, and S 2p XPS spectra signifies the presence of interaction between Cd NPs and UiO-66-IPy, which is beneficial for the formation of a heterojunction structure, facilitating light absorption, and charge carrier separation and migration, further enhancing the photocatalytic activity of the CdS-20/UiO-66-IPy(Co) composite. Additionally, the valence state of Cd in CdS-20/UiO-66-IPy(Co) was revealed to be +2 by Cd 3d XPS spectra, with the peaks located at 405.1 (Cd 3d_{5/2}) and 411.8 eV (Cd 3d_{3/2}). For the Co 2p spectra, the peaks located at 781.3, 784.0, 796.8, and 800.4 eV are assigned to Co 2p_{3/2} and Co 2p_{1/2}, respectively, corroborating the successful introduction of Co ions into the framework. Moreover, to probe the coordination environment of Co centers in CdS-20/UiO-66-IPy(Co), X-ray absorption fine structure (XAFS) spectroscopy, including synchrotron-radiation-based X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine

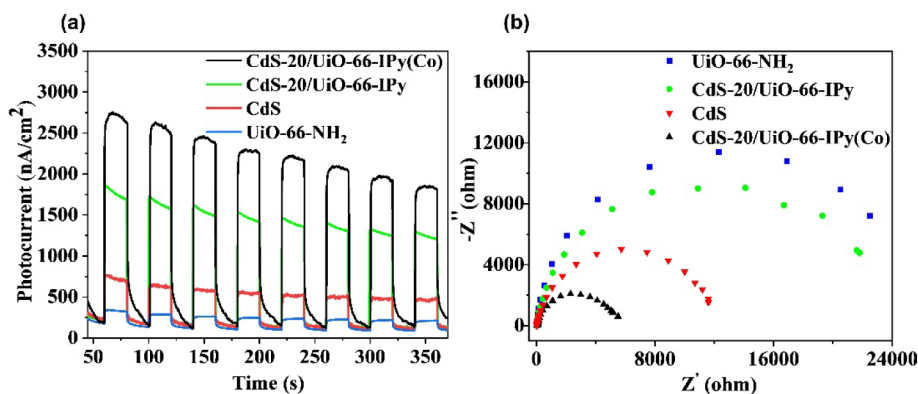


Figure 4. (a) Photocurrent spectra of CdS, UiO-66-NH₂, CdS-20/Uio-66-IPy, and CdS-20/Uio-66-IPy(Co); (b) electrochemical impedance spectroscopy of CdS, UiO-66-NH₂, CdS-20/Uio-66-IPy, and CdS-20/Uio-66-IPy(Co).

structure (EXAFS) spectroscopy, was performed (Figure S11). The XANES measurement revealed that the valence state of Co fell between +2 and +3, consistent with the XPS results (Figure S9). A peak located at 1.60 Å based on the EXAFS spectra could be observed, corresponding to the Co–N/O coordination bond, while no Co–Co peaks could be observed, indicating the atomic dispersion of Co sites in CdS-20/Uio-66-IPy(Co). Additionally, the quantitative EXAFS fitting was implemented to determine the coordination environment of Co species, revealing that the coordination number of Co–N is 6.0 ± 0.4 with the Co–N/O distance of ~ 2.08 Å (Table S3). Considering that CdS-20/Uio-66-IPy(Co) was synthesized in acetonitrile solution, it could be inferred that each Co ion was ligated by two N atoms from one pyridine-2-imine motif, two O atoms from two different NO₃[−] anions, and two N atoms from two acetonitrile molecules, respectively, thus forming a stabilized octahedral configuration.

