In Situ Grown Single-Atom Cobalt on Polymeric Carbon Nitride with Bidentate Ligand for Efficient Photocatalytic Degradation of Refractory Antibiotics

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Semiconductor photocatalysis is a promising technology to tackle antibiotics contamination in water. Herein, a facile in-situ growth strategy reloped to implant singleatom cobalt in polymeric carbon nitride (pCN) via the bi ntate ligand for efficient mic characterizations indicate photocatalytic degradation of oxytetracycline (OT that single-atom cobalt is successfully anchored on pCN by covalently forming the Co-O bond and Co-N bond, which will strengthen the interaction between single-atom cobalt and pCN. This single-atom cobalt car ten ly expand optical absorption, increased electron density, facilitate charge se d transfer, and promote OTC degradation. As the aráth optimal sample, Co(1.28)presents an outstanding apparent rate constant for OTC degradation (0.038 min⁻¹) under visible light irradiation, which is about 3.7 times than that of the pristine pCN. The electron spin resonance (ESR) tests and reactive species trapping experiments demonstrate that the ${}^{1}O_{2}$, h^{+} , $\bullet O_{2}^{-}$ and $\bullet OH$ are responsible for OTC degradation. This work develops a new way to construct single-atom modified pCN, and provides a green and highly efficient strategy for refractory antibiotics removal.

1. Introduction

Antibiotics contamination in water is becoming a severe environmental problem that threatens human public health security.^[1] Oxytetracycline (OTC) is a typical tetracycline which is widely used as a prophylactic antibiotic in agriculture and aquaculture.^[2] Because of the limited absorption by animals after ingestion, large amounts of undigested OTC are released into the environment through feces or urine. The OTC discharged into water can adversely affect ecological systems by suppressing the growth of microorganisms, inducing the formation of antibiotic resistant genes and leading to other ecotoxicological effects.^[3] Accordingly, highly efficient and convenient methods are demanded for the removal of residual OTC in water.

Semiconductor photocatalysis is a novel and desirable technology for the treatment of organic pollutants, which can directly utilize solar energy and outs a require exogenous chemical reagents or electrical energy.^[4] Polymeric earbon nitrite (pCN), as a metal-free organic semiconductor, has drawn tremendous attention due to its favorable band structure, environmental benignity, earth-abundance and excelent/hermal and chemical stability.^[5] Since the pioneering work reported in 2009 by Wang and co-workers,^[6] pCN has been extensively utilized in photocatalytic applications such as water splitting, CO₂ reduction, artificial photosynthesis and environmental mediation.^[7] Nevertheless, pristine pCN suffers from limited visible light absorption, flw electronic conductivity, rapid charge carrier recombination behavior and relatively ew surface active sites, leading to very poor photocatalytic activity.

Within the last decade, various strategies, including heteroatom doping, heterojunction construction and nanostructural engineering, have emerged to effectively resolve these troubles to enhance the photocatalytic performance of pCN.^[8] Among them, introducing metal species into the pCN framework has stimulated much interest, as it can modulate the band gap structure, extend the light absorption range, accelerate charge transfer as well as provide more active sites.^[9] More interestingly, the presence of electron-rich "nitrogen pot" in pCN would provide an ideal site for metal incorporation.^[10] Cobalt-based materials have been attractive in photocatalysis recently owing to their low toxicity, high abundance and low cost.^[11] In general,

cobalt was introduced into pCN structure in the form of nanoparticles (*e.g.*, metallic cobalt, CoO, Co₃O₄, CoP), and activity of the photocatalytic reactions was improved.^[12] Unfortunately, the photocatalytic performances are still poor because only the atoms exposed on the surface of nanoparticles can participate in the reactions.^[13] Therefore, how to increase the atom utilization efficiency of nanoparticles is the key issue.

Recently, uniformly anchoring single-atom onto the pCN network via coordination bonds has been a research frontier in photocatalysis, owing to the maximum metal utilization.^[14] Moreover, single-atom cobalt dispersed in pCN could greatly accelerate charge separation by the chemical bonding, and hence significantly improve the photocatarytic activity. For instance, Liu and co-workers designed a single Co_1 -P₄ site confined on CN by CNa pyrolysis reaction and a following phosphidation route.^[15] This single Co site could efficiently restrain charge recombination and prolong carrier lifetime, and promote absorption and activation of water molecular. As a result, this Co₁-phosphide/nCN composite photocatalyst presented superior ol h photocatalytic H₂ evolution rate of 410.3 \checkmark^1 under simulated sunlight irradiation. Cao om cobalt on pCN in the form of Co₁-N₄ site by and co-workers successfully grafted stip) the method of atomic layer derosition. ¹⁰ The existence of coordinated donor nitrogen could assist the formation of key hydrile intermediate on active Co center in the single Co₁-N₄ site, resulting in accelerated A-H coupling and enhanced H₂ production. Besides, Huang and coworkers achieved superior CO production with a turnover number of more than 200 on the process of photocatalytic CO₂ reduction under visible light irradiation ($\lambda > 420$ nm), by dispersing single Co^{2+} site on pCN through a simple deposition method, to improve the photocatalytic activity and promote the selective formation of CO.^[17] However, in these studies, single-atom cobalt was generally incorporated into pCN by the postloading method, which would weaken the interfacial contact between the Co atom and pCN, and reduce the stability of the composite. In addition, the postloading method was a multi-step process, which would increase the complexity and cost of practical application. Accordingly, it is urgent to develop a

simple method for the implantation of single-atom cobalt in pCN to significantly improve the photocatalytic performance.