To assess the photocatalytic activity of all the synthesized materials, UV–vis diffuse reflectance spectroscopy (DRS) was measured (Figures 2 and S12). As depicted in Figure 2a, the prototypical UiO-66-NH₂ presents a narrow optical absorption extending to 450 nm, while CdS NPs exhibit an intense optical absorption from 300 to 550 nm, suggesting a better optical response for CdS NPs. After dispersing CdS NPs on UiO-66-IPy, the optical absorption ability of CdS-*x*/UiO-66-IPy is effectively enhanced compared with that of the parent UiO-66-NH₂, which inherits the optical properties of CdS NPs. Moreover, the introduction of Co ions further enhances the optical absorption capacity, in which a new absorption band emerges between 600 and 700 nm. The band gap of UiO-66-NH₂ is estimated to be 2.83 eV based on its UV–vis spectra (Figure 2b), whereas that of CdS NPs is 2.23 eV. Along with the continuous introduction of CdS NPs and Co ions, the band gap gradually decreases from 2.83 eV (UiO-66-NH₂) to 2.81 eV (CdS-20/Uio-66-IPy) and 2.80 eV (CdS-20/Uio-66-IPy(Co)), which falls in between the parent UiO-66-NH₂ and CdS NPs, manifesting the presence of interactions between the pristine MOF and NPs, indicative of the formation of a heterojunction structure.

To determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), Mott–Schottky (M–S) measurements were conducted at different frequencies (Figure 3a–c). The positive slope of M–S plots indicates that all of the materials, including UiO-66-NH₂, CdS, and CdS-20/Uio-66-IPy(Co), are n-type semiconductors. Generally, the flat-band potential in typical n-

type semiconductors is approximately equal to the bottom of the LUMO. The LUMO positions of UiO-66-NH₂ and CdS are estimated to be approximately -0.80 and -0.66 eV (vs. NHE), respectively. Considering the band gaps and LUMO positions, the HOMO positions of CdS and UiO-66-NH₂ are calculated to be 1.43 and 2.17 eV (vs. NHE), respectively. It is important to highlight that the LUMO edge of CdS is more negative than that of UiO-66-NH₂, which injects more driving forces to facilitate electron transfer from CdS to UiO-66-NH₂, thus being beneficial for improving photocatalytic activity via forming a heterojunction structure. For CdS-20/Uio-66-IPy(Co), the HOMO and LUMO positions are calculated to be -0.76 and 2.04 eV, respectively, which falls between those of the parent CdS and UiO-66-NH₂, further revealing the formation of a heterojunction structure.

To gain further insight into the efficacy of the photo-generated charge separation and migration, photoelectrochemical measurements were carried out. The transient photocurrent spectra clearly show that the photocurrent intensity of CdS-20/Uio-66-IPy is higher than those of CdS and UiO-66-NH₂ (Figure 4a). The photocurrent intensity further augments upon immobilizing Co ions into CdS-20/Uio-66-IPy, indicative of more efficient photoinduced charge carrier separation in the CdS-20/Uio-66-IPy(Co) composite. It is worth mentioning that there is a noticeable tail after the end of illumination and a decay of photocurrent over the course of the measurement for CdS-20/Uio-66-IPy(Co), which are probably due to the long-lived charges caused by the existence of a charge separation and transport approach: from CdS to MOF, followed by Co species. Moreover, the electrochemical impedance spectroscopy (EIS) measurements were conducted to evaluate the internal resistance of all the prepared samples (Figure 4b). In comparison with the parent UiO-66-NH₂ and CdS, CdS-20/Uio-66-IPy(Co) showcases the smallest semicircular diameter, suggesting the smallest charge carrier migration resistance, which probably could be attributed to the synergistic effects of different components through the structure regulation. Especially, the immobilization of Co sites could reduce the overpotential and enrich electrons to achieve effective charge separation. Overall, it can be concluded that the suitable band gaps, high photocurrent intensity, and small impedance for CdS-20/Uio-66-IPy(Co) guarantee a constant flow of photogenerated charge carriers under visible-light irradiation, efficient electron separation, and rapid electron migration, thus enabling the composite with outstanding photocatalytic potential.

Catalytic Studies. Prompted by the distinct characteristics of CdS-20/Uio-66-IPy(Co), involving appropriate band gaps, excellent optical response, and rapid charge carrier separation and migration, the photocatalytic amine oxidation was chosen as a model reaction to examine its catalytic activity under visible-light irradiation ($\lambda > 400$ nm) with a 300 W Xe lamp at room temperature (Table 1). Initially, the reaction was tested

Table 1. Photocatalytic Oxidative Coupling of Benzylamine^a

Reaction scheme: Benzylamine (1a) $\xrightarrow[\lambda > 400 \text{ nm, air, 4 h}]{\text{Catalyst}}$ N-benzylidenebenzylamine (2a)

Entry	Catalyst	Conv./%	Sel./%
1	UiO-66-NH ₂	39	72
2	CdS	5	>99
3	CdS-20/UiO-66-IPy	77	>99
4	UiO-66-IPy(Co)	59	68
5	CdS-5/UiO-66-IPy(Co)	12	>99
6	CdS-10/UiO-66-IPy(Co)	63	>99
7	CdS-15/UiO-66-IPy(Co)	97	97
8	CdS-20/UiO-66-IPy(Co)	99	>99
9	CdS-30/UiO-66-IPy(Co)	98	98
10 ^b	CdS-20/UiO-66-IPy(Co)	69	89
11 ^c	CdS-20/UiO-66-IPy(Co)	94	>99
12 ^d	CdS-20/UiO-66-IPy(Co)	75	>99
13 ^e	CdS-20/UiO-66-IPy(Co)	78	>99
14	none	-	-
15 ^f	CdS-20/UiO-66-IPy(Co)	-	-
16 ^g	CdS-20/UiO-66-IPy(Co)	-	-

^aReaction conditions: 0.2 mmol benzylamine, 10 mg of catalyst, 300 W Xe lamp ($\lambda > 400$ nm), air, 1.5 mL of acetonitrile, 4 h. ^bReaction time: 2 h. ^cDMF as the solvent. ^dEthyl acetate as the solvent. ^eBenzotrifluoride as the solvent. ^fWithout light irradiation. ^gUnder an Ar atmosphere.

by using benzylamine (1a) as the substrate, in which the parent UiO-66-NH₂ can drive the oxidation reaction to a conversion of 39% within 4 h, with a selectivity of 72% toward the desired product, N-benzylidenebenzylamine (2a) (Table 1, entry 1). Conversely, only 5% conversion was achieved when using pure CdS NPs as catalysts (Table 1, entry 2). Strikingly, the conversion of benzylamine was greatly improved to 77% with an impressive >99% selectivity when CdS-20/UiO-66-IPy was used as a catalyst, revealing the crucial role of CdS NPs in the amine oxidation (Table 1, entry 3). In addition, UiO-66-IPy(Co) also presented dramatically improved photocatalytic activity, indicating the important role of a molecular Co catalyst (Table 1, entry 4). Whereafter, the benzylamine oxidation efficacy for CdS-*x*/UiO-66-IPy(Co) was evaluated, revealing that CdS-20/UiO-66-IPy(Co) presents the highest conversion (99%) and selectivity (>99%) (Table 1, entries 5–9). Thus, CdS-20/UiO-66-IPy(Co) was screened out to be the photocatalyst for this reaction system. First, the effect of solvents was investigated under air conditions at room temperature for 4 h, which revealed that the oxidation reaction proceeded most smoothly in acetonitrile (Table 1, entries 8 and 11–13). Afterward, the reaction time was examined, revealing that the reduction of reaction duration to 2 h lowered the conversion to 69% with an 89% selectivity (Table 1, entry 10 and Figure S13). Further optimization revealed that the oxidation reaction proceeded poorly in the absence of the

catalyst, light, or under an Ar atmosphere, proving the important roles of CdS-20/UiO-66-IPy(Co), light irradiation, and O₂ in promoting the reaction (Table 1, entries 14–16). It is worth noting that the yield and selectivity toward 2a increased gradually along with the increasing CdS contents in CdS-*x*/UiO-66-IPy(Co), further demonstrating the pivotal role of CdS NPs in photocatalytic amine oxidation (Table 1, entries 5–8). To gain further insights into the role of CdS NPs, a series of control experiments were conducted, revealing that CdS-20/UiO-66-IPy could promote the amine oxidation reaction with 92% conversion and more than 99% selectivity of imine (Table S4, entry 4), while UiO-66-IPy(Co) displayed a moderate yield and selectivity toward 2a (58% and 68%) under the optimized conditions (Table S4, entry 6). Considering that CdS-20/UiO-66-IPy(Co) exactly presented superior catalytic performance compared to CdS-20/UiO-66-IPy, it can be inferred that CdS NPs and molecular Co centers acted in concert in amine oxidation.