In this work, we develop a facile in-situ growth strategy to implant single-atom cobalt in pCN by the bidentate ligand. The atomic characterizations demonstrate that single-atom cobalt is successfully immobilized on pCN by covalently forming a Co-O bond and a Co-N bond. The Co-O bond and Co-N bond act as the links through which the interaction between single-atom cobalt and pCN is strengthened. Anchoring single-atom cobalt onto pCN not only extends optical absorption in the visible region but also accelerates photogenerated charge carrier separation, increases electron density and facilitates electron transfer. These positive effects endow the single-atom cobalt incorporated pCN (Co-pCN) with superior photocatalytic activity for oxytetracycline (OTC) degradation under visible light irradiation.

2. Results and Discussion

The Co-pCN is synthesized via an **in-situ bato-ener** cyclization process of urea and cobalt (II) acetylacetonate to implant single-atom object in pCN framework by the bidentate ligand, as shown in **Figure 1**a. First is theformation of 2-hydroxy-4,6-dimethylpyrimidine (HDMP) and tri-s-triazine ring, which ar originated from the cyclization of acetylacetone with urea and the polymerization of urear respectively. Then a bimolecular condensation occurs between the HDMP and tri-s-triazine ring. Finally, a single-atom cobalt implanted pCN is generated through the chelation of hydroxyl group and nitrogen lone pair on HDMP with the Co²⁺.

Solid-state ¹³C nuclear magnetic resonance (NMR) spectra are utilized to analyze the carbon species of the samples. As shown in Figure 1b, the two carbon peaks at 165 and 157 ppm are obviously observed on pCN, which can be assigned to the C_1 (CN₃) and C_2 (CN₂(NH_x)) carbons, respectively.^[18] During the cyclization and condensation process, the HDMP will be generated and incorporated into the pCN framework. Figure S1 (Supporting Information) demonstrates that the pure HDMP owns four distinct peaks at 181, 161, 157 and 108 ppm.

Nevertheless, because of the formation of self-assembled structures between pyrimidine derivatives, the only peak that can be determined is 108 ppm, corresponding the C₃ (CC₂) carbon.^[19] As for Co(1.28%)-pCN (Figure 1c), the two prominent peaks are detected at 165 and 157 ppm, similar to the spectrum of pCN. However, no obvious peaks of HDMP can be observed on Co(1.28%)-pCN due to the paramagnetic effect of Co. Thus, the solid-state ¹³C NMR spectrum of aa-PCN is detected to verify the incorporation of HDMP. As shown in Figure 1d, the aa-pCN presents a new peak located at 90 ppm, which can be ascribed to the C γ (CC₃) *para* to the hydroxyl group of HDMP. Compared to the pure HDMP, this peak is downshifted because the carbon is in a more electron-rich environment. These results indicate the successful implantation of HDMP into the pCN framework, which will provide be xygen and nitrogen ligands as the efficient and strong coordination center for the Co atoms.

The crystal structures of the samples are characterized by X-ray diffraction (XRD) and presented in Figure 1e. Two characteristic peaks a 3.0° and 27.5° in pCN can be assigned to the (100) and (200) crystal planes, represe ng the intralayer repeated packing of tri-s-triazine units and the interlayer stacking of gapite ke materials, respectively.^[20] In comparison with pCN, it is clear that the (100) peak disappears and the (002) peak becomes weaker and broader with increasing the Go concent in Co-pCN. This is mainly due to the distortion of the planar structure around the Centers in Co-pCN. Raman spectra are then used to confirm the difference of frameworks on pCN and Co-pCN (Figure 1f). A series of characteristic peaks belonging to pCN can be detected in the all samples. The peaks observed at 707 cm⁻¹ and 975 cm⁻¹ correspond to the in-plane bending and the symmetric N-breathing mode of tri-s-triazine, and those at 1100-1700 cm⁻¹ correspond to the disordered graphitic C-N vibrations.^[21] This shows that the basic framework of pCN is well maintained in Co-pCN. From pCN to Co-pCN, the intensity of Raman signals is gradually weakened, which is ascribed to the formation of disordered structure around the Co centers. The microstructures of pCN and Co-pCN are further investigated by Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra.

As shown in Figure 1g, both pCN and Co-pCN exhibit the feature peaks at around 810 cm⁻¹, 1200-1600 cm⁻¹ and 3000-3300 cm⁻¹, corresponding to the breathing mode of tri-s-triazine rings, stretching mode of C-N heterocycles and N-H stretching vibrations, respectively.^[22] This demonstrates that the Co-pCN still keeps the basic structure of pCN, which is in agreement with the Raman results. Compared to pCN, these peaks of Co-pCN are gradually getting weaker as the amount of Co increases due to the localized disorder structures around the Co centers. In addition, the intensity of C-O stretching at 1062-1134 cm⁻¹ increases from pCN to Co-pCN owing to the incorporation of HDMP.^[23] Meanwhile, new peaks emerge at 2820-2970 cm⁻¹ in Co-pCN, which is ascribed to the stretching vibration of -CH₃ in HDMP.^[24] Moreover, N₂ adsorption-desorption isotherms are used to measure the Brunner Formett-Teller (BET) surface areas of the samples. As exhibited in Figure §2a (Supporting Information), all the samples present type IV adsorption curves, manifesting that they are mesoporous materials. The pore size distributions of them (Figure S2b, Supporting Information) also verify this result. The m^2 of Co(1.28%)-pCN, which is similar than BET surface area is determined to be 68 surface area effect for the photocatalytic activity that of pCN (72.13 $m^2 g^{-1}$), indicatin can be ignored.