With the optimized reaction conditions in hand, we moved on to investigate the universal applicability of CdS-20/UiO-66-IPy(Co) in the photocatalytic oxidation of amines with diverse substituents (Table 2). Various electron-rich, electron-neutral, and electron-poor benzylamines underwent the photocatalytic amine oxidation reaction with excellent conversion (95–99%) and selectivity (95–99%). As mentioned above, benzylamine (1a) could be smoothly transformed into N-benzylidenebenzylamine (2a) with 99% conversion and >99% selectivity (Table 2, entry 1). Noteworthy, the presence of electron-withdrawing groups like fluoro- (conversion: >99%, selectivity: 98%) or chloro- (conversion: 98%, selectivity: >99%) at the *para*-position of benzylamine did not compromise the high conversion and selectivity of the system (Table 2, entries 2 and 3). The electron-rich benzylamines also steadily participated in the amine oxidation reaction, delivering the corresponding products with excellent yield and selectivity (Table 2, entries 4 and 5). Furthermore, the electronically biased benzylamine bearing a methoxy group at the *ortho*- or *meta*-positions also reacted smoothly, furnishing the corresponding imine products with excellent yields and selectivity (Table 2, entries 6 and 7). Note that the CdS-20/UiO-66-IPy(Co) showcased high photocatalytic activity in amine oxidation with a wide substrate scope compatibility, which was comparable with many reported porous materials involving MOFs, COFs, etc. (Table S5).^{39,47–51}

To examine the recyclability and durability of CdS-20/UiO-66-IPy(Co), recycling experiments were conducted under standard conditions. As shown in Figure S14, the catalyst could be reused for at least five runs without significant loss of activity and selectivity. The conversion and selectivity were 96% and 99% in the fifth run. Moreover, the structural integrity of the material after five consecutive runs of catalysis was validated by PXRD, SEM, and XPS analyses, agreeing well with that of the as-prepared fresh sample (Figures S15–S17). In addition, N₂ adsorption for CdS-20/UiO-66-IPy(Co) after five consecutive rounds of experiments at 77 K was implemented to reveal that the BET surface area decreased from 667 to 136 m²/g (Figure S18), suggesting that the samples decomposed partly after the recycling experiments. In summary, the samples of the CdS-20/UiO-66-IPy(Co) material underwent changes in the pore structure after five consecutive runs of catalysis to some extent, but the long-range order and catalytic activity remained almost unchanged, which might be ascribed to the effective integration of CdS NPs and molecular Co catalysts in

Table 2. Substrate Scope for the Photocatalytic Oxidative Coupling of Amines^a

Entry	Substrates	Products	Conv. /%	Sel. /%
1			99	>99
2			>99	98
3			98	>99
4			99	98
5			96	97
6			97	95
7			95	96

^aReaction conditions: 0.2 mmol benzylamine, 10 mg of CdS-20/Uio-66-IPy(Co), 300 W Xe lamp ($\lambda > 400$ nm), air, 1.5 mL of CH₃CN, 4 h.

UiO-66-NH₂, which enables the frameworks with outstanding photocatalytic amine oxidation performance with wide substrate scope via synergy.