The morphologies of pCI and Co(1.28%)-pCN are observed by scanning electron microscopy (SEM) and ransmission electron microscopy (TEM). The SEM image in **Figure 2**a shows that pCN has a blocky stacked structure. Compare to pCN, the morphology of Co(1.28%)-pCN is transferred to distorted and curled structure (Figure 2b) because the cobalt chelating pyrimidine derivative restrains the extension of tri-s-triazine units. For TEM images, the pCN exhibits the structure of layered silk-like sheets with wrinkles (Figure 2c), while Co(1.28%)-pCN displays a structure consisting of curly sheets (Figure 2d). No accumulation of nanoparticles or nanoclusters can be observed on the surface of Co(1.28%)-pCN. To confirm the distribution of the Co species, aberration-corrected high-angle-annular-dark-field scanning transmission electron microscopy (HAADF-STEM) characterization is performed. As

displayed in Figure 2e, the HAADF-STEM image exhibits abundant bright dots, which are in atomic size, as highlighted by the red circles. Those bright dots correspond to the Co atoms, which are uniformly implanted in the pCN support, indicating that cobalt predominantly exists in the form of single atoms. The energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Figure 2f) further reveal that the Co atoms are homogeneously distributed on the pCN support. Therefore, these results demonstrate that Co species are mainly dispersed as isolated atoms on the pCN nanosheets.

To determine the electronic structure and coordination, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (FKAFS) spectroscopy at the Co K-edge are recorded. As shown in Figure 3a, the absorption -eite portion of Co(1.28%)pCN is close to that of CoO and is located between the Co foil and Co₃O₄, demonstrating that the valence state of Co is around +2. The formation of Coand Co-N bonds in Co(1.28%)shtel $\chi(k)$ function. As exhibited in Figure pCN is verified by Fourier transformed (FT) We 6)-p is observed, which is apparently different 3b, a Co-ligand peak at ca. 1.5 Å in Co(1 from the Co-Co coordination peak a Co foil and the Co-O coordination peak at 1.7 Å in CoO, further demonstrating the atomically dispersed Co species.^[25] The 1.5 Å FT peak is similar to Co-N bond of CPc, but with slight differences, which may be caused by the Co-O otain the quantitative structural parameters of Co in the Co(1.28%)coordination bond. To pCN, a least-squares EXAFS curve fit is conducted, as displayed in Figure 3c, Figure S3 and Table S1 (Supporting Information). These results indicate that the Co is likely to be coordinated with the O and N atoms, and the coordination number is determined to be 2.6 and 2.6 for Co-O and Co-N, respectively. The coordination structure is also confirmed by the optimized density functional theory (DFT) calculation model as the most thermodynamically stable structure can be formed when both O and N atoms of HDMP participate in the Co coordination, shown in Figure 3d.

Furthermore, X-ray photoelectron spectroscopy (XPS) spectra are used to investigate the surface chemical state of pCN and Co(1.28%)-pCN. As exhibited in Figure S4 (Supporting Information), C, N, O and Co elements are all detected in Co(1.28%)-pCN, but there is no Co element appearing in pCN. The C 1s spectrum of pCN (Figure 4a) possesses three peaks at 288.3, 285.3 and 284.8 eV, which are corresponded to sp²-hybridized carbon (N-C=N), sp³coordinated carbon (C-N) and pure graphitic species (C-C/C=C), respectively.^[26] In comparison with pCN, the Co(1.28%)-pCN has a new peak at 287.1 eV and stronger peaks at 285.3 and 284.8 eV. The new peak located at 287.1 eV is ascribed to the C-O in HDMP.^[27] And the increment in C-N and C-C/C=C intensity should be also attributed to the incorporation of HDMP. In N 1s spectrum of pCN (Figure 4b), three peaks a 400 300 and 398.8 eV are owing to terminal C-NH_x amino functions, N-C₃ groups of skeleton and sp²-bonded nitrogen in C=N-C, respectively.^[28] For Co(1.28%)-pCN, the N-C₂ peak shift to the higher binding energy because the lone pair of electrons on the nitrogen top transfer to the Co atom through the coordinative Co-N bond. In O 1s spectry f p \bigcirc (Figure 4c), the peaks at 532.4 and 531.5 eV are assigned to adsorbed CO₂ or HPD C-O, respectively.^[29] Compared to pCN, these two peaks in Co(1.28%)-pCN are strengthened owing to the incorporation of HDMP. And a new peak at 530.8 eV is merged in Co(1.28%)-pCN, which can be assigned to the Co-O bond.^[30] Moreover, the to 2p band is observed only with the Co(1.28%)-pCN (Figure 4d). The Co 2p spectrum of Co(1.28%)-pCN can be deconvoluted into two pairs of peaks, where the two pairs of peaks at 803.5/797.1 and 786.0/781.3/780.3 eV correspond to Co 2p_{1/2} and Co 2p_{3/2}, respectively. The sharp peaks at 781.3 and 780.3eV are attributed to Co-N and Co-O bonds, respectively.^[31] The above XAS and XPS results corroborate the distribution of Co atoms on the pCN support, which are stabilized by the strong interactions of Co-O/N bonds.

Light-harvesting ability of the photocatalyst is an important factor affecting its photocatalytic performance. As displayed by the ultraviolet visible diffuse reflectance spectra (UV-vis DRS) in Figure S5a (Supporting Information), the introduction of Co atoms causes an

enhanced optical absorption for pCN in visible light region because of the optical absorption of surface Co atoms. This change is also evidenced by the physical appearance changes. With the increase of Co concentration, the color of the sample changes from faint yellow to brown (inset image of Figure S5a, Supporting Information). The bandgap energy (E_g) is calculated by the Kubelka-Munk method. Based upon the Tauc plots in Figure S5b (Supporting Information), the E_g value of pCN and Co(1.28%)-pCN is deduced to be 2.62 and 1.91 eV, respectively. In addition, the potentials of the valence band (VB) are estimated to be 1.81 and 1.26 V for pCN and Co(1.28%)-pCN according to the VB-XPS spectra (Figure S5c, Supporting Information). Therefore, the conduction band (CB) potentials of pCN and Co(1.26%)-pCN are evaluated to be -0.81 and -0.65 V from the formula $E_{CB} = E_{VB} - E_g$ (E_{CB} and E_{CB} and E_{CB} and VB energy), and the detailed band structure alignments is displayed in Figure S5d (Supporting Information).

Except for the optical absorption, Co(1.28%)-teN ilso has more unpaired electrons in the aromatic system than pCN, as verified by lectron spin resonance (ESR) spectra displayed in **Figure 5**a. Obviously, both pCN and Co(1.28%)-pCN exhibit a single Lorentzian line centered at a g value of 2.003 owing to the unpaired electrons on the carbon atoms of the π -conjugated aromatic rings.^[32] But the HR intensity of Co(1.28%)-pCN is increased significantly compared to that of pCN, suggesting the enhanced delocalization of π system and the improved electron mobility. Thus, the density of charge carriers will be increased, which can be evidenced by the Mott-Schottky analysis. As displayed in Figure 5b, both pCN and Co(1.28%)-pCN present positive slopes, suggesting that they are n-type semiconductors with electron conduction. Accordingly, the charge carrier density (N_D) can be calculated from the slope of the Mott-Schottky curve using the Equation (1):^[33]

$$N_{\rm D} = \frac{2}{q\varepsilon\varepsilon_0} \frac{\mathrm{d}E}{\mathrm{d}(1/C^2)} = \frac{2}{q\varepsilon\varepsilon_0} \frac{1}{\mathrm{slope}} \tag{1}$$

Where q represents the electronic charge (1.602 × 10⁻¹⁹ C), ε and ε_0 are the dielectric constant of carbon nitride (5.25) and the permittivity in vacuum (8.85 × 10⁻¹⁴ F cm⁻²). On the basis of the slopes of the Mott-Schottky curves, the N_D of pCN and Co(1.28%)-pCN are computed to be 1.68 × 10²⁴ and 1.88 × 10²⁴ cm⁻³, respectively. The larger carrier density in the Co(1.28%)pCN will contribute to the participation of free charges in photocatalytic reaction.

Next, the photogenerated charge transfer behaviors, which are the key factors in determining the photocatalytic activity, are investigated. The separation and recombination efficiency of the photogenerated electron-hole pairs are analyzed by photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra. As displayed in Figure 5c, compared with pCN, the Co(1.28%)-pCN shows significant decrease of the 2Leinensity, suggesting a larger barrier to charge recombination in Co(1.28%)-pCN. The ensistion peak is red shifted, which is attributed to the extended π -conjugation induced by HDMP.^[34] In order to investigate the lifetimes of photogenerated charges and to further validate the processes of charge separation, the TRPL decay curves are callected on pCN and Co(1.28%)-pCN, as shown in Figure 5d. The TRPL decay curves are callected on pCN and Co(1.28%)-pCN, as shown in

$$R(t) = B_1 \exp\left(-\frac{t}{\tau_1}\right) + B_2 \exp\left(-\frac{t}{\tau}\right)$$
(2)

Where B_1 and B_2 represent the formalized amplitudes of each decay component and τ_1 and τ_2 are values of the lifetime components, respectively. All of the fitting TRPL decay data are listed in the Figure 5e. The average lifetime (τ_{ave}) is calculated from the two lifetime components using the Equation (3):

$$\tau_{\text{ave}} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2} \tag{3}$$

From Equation (3), the average lifetimes of pCN and Co(1.28%)-pCN are calculated to be 8.81 and 7.43 ns, respectively. In comparison to pCN, the lifetime of Co(1.28%)-pCN is decreased, suggesting the faster quenching of the Co(1.28%)-pCN luminescence. Generally, the fast quenching is because of the improved charge separation or stronger nonradiative transitions.

Therefore, the decreased lifetime in Co(1.28%)-pCN is indicative of the enhanced dissociation and transfer efficiency of photogenerated excitons.^[14b, 36]

The transfer ability of photogenerated charge carriers are further studied by the photoelectrochemistry. Firstly, the electrochemical impedance spectroscopy (EIS) analysis is performed to investigate the electronic conductivity of the samples. As shown by EIS Nyquist plots in Figure 5f, the electronic resistance of Co(1.28%)-pCN is smaller than that of pCN, suggesting much lower electron-transfer resistance. Meanwhile, the bode phase spectra (Figure 5g) shows that the frequency peak of Co(1.28%)-pCN shifts slightly to a lower frequency compared with pCN, which indicates a more rapid electron transfer process on Co(1.28%)-pCN. In addition, the linear sweep voltammetry (LSV) curves and transplotocurrent response curves are collected. As exhibited in Figure 5h, the current density of pCN and Co(1.28%)-pCN are 0.72 and 2.52 μ A cm⁻² under dark and 0.81 and 2.96 A cm⁻² under light at 1.0 V vs. Ag/AgCl, respectively. The increased current density in Co(1.28%)-pCN suggests its enhanced charges separation and accelerated charge rans Figure 5i displays the comparison of the Co(1.28%)-pCN. When the light is switched on, transient photocurrent responses of CI an the photocurrents of the sample increase to their maximum level and keep nearly unchanged. Then the photocurrents decrease to the background value when the light is switched off. It is p-pCN presents a larger photocurrent than pCN, indicating that obvious that Co(1.28)Co(1.28%)-pCN possesses superior ability for the separation and transfer of the photogenerated electron-hole pairs. Overall, these results demonstrate well that the light-harvesting ability and charge transfer and separation efficiency of pCN are improved because of the implantation of single-atom cobalt. Therefore, better photocatalytic performance can be anticipated.