Catalytic Mechanism. To qualitatively probe the recombination process of photogenerated electron–hole pairs, steady-state photoluminescence (PL) measurements were conducted, in which the PL spectra of UiO-66-NH₂ and CdS-*x*/UiO-66-IPy(Co) were collected under an excitation wavelength of 350 nm (Figure 3d). The PL intensity systematically diminished after the integration of CdS NPs, Co-based molecular catalyst with UiO-66-NH₂, signifying the improved electron–hole separation ability as a result of the formation of the heterojunction structure. It is worth mentioning that the PL intensity of CdS-*x*/UiO-66-IPy(Co) with different amounts of CdS followed the sequence: 5 wt % > 10 wt % > 30 wt % > 15 wt % > 20 wt %, implying that CdS-20/UiO-66-IPy(Co) possesses the highest charge-separation efficiency and theoretically the best photocatalytic activity, which is consistent with the trend observed in the photocatalytic amine oxidation results as illustrated in Table 1. Moreover, ultrafast transient absorption (TA) spectroscopy was performed to further assess the photogenerated charge separation properties (Figures S19–S29). The TA spectrum was measured in Helios mode with a time resolution of 140 fs. The center wavelength of the pump pulses was chosen to be 370 and 400 nm. UiO-66-NH₂, UiO-66-IPy, CdS-20/UiO-66-IPy, UiO-IPy(Co), and CdS-20/UiO-66-IPy(Co), absorbed energy from the pump light at 370 or 400 nm to be excited to the excited state, resulting in increasing numbers of molecules in the excited state. For UiO-66-NH₂, UiO-66-IPy, CdS-20/UiO-66-IPy, and UiO-IPy(Co), they all displayed broad excited-state absorption (ESA) around 623 nm, accompanied by positive absorbance changes, respectively, whereas CdS-20/

UiO-66-IPy(Co) presented both negative ground-state bleaching (GSB) and positive ESA absorption. The intensity of ESA signals for all the samples gradually decreased along with an increase in delay time from 1 to 200 ps. Considering that the steady-state PL intensity of CdS-20/UiO-66-IPy(Co) was much lower than that of the parent UiO-66-NH₂, it could be inferred that the reason for the reduced ESA signal of CdS-20/UiO-66-IPy(Co) might stem from the migration of the photogenerated electrons from the CB to the catalytic active Co centers. The recovery around 623 nm with the excited wavelength of 370 nm was characterized by two or three or four time constants, that are $\tau_1 = 6.01$ ps (42.6%), $\tau_2 = 75.00$ ps (37.1%), and $\tau_3 = 788.00$ ps (20.2%) for UiO-66-NH₂, $\tau_1 = 6.13$ ps (40.2%), $\tau_2 = 867.00$ ps (11.8%), $\tau_3 = 65.30$ ps (36.8%), and $\tau_4 = 432.00$ ps (11.1%) for UiO-66-IPy, $\tau_1 = 2.70$ ps (51.1%), $\tau_2 = 362.00$ ps (16.3%), and $\tau_3 = 26.10$ ps (36.2%) for CdS-20/UiO-66-IPy, $\tau_1 = 1.35$ ps (40.3%), $\tau_2 = 9.00$ ps (31.6%), and $\tau_3 = 141.00$ ps (28.1%) for UiO-66-IPy(Co), and $\tau_1 = 81.6$ ps (39.2%) and $\tau_2 = 3.86$ ps (60.8%) for CdS-20/UiO-66-IPy(Co). It was found that the decay time was significantly shortened after the merger of CdS NPs and Co sites into UiO-66-NH₂, suggesting accelerated TA kinetics. The similar phenomenon was found under the excitation of a longer wavelength light (400 nm) (Figures S24–S28). Given that the introduction of Co ions can result in enhanced charge separation efficiency through the polarization effect of organic functional groups,⁵² the kinetic decay plots were fitted at a longer wavelength (720 nm under the excitation of 400 nm) to evaluate the role of CdS NPs during the photocatalytic amine oxidation process. For CdS-20@UiO-66-IPy, the decay time at 720 nm ($\tau_{\text{ave.}} = 81.87$ ps) was much longer than that at 623 nm ($\tau_{\text{ave.}} = 11.08$ ps), similar with CdS-20/UiO-66-IPy(Co) ($\tau_{\text{ave.}} = 26.79$ ps at 720 nm, $\tau_{\text{ave.}} = 12.60$ ps at 623 nm), while UiO-66-