The photocatalytic performance of the Co-pCN samples is evaluated by the degradation of OTC under visible light irradiation ($\lambda > 420$ nm). As shown in Figure S6 (Supporting Information), the adsorption ability of the samples for OTC increases with the increase of single-atom cobalt content, while the difference in BET surface area of these samples is not

obvious. This result indicates that the single-atom cobalt can promote the adsorption of OTC, which will be beneficial to the OTC degradation. The photocatalytic degradation efficiency (DE, %) for OTC is calculated using the Equation (4):

$$DE(\%) = \left(1 - \frac{c_t}{c_0}\right) \times 100\% \tag{4}$$

Where C_t is the concentration of OTC solution after t minutes of photocatalytic reaction, C_0 is the initial concentration of OTC. As shown in Figure 6a, no obvious change in OTC concentration can be observed in the absence of photocatalyst, suggesting that the photolysis plays a negligible role in OTC degradation. pCN presents 33.2% degradation efficiency for OTC after 40 min of photocatalytic reaction. Compared to pCN, the CTC the gradation efficiency of Co-incorporated samples are all significantly enhanced. Among o-incorporated samples, the Co(1.28%)-pCN sample exhibits the highest activity for OTC degradation (75.7%). The time-dependent UV-vis spectra of OTC solution over .28%)-pCN photocatalyst (Figure O(S7, Supporting Information) apparently demonstrates at the absorbance of OTC characteristic absorption peak (353 nm) decreases with the madiation time prolongs. However, as the content of single-atom cobalt increases, ytic activity of the sample (Co(2.52%)-pCN) is decreased due to the rap ination of photogenerated charges. Interestingly, the acetylacetone modified pCN) shows some improvement in photocatalytic degradation of OTC, while the activity improvement is more pronounced in the presence of single-atom cobalt, implying that the single-atom cobalt is crucial for high photocatalytic performance. Moreover, the curves of $\ln(C_0/C_t)$ versus t over the samples show a linear relationship (Figure 6b), which is in agreement with the pseudo-first-order model. Thus, the apparent rate constants (k) for OTC degradation over the samples can be deduced by the Equation (5):

$$k = \frac{\ln(C_0/C_t)}{t} \tag{5}$$

The *k* value of the Co(1.28%)-pCN is 0.038 min⁻¹, which is 3.7 times than that of pCN. These results suggest that the single-atom cobalt can highly efficient enhance the photocatalytic

performance of pCN. The photocatalytic stability of the Co(1.28%)-pCN sample is studied by cyclic photocatalytic OTC degradation reactions and a series of characterizations. As displayed in Figure 6c, the Co(1.28%)-pCN photocatalyst still presents high photocatalytic activity for OTC degradation in the subsequent runs and shows no noticeable decrease after four runs. Besides, the XPS, XRD, Raman and ATR-FTIR spectra of the Co(1.28%)-pCN sample (Figure S8, Supporting Information) remain almost unchanged after the photocatalytic reaction, further verifying the physicochemical stability of the Co (1.28%)-pCN photocatalyst. Meanwhile, the photocatalytic degradation activity of Co-pCN is higher than most of other pCN-based photocatalysts reported previously (**Table 1**), demonstrating the **Co**-pCN is a promising photocatalyst for degradation of organic pollutants.

For deeply understanding the transformation pathways of OTC degradation over Co(1.28)pCN, the degradation intermediates of OTC are identified by the liquid chromatography T technology, and the results are shown in coupled with tandem mass spectrometry (LC/MS-I Figure S9 and Table S2 (Supporting Info ation. On the basis of the detected intermediates n process is displayed in Scheme S1 (Supporting and related reports,^[49] the proposed d ego da Information). First OTC (m/z 46141) is decomposed to OTC 1 (m/z = 382.9) through the deamidation, dehydroxylation and dehydration. OTC 1 is then fragmented into OTC 4 (m/z =279.1), and transformed to OTC 6 (m/z = 262.9) via dehydroxylation. Meanwhile, OTC also can be decomposed to OTC 2 (m/z = 362.3) via the N-d-methylation, decarbonylation, dehydroxylation and deamidation. And due to the demethylation, decarbonylation and dehydroxylation, the OTC 2 is transformed to OTC 3 (m/z = 318.3). Then the OTC 3 is decomposed to OTC 5 (m/z = 274.5) via the deamination and dehydroxylation. Subsequently, these intermediates are oxidized to produce opening ring products including OTC 7 (m/z =198.1), OTC 8 (m/z = 194.0), OTC 9 (m/z = 180.0) and OTC 10 (m/z = 143.0). Lastly, these ring-opening products are oxidized into CO₂ and H₂O. The TOC removal efficiency is investigated to assess the mineralization ability of Co(1.28%)-pCN for OTC. As exhibited in

Figure S10 (Supporting Information), the total organic carbon (TOC) removal efficiency in OTC aqueous solution is 18.3% in 40 min under visible light irradiation, further confirming the enhanced photocatalytic performance for Co(1.28%)-pCN.

Furthermore, the generation of reactive species over the Co(1.28%)-pCN photocatalysts is probed by the 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetramethylpiperidine (TEMP) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) spin-trapping ESR technique. Figure 6d and e shows that no ESR signals are monitored in the dark, but two obvious ESR signals are recorded under visible light irradiation. The intensity ratios of these two signals are 1:1:1:1 and 1:2:2:1, which is attributed to the DMPO- $\bullet O_2^-$ and DMPO- $\bullet OH$ adducts, respectively. Meanwhile, a three-line ESR signal of TEMP-¹ adduct th an intensity ratio of 1:1:1 is observed (Figure 6f). The signal of TEMP- $^{1}Q_{2}$ adduct in the dark may be originated from the energy transfer of molecule oxygen.^[50] Besides, Figure 6g displays the signal of TEMPO-h⁺ adduct in the dark and under visible li tradiation, which possesses three peaks with intensity of 1:1:1. The ESR signa TEN •O-h⁺ adduct decreases upon visible light ogenerated holes.^[51] With the irradiation time irradiation, indicating the generation prolongs, the signal intensity of the four adducts all changes, demonstrating their continuous generation by the Co(1.28%)-pNN photocatalyst during the irradiation process. In order to clarify the contribution of specific reactive species generated in the Co(1.28%)-pCN photocatalytic system for OTC degradation, reactive species trapping experiments are carried out by adding quenchers. The quenchers for $\bullet O_2^-$, $\bullet OH$, 1O_2 and h^+ are 4-hydroxy-2,2,6,6tetramethylpiperidinyloxy (TEMPOL), isopropanol (IPA), L-tryptophan and ethylenediaminetetraacetic acid disodium (EDTA-2Na), respectively. As shown in Figure 6h, different quenchers have different effects on OTC degradation in the presence of Co(1.28%)pCN photocatalyst. Specifically, the degradation efficiency of OTC after 40 min of irradiation on solutions containing TEMPOL, IPA, L-tryptophan and EDTA-2Na are 66.6%, 72.9%, 32.4% and 52.9%, respectively. And the corresponding apparent rate constants are 0.029, 0.035, 0.011

and 0.020 min⁻¹, respectively (Figure 6i). The relative contributions of $\bullet O_2^-$, $\bullet OH$, 1O_2 and h^+ to the overall OTC degradation can be deduced by the Equations (6)-(9):

$$R_{\cdot O_2^-} = \frac{k_{\cdot O_2^-}}{k} \approx \frac{(k - k_{\text{TEMPOL}})}{k} \tag{6}$$

$$R_{\cdot \text{OH}} = \frac{k_{\cdot \text{OH}}}{k} \approx \frac{(k - k_{\text{IPA}})}{k}$$
(7)

$$R_{1}_{0_2} = \frac{k_{1}_{0_2}}{k} \approx \frac{(k - k_{\text{L-tryptophan}})}{k}$$
(8)

$$R_{\rm h^+} = \frac{k_{\rm h^+}}{k} \approx \frac{(k - k_{\rm EDTA-2Na})}{k} \tag{9}$$

Accordingly, they are 23.7%, 7.9%, 71.1% and 47.4%, respectively. Because of the complex radical chemistry involved in the photocatalytic reaction the contributions of these four reactive species exceed 100%. These results demonstrate te that ${}^{1}O_{2}$, h⁺ and ${}^{\bullet}O_{2}^{-}$ play significant roles in the Co(1.28%)-pCN photocatactic system for OTC degradation. In addition, the major reactive species in the OTC de riven by pure pCN are identified to be $\bullet O_2^-$, 1O_2 and h^+ (Figure S11a, Supporting Info tion). And the relative contributions of $\bullet O_2^{-}$, 1O_2 , h^+ and $\bullet OH$ to the overall OTC legal dation are estimated to be 64.6%, 44.9%, 35.1% and 6.4%, respectively (Figure orting Information). After single-atom cobalt ve specie changes from $\bullet O_2^-$ to 1O_2 , indicating that the incorporation, the most prin single-atom cobalt mat formation of ¹O₂.

On the basis of the bove results and discussion, the mechanism of OTC degradation in the Co-pCN photocatalyst can be proposed, as shown in **Scheme 1**. Under visible light irradiation ($\lambda > 420$ nm), the Co-pCN is excited to generate electrons (e⁻) and holes (h⁺) (Equation (10)). As the CB potential of Co(1.28%)-pCN (-0.65 V vs NHE) is lower than the redox potential of O₂/•O₂⁻ (-0.33 V vs NHE), the photogenerated electrons on the CB can be captured by molecular oxygen to form •O₂⁻ (Equation (11)). Furthermore, •O₂⁻ can respectively react with h⁺ to form ¹O₂ (Equation (12)), and react with e⁻ and H⁺ to form •OH (Equation (13) and (14)). The generated reactive species (h⁺, •O₂⁻, ¹O₂ and •OH) will then react with the OTC

molecule, leading to its degradation (Equation (15)).

$$\operatorname{CopCN} + hv \to \operatorname{CopCN} \left(e^{-} + h^{+}\right) \tag{10}$$

$$e^- + 0_2 \rightarrow 0_2^- \tag{11}$$

$$\cdot \mathbf{0}_2^- + h^+ \to \ ^1\mathbf{0}_2 \tag{12}$$

$$\cdot 0_2^- + e^- + 2H^+ \to H_2 0_2$$
 (13)

$$H_2O_2 + e^- \to OH^- + OH \tag{14}$$

$$(h^+, O_2^-, O_2^-, OH) + OTC \rightarrow \text{products}$$
 (15)

3. Conclusion

In conclusion, a simple in-situ growth strategy is developed b ingle-atom cobalt in pCN by the bidentate ligand. HAADF-STEM images demonstrate that the Co atoms are atomically dispersed in pCN. EXAFS analysis further indicate that the single-atom cobalt is bond and a Co-N bond. Benefiting from immobilized on pCN by covalently forming Cothe extended optical absorption in visible region, increased electron density, and accelerated separation and transfer of charge cr the Co-pCN photocatalysts present excellent TC legradation under visible light irradiation ($\lambda > 420$ nm). photocatalytic performance for C degradation for optimal sample (Co(1.28%)-pCN) is 0.038 The apparent rate conant d min⁻¹, which is about 3. times than that of pristine pCN. This work develops a novel process to synthesize single-atom modified pCN, and provides a green and highly efficient strategy for the OTC removal.