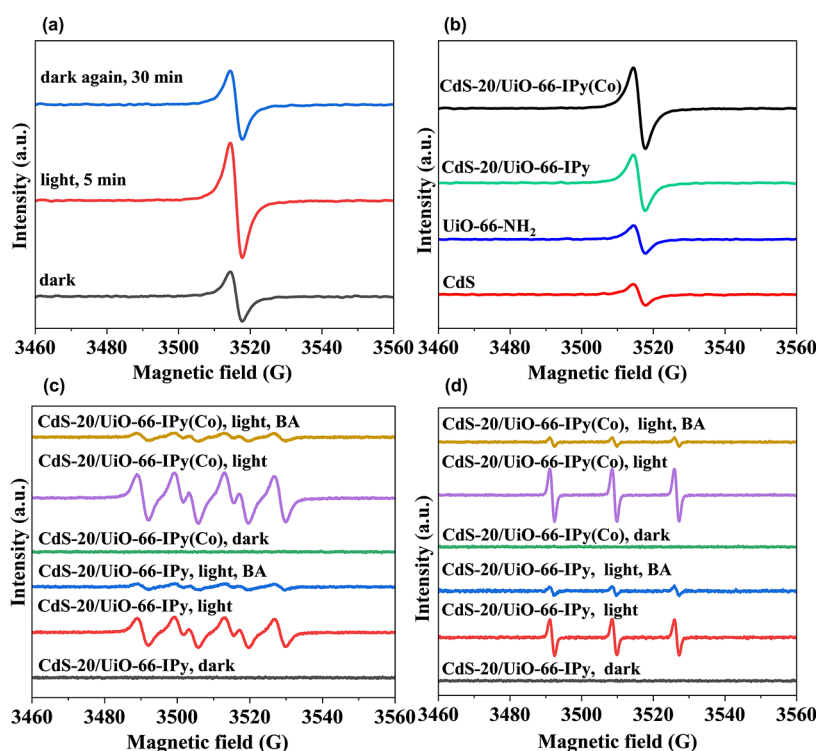


Figure 5. (a) EPR detection of photogenerated radicals for CdS-20/Uio-66-IPy(Co) under different conditions; (b) EPR detection of photogenerated radicals for different catalysts; (c) EPR detection of the generation of $\text{O}_2^{\bullet-}$ over CdS-20/Uio-66-IPy(Co) trapped by DMPO; and (d) EPR detection of $^1\text{O}_2$ generation over CdS-20/Uio-66-IPy(Co) trapped by TEMP. BA: benzylamine.

IPy ($\tau_{\text{ave.}} = 110.13$ ps at 720 nm, $\tau_{\text{ave.}} = 203.63$ ps at 623 nm) and UiO-66-IPy(Co) ($\tau_{\text{ave.}} = 46.36$ ps at 720 nm, $\tau_{\text{ave.}} = 52.88$ ps at 623 nm) displayed opposite results, indicating that the introduction of CdS NPs onto UiO-66-IPy inhibited the photogenerated electron–hole recombination. Moreover, the kinetics decay plots for all the samples followed the same rule as those observed at 623 nm, in which CdS-20/Uio-66-IPy(Co) exhibited the shortest decay time, indicating faster charge transfer kinetics.

To clarify the reaction mechanism and identify the active oxygen species, a series of control experiments were designed and conducted using different scavengers. In the presence of the electron scavenger, AgNO_3 , a significant decrease in both the conversion and selectivity, dropping to 38% and 19%, respectively, was observed due to the fact that the reactive oxygen species production was severely prevented (Table S6, entry 1). The addition of the hole scavenger, KI, markedly impeded the imine formation by restraining the oxidation of benzylamine (Table S6, entry 2). Furthermore, the addition of benzoquinone as a superoxide anion ($\text{O}_2^{\bullet-}$) scavenger, or β -carotene as a singlet oxygen ($^1\text{O}_2$) scavenger, almost entirely inhibited the formation of the desired product (Table S6, entries 3 and 4). However, the use of $t\text{BuOH}$ as a $\bullet\text{OH}$ scavenger had little effect on the oxidation reaction (Table S6, entry 5). Based on the above results, it can be concluded that the photogenerated electrons and holes, and the reactive oxygen species, $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$, play vital roles in the photocatalytic oxidative coupling process.