4. Experimental Section

Preparation of samples: Co-pCN was prepared via thermal polymerization of urea and cobalt (II) acetylacetonate. Typically, 10 g of urea and a certain amount of cobalt (II) acetylacetonate (0, 0.01, 0.05 and 0.1 g) were added into an agate mortar and ground to achieve

complete homogeneity. Then, the obtained powders were transferred to a covered crucible and calcined at 550 °C for 2 h with the heating rate of 5 °C min⁻¹, followed by cooling to room temperature naturally. Finally, the product was washed with deionized water and dried at 60 °C for 12 h. The contents of cobalt in pCN were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7800) method to be 0.29, 1.28 and 2.52 wt%. And the samples were denoted as Co(0.29%)-pCN, Co(1.28%)-pCN and Co(2.52%)-pCN, respectively. Besides, the acetylacetone modified pCN (aa-pCN) was prepared for solid-state ¹³C nuclear magnetic resonance (NMR) spectra analysis. The added molar amount of acetylacetone and heating process was consistent with the preparation of Co(1.28%)-pCN.

Characterization: Solid-state ¹³C NMR spectra were channel cross-polarization magic angle spinning on a Bruker Avance III 600 spectrometer. XCD patterns were recorded on a Bruker D8 Advance diffractometer with Cu Ka radiation Raman tests were performed on a Horiba Jobin Yvon LabRAM HR800 Raman spectroscopy with a He-Cd laser excitation at Hermo Nicolet 5700 spectrophotometer. N₂ 325 nm. ATR-FTIR spectra were acquire n a` adsorption-desorption isotherms and pope distribution curves were investigated using the BET method on a Micromeritic ASAP 2020 HD88 instrument. SEM images were obtained on a Zeiss Sigma HD electron microscope. TEM and EDS mapping images were collected on a FEI Tecnai G2 F20 S-TVIN electron microscope. HAADF-STEM images were collected on a Cs-corrected FEI Titan G2 60-300 electron microscope. X-ray adsorption spectroscopy (XAS) of Co K-edge were recorded on the beamline BL01C1 in National Synchrotron Radiation Research Center (NSRRC), and were provided technical support by Ceshigo Research Service "www.ceshigo.com". The radiation was monochromatized by a Si (111) double-crystal monochromator. The data of XANES and EXAFS were analyzed by Athena software. XPS spectra were acquired on a Thermo Escalab 250Xi spectrometer with monochromatized Al Ka line source (150 W). UV-vis DRS were collected on a PerkinElmer Lambda 750 UV/vis/NIR spectrometer. ESR spectra were measured on a JEOL JES-FA200 spectrometer at room

temperature. PL emission spectra were recorded on a PerkinElmer LS-55 fluorescence spectrophotometer with an excitation wavelength of 350 nm. TRPL decay curves were acquired from a FLS 980 fluorescence lifetime spectrophotometer.

Theoretical computation: Gaussian program was employed for DFT calculations. Geometry optimization was performed at B3LYP-D3BJ/def2-SVP level.

Photoelectrochemical measurement: The photoeletrochemical measurements were conducted on a Chenhua CHI 760E electrochemical workstation using a standard threecompartment electrochemical cell. The platinum foil and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The working electrone was prepared as follows: 5 mg of the sample was dispersed into 1 mL of 10% nation colution to r ultrasonication to get a slurry. 100 µL of the slurry was then coated on a fluorine-doled tinoxide (FTO) glass (1 $cm \times 2 cm$) with an effective working area of 1 cm². After diving at 60 °C for 2 h, the working electrode was calcined at 120 °C for 1 h to enhance adhision. 0.2 M Na₂SO₄ aqueous solution enon amp (PLS-SXE300/300UV, Perfect Light) was employed as the electrolyte. A 300 6 produce light source. Mott-Schottky plots were equipped with a 420 nm cutoff filter as collected at the frequency of 1000 He. EIS was obtained at an applied voltage of 0.15 V with an amplitude of 0.005 V. SV jurves were conducted at the scanning speed of 0.02 V s^{-1} . esponse curves were recorded at an applied voltage of 0 V with the Transient photocurrent light on or off.

Photocatalysis experiment: The photocatalytic performance of the samples was assessed by the degradation of OTC under visible light irradiation ($\lambda > 420$ nm). Typically, 30 mg of the photocatalyst was added into 100 mL of 20 mg L⁻¹ OTC aqueous solution. Prior to irradiation, this suspension was magnetically stirred in the darkness for 30 min to establish the adsorptiondesorption equilibrium of the OTC on the photocatalyst surface. Then, the suspension was irradiated under a 300 W xenon lamp (PLS-SXE300/300UV, Perfect Light) equipped with a 420 nm cutoff filter. At the given irradiation time intervals, 3 mL of the specimen was taken out

and centrifuged to separate the photocatalyst powders. The concentration of OTC aqueous solution was determined using a Shimadzu UV-2700 spectrophotometer at 353 nm by measuring its absorbance. The TOC contents were analyzed a Shimadzu TOC-VCPH analyzer. The degradation intermediates of OTC were analyzed by the LC-MS/MS technology, and the specifically method was provided in Supporting Information. To evaluate the stability of the photocatalyst, the photocatalyst powders were collected via vacuum filtration after one trial with washed by deionized water and ethanol, and dried for the cycle experiment.

Reactive species examination: ESR spin-trapping technique was utilized to detect reactive species generated in the photocatalytic system. DMPO was used is the trapping reagent for $\cdot O_2^-$ and $\cdot OH$, TEMP was used as the trapping reagent for $1^{-1}O_2$ and TEMPO was used as the trapping reagent for h^+ . Furthermore, chemical quenchers were added into the experimental solutions to investigate the contribution of specific reactive species to OTC degradation. The quenching agents for $\cdot O_2^-$, $\cdot OH$, $1^{-1}O_2$ and h^+ were TEMPOL (5 mM), IPA (5 mM), L-tryptophan

(5 mM) and EDTA-2Na (5 mM), respectively

Supporting Information

Supporting Information is a ratio from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Figure 1. a) The proposed synthetic properts of \bigcirc -pCN. Solid-state ¹³C NMR spectra for b) pCN, c) Co(1.28%)-pCN and d) aa-pCU (th) symbols of *, \checkmark and \blacklozenge indicate the spinning sidebands of solid-state ¹³C NMR spectre, the characteristic peaks of pCN and the characteristic peaks of HDMP, respectively. e) YRC patterns, f) Raman spectra and g) ATR-FTIR spectra of the samples.



Figure 2. SEM images of a) p/N and b) Co(1.28%)-pCN. TEM images of c) pCN and d) Co(1.28%)-pCN. e) HAIDF-STEM image and f) EDS elemental mapping images of Co(1.28%)-pCN.



Figure 3. a) Co k-edge XANES spectra of Co foil, CoO, Co₃O₄ and Co(1.28%)-pCN. b) Corresponding Fourier transform spectra of Co foil, CoO and Co(1.28%)-pCN. c) EXAFS r space-fitting curve of Co(1.28%)-pCN (aser. k space-fitting curve of Co(1.28%)-pCN). d) Optimized DFT calculation model of Co(1.28%)-pCN.



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Figure 5. a) ESR spectra, b) Mott-Schottky curves, c) PL spectra, d) TRPL spectra, e) TRPL lifetimes, f) Nyquist plots of EIS, g) Fore phase spectra, h) LSV curves and i) transient photocurrent curves of the samples.



Figure 6. a) Photocatalytic degradation efficience over different samples under visible light irradiation ($\lambda > 420$ nm). b) Pseudo first-on er kinetic fitting curves and the corresponding on OTC by Co(1.28%)-pCN. ESR spectra of kinetic constants. c) Four cycles of degr the d) DMPO- \bullet O₂⁻ adduct, e) DMPO- \bullet H a duct, f) TEMP- $^{1}O_{2}$ adduct and g) TEMPO-h⁺ adduct for Co(1.28%)-pCN under vi 10 irradiation. h) Photocatalytic degradation curves of OTC with different quenchers %)-pCN under visible light irradiation and i) the Col .28 corresponding kinetic constants as well as the relative contributions of different quenchers.



Scheme 1. The proposed photocatalytic degradation mechanism of OTC in Co-pCN.



	Table 1.	. Comparison	with other pCN-	based photocatalysts	for degradation.
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Photocatalysts	Pollutant concentration $(mg L^{-1})$	Dosage $(g L^{-1})$	Light source	$k^{a}(\min^{-1})$	Ref. (year)
β-Bi2O3@g-C3N4	$\frac{(mg 2)}{TC^{b}(10)}$	0.50	250 W XL ^{c)} ($\lambda > 420$ nm)	0.031	[37] (2018)
$Co_3O_4/g-C_3N_4$	TC (10)	0.50	500 W XL ($\lambda > 420$ nm)	0.010	[38] (2018)
γ-Fe ₂ O ₃ /g-C ₃ N ₄	TC (10)	0.50	500 W XL ($\lambda > 420$ nm)	0.014	[39] (2018)
Co ₃ O ₄ @CoO/g-C ₃ N ₄	TC (10)	0.60	500 W XL ($\lambda > 420$ nm)	0.021	[40] (2019)
h-BN/g-C ₃ N ₄	TC (10)	1.00	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.028	[41] (2018)
CDs/g-C3N4/MoO3	TC (20)	0.60	350 W XL ($\lambda > 420$ nm)	0.023	[42] (2018)
KMCN	TC (20)	1.00	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.028	[43] (2018)
HTCN-C	TC (20)	1.00	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.029	[44] (2019)
CNF	TC (21)	0.50	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.014	[45] (2018)
BPTCN	OTC (10)	0.60	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.028	[46] (2020)
BNQDs/UPCN	OTC (10)	1.00	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.031	[47] (2019)
OCN	OTC (20)	1.00	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.016	[48] (2020)
Co-pCN	OTC (20)	0.30	$300 \text{ W XL} (\lambda > 420 \text{ nm})$	0.038	This work

^{a)}k is apparent rate constant; ^{b)}TC is tetracycline; ^{c)}XL is Xenon lamp.

Acerted

Single-atom cobalt is in situ grown on polymeric carbon nitride by the Co-O and Co-N bidentate ligand, exhibiting superb photocatalytic performance in the degradation of oxytetracycline under visible light irradiation ($\lambda > 420$ nm) due to the improved molecular oxygen activation ability induced by the boosted exciton dissociation and accelerated charge transfer.

single atom

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In Situ Grown Single-Atom Cobalt on Polymeric Carbon Nitride with Bidentate Ligand for Efficient Photocatalytic Degradation of Refractory Antibiotics