To evaluate the ability to produce photogenerated radicals and further determine the reactive oxygen species, we designed and conducted electron paramagnetic resonance (EPR) measurements. As shown in Figure 5a, a signal with $g \approx 2.002$, ascribed to the unpaired electrons trapped in oxygen

vacancies, was observed for CdS-20/Uio-66-IPy(Co), indicating the feasibility of generating active radical pairs in the photocatalytic reaction. Notably, the EPR signal was obviously enhanced upon light irradiation and decreased after restoring the sample in dark conditions for 30 min, suggesting the important role of light. In addition, the hybrid CdS-20/Uio-66-IPy(Co) displayed a stronger EPR signal than CdS, UiO-66- NH_2 , and CdS-20/Uio-66-IPy, signifying that CdS-20/Uio-66-IPy(Co) can produce more charge carriers under light irradiation (Figure 5b).

To identify the types of reactive oxygen species during the photocatalytic process, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were used to trap the possible transient-state radicals $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$, respectively. No obvious EPR signals could be detected under the dark conditions. However, a clearly characteristic quadruple signal of $\text{O}_2^{\bullet-}$ (1:2:2:1) was observed after illuminating the reaction system for 5 min in air (Figure 5c). Similarly, a clear triplet peak signal (1:1:1) was observed in the presence of TEMP, implying the generation of singlet oxygen species in the reaction system (Figure 5d). Further addition of substrate **1a** (benzylamine, BA) into the reaction system significantly decreased the peak intensities of the DMPO- $\text{O}_2^{\bullet-}$ and TEMP- $^1\text{O}_2$ adducts, demonstrating the strong interaction between **1a** and the reactive oxygen species. The higher EPR signal intensity for CdS-20/Uio-66-IPy(Co) compared with CdS-20/Uio-66-IPy indicated the important role of the Co-based molecular catalyst in facilitating the production of reactive oxygen species.

To detangle the electron transfer pathway in the photocatalytic process, in situ EPR trapping studies with triethanolamine (TEOA) as a hole sacrificial agent or AgNO_3 as an electron scavenger were conducted (Figure S30). In the

presence of TEOA, aiming to consume the photogenerated hole, an EPR signal at $g = 2.002$ corresponding to free electrons was observed under an N_2 atmosphere, which was enhanced under visible light irradiation and subsequently diminished to the initial state after exposure to an O_2 atmosphere, revealing that the photogenerated electrons transfer from the catalyst to O_2 to afford $O_2^{\bullet-}$ and 1O_2 species. Similarly, with the addition of the electron scavenger, $AgNO_3$, an EPR signal at $g = 2.003$, assignable to photo-generated holes, was observed, which was enhanced upon illumination and reduced after the introduction of BA, implying the interaction between benzylamine and the holes.

In view of the above experimental results and previous reports,^{51,53,54} a plausible photocatalytic mechanism was proposed as illustrated in Figure 6. Upon visible-light

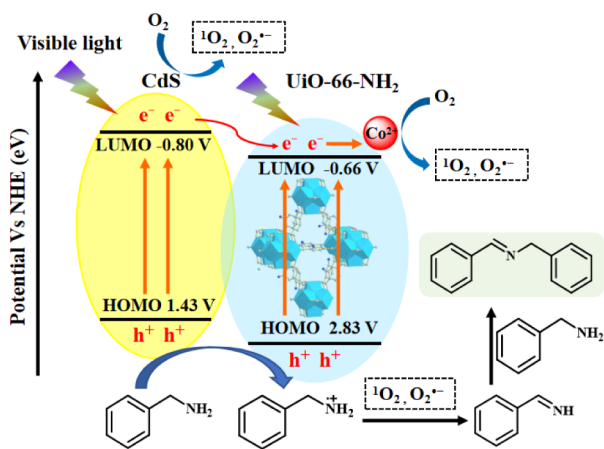


Figure 6. Proposed reaction mechanism for the photocatalytic oxidative coupling of benzylamine over the ternary composite CdS-20/Uio-66-IPy(Co).

irradiation, CdS NPs serving as the light-harvesting center were excited to generate electrons, which were transferred from the LUMO of CdS to the LUMO of Uio-66-NH₂ via the heterojunction interface, aiming to realize electron–hole separation. Whereafter, the electrons were then transmitted to the Co centers so as to capture the photogenerated electrons immediately, hence greatly boosting the transportation of photoelectrons and minimizing the recombination of photoinduced carriers. Furthermore, oxygen was then activated to generate a superoxide radical ($O_2^{\bullet-}$) and singlet oxygen (1O_2) by the photogenerated electrons accumulated on the Co molecular catalyst. Meanwhile, benzylamine was oxidized to cationic radical $PhCH_2NH_2^{\bullet+}$ by the holes from the HOMO position, which then reacted with the active oxygen species $O_2^{\bullet-}$ and 1O_2 to form the $PhCH=NH$ intermediate. Finally, a nucleophilic addition reaction of $PhCH=NH$ with another benzylamine gave rise to the desired *N*-benzylidenebenzylamine product. Considering the poor catalytic activity of CdS NPs and the good catalytic activity of CdS-20/Uio-66-IPy, it cannot be excluded that the photogenerated electrons from CdS NPs directly participate in the activation process of O_2 to convert O_2 to $O_2^{\bullet-}$ and 1O_2 to accomplish the benzylamine oxidation reaction. Therefore, the actual photocatalytic mechanism for CdS-20/Uio-66-IPy(Co) might involve multiple electron transfer pathways, beneficial for enhancing the photocatalytic amine oxidation performance. In addition, it should be noted that the proposed reaction

mechanism highlights the crucial role of the CdS semiconductor and Co-based molecular catalyst in enhancing the photogenerated charge carrier separation and migration processes and elucidating the active sites of the photocatalytic oxidative coupling reaction.

CONCLUSION

In summary, we reported a series of multifunctional composites featuring photosensitive CdS NPs and catalytically active Co sites with precise location via an SSA strategy for photocatalytic amine oxidation applications. Remarkably, the introduction of potential metal-chelating sites into the parent Uio-66-NH₂ via postsynthetic covalent modification not only guarantees the favorable spatial distribution of small-size CdS on Uio-66-NH₂ with precise positioning but also concurrently immobilizes abundant active Co sites within the MOF structure, thus resulting in dramatically enhanced photocatalytic amine oxidation performance. Especially, the resultant CdS-20/Uio-66-IPy(Co) presents superior amine oxidation performance with conversion and selectivity both exceeding 95% under visible-light irradiation and ambient air, much higher than the parent CdS NPs and Uio-66-NH₂, and comparable with many reported porous materials, due to the synergistic effect of CdS NPs, Uio-66-NH₂, and Co-based molecular catalysts. It is expected that the SSA strategy will pave a new avenue to construct multifunctional MOFs for sophisticated photocatalysis applications and even practical applications in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c07398>.

Materials and instrumentation, full experimental details, PXRD patterns, FT-IR spectra, ICP-AES results, N_2 sorption isotherms, XPS, UV–visible diffuse reflectance spectra, catalytic screening on reaction time, recycling experiments, PXRD patterns after catalysis, and results of the trapping experiment and EPR experiment with TEOA/ $AgNO_3$ (PDF)

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Author Contributions

L.C., Y.C., C.-X.C., and S.M. conceived the project and designed the experiments. L.C., Y.C., Z.L., D.K., and Q.T. carried out the syntheses and measurements. C.-X.C. and L.C. drafted and revised the manuscript. L.-L.T. and Z.-M.L. helped with the experiments. All authors provided valuable discussions and suggestions for the final manuscript.

Notes

The authors declare no competing financial interest.

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