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Lattice Engineering on Metal Cocatalysts for Enhanced Photocatalytic Reduction of CO₂ into CH₄: Synergism of Alloying and Hydriding

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Abstract: Photocatalytic conversion of CO2 to CH4 represents an appealing approach to alleviate the world's continued reliance on fossil fuels and global warming resulted from the rise of CO2 concentrations in the atmosphere. However, its practical application is greatly limited by the serious electron-hole recombination in the photocatalysts as well as the production of CO and H₂ as side reactions. In this paper, for the first time, we demonstrate that the photocatalytic reduction of CO₂ to CH₄ can be significantly improved through the simultaneous alloving and hydriding of metal cocatalysts. It is found that the isolation of Cu and H atoms in Pd lattices play three roles in the enhancement of CO₂-to-CH₄ conversion: (1) Cu atoms provide catalytic sites in reduction of CO₂ to CO and then to CH₄ in suppression of H₂ evolution; (2) H atoms improve the electron trapping ability of cocatalysts; (3) H atoms accelerate the reduction of CO to CH₄, the rate-limiting procedure in the conversion of CO₂ to CH₄. Arised from the synergistic interplay between Pd-H and Cu-CO sites, 15 mg of C₃N₄-Pd₉Cu₁H_x achieves 100% selectivity for CH₄ production with an average rate of 0.018 µmol h⁻¹ under visible light irradiation. This work provides insights into the cocatalyst design for highly selective CO₂ conversion through lattice engineering at atomic precision.

Introduction

Photocatalytic reduction of CO_2 into value-added fuels (e.g. methane) by H_2O is of particular interest because of its capability of mimicking natural photosynthesis to convert solar energy into chemical energy, which is a promising approach to address the increasing environmental and energy related concerns.^[1-4] Since the pioneering study by Inoue et al. in 1979, various semiconductor materials have been developed as photocatalysts for CO_2 reduction reaction.^[5-10] Despite the

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promising future and great efforts, this approach is faced with a serious of challenges.^[11,12] On one hand, inevitable electronhole recombination in light-harvesting semiconductors reduces the solar-to-chemical energy conversion efficiency.^[13,14] On the other hand, low adsorption and activation abilities of stable CO₂ molecules on the surface of photocatalysts reduce the catalytic activity. Combination of semiconductors with cocatalysts is a potential method to improve the photocatalytic activity and selectivity.^[15-19] Cocatalysts not only trap the photogenerated electrons from semiconductors in promoting the electron-hole separation, but also serve as catalytic sites for surface reactions. Recently, metal cocatalysts such as Pt,^[20,21] Pd,^[22,23] Ag,^[24] Au^[25] and $Rh^{[26]}$ have been used in photocatalytic CO_2 reduction reactions. In spite of the efforts, multiple reactive routes (e.g. $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O; CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O)$ as well as the side reactions such as the reduction of H₂O to H₂ (e.g. $2H^+ + 2e^- \rightarrow H_2$) take place simultaneously on the surface of cocatalysts, lowering the catalytic activity and product selectivity, which is mainly attributed to the lack of rational design of cocatalysts.^[17]

In the design of cocatalysts, lattice engineering offers a promising opportunity to further improving the activity and selectivity in photocatalytic reactions. Both of the surface and electronic structure of cocatalysts related to catalytic sites can be tailored by lattice engineering, which are two versatile knobs for tuning the catalytic activity and selectivity.^[27] Alloving strategy represents the most promising method to improving the catalytic performance of metal from the angle of lattice engineering. Alloys not only supply various local atomic arrangements on the surface to maneuver the adsorption configuration of CO2 molecules, but also steer the d-band centers of active sites. For instance, resulted from the adjustment of surface and electronic structures, alloying of Cu with Pd, Pt and Au have been reported to achieve giant enhancements on the conversion of CO_2 to CH_4 .^[27-29] When alloying is considered as the doping of foreign atoms into the host lattice substituting the existing atoms, doping of foreign atoms into the interstitial positions of the lattice represents another promising method to improve the photocatalytic performance through controllable lattice engineering. For instance, our previous report has shown that incorporation of H atoms into the lattice of Pd cocatalysts successfully steers both the reactive and charge kinetics in reduction of CO₂ with H₂O into CH₄.^[30] Taken together, the synergism of alloying strategy and interstitial doping method should be a promising approach to further boost the CO₂ conversion efficiency through taking full advantage of lattice engineering on cocatalysts. 1

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Figure 1. (a) Schematic illustrating the synthesis of C_3N_4 based photocatalysts; (b-f) TEM and HRTEM (inset) images of (b) C_3N_4 -Pd, (c) C_3N_4 -Pd₉Cu₁, (d) C_3N_4 -Pd₇Cu₃, (e) C_3N_4 -PdH_x, (f) C_3N_4 -Pd₉Cu₁H_x and (g) C_3N_4 -Pd₇Cu₃H_x; (h) STEM image and (i-l) EDS mapping profiles of C_3N_4 -Pd₉Cu₁H_x showing the element (i) C, (j) N, (k) Pd and (l) Cu.

Herein, we report that the simultaneous incorporation of Cu and H atoms into the lattice of Pd cocatalysts achieves the excellent photocatalytic activity and selectivity in reduction of CO_2 to CH₄. The Cu atoms isolated in Pd lattice facilitate the CO_2 adsorption and activation, which provide highly active sites for the reduction of CO to CH₄ as well as the following reduction of CO₂ to CO, while H atoms in the interstitial voids not only improve the electron trapping ability of cocatalysts, but also participate in the hydrogenation reaction in reduction of CO to CH₄. As a proof of concept, 15 mg of the designed C_3N_4 - $Pd_9Cu_1H_x$ photocatalyst achieves excellent photocatalytic CH_4 production with an average evolution rate of 0.018 μ mol h⁻¹ and selectivity of 100% under visible light irradiation. This work offers a lattice engineering approach to high-selectivity conversion of CO_2 to fuels through the synergism of alloying and hydriding of metal cocatalysts.

Results and Discussion

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Figure 2. (a) XRD pattern and (b) FTIR spectra of C_3N_4 based photocatalysts; (c-f) XPS spectra of C_3N_4 -Pd₉Cu₁ and C_3N_4 -Pd₉Cu₁H_x: (c) C1s, (d) N1s, (e) Pd3d and (f) Cu2p high-resolution spectra.

Sample synthesis and characterization

Graphitic-phase C_3N_4 (g- C_3N_4) is used as the visible light excitable semiconductor in the design of the photocatalysts. Since the discovery by Wang et al. in 2009, polymeric C_3N_4 has become a promising candidate for photocatalytic H₂ evolution and CO_2 reduction due to its low costs, robust stability, environmental friendliness, unique layered architecture and proper band structure.^[31-37] Bulk C_3N_4 is firstly prepared according to previous literature,^[38] which is then ultrasonically exfoliated into C_3N_4 nanosheets (Figure 1a). The as-obtained C_3N_4 nanosheets are wrinkled with a nanoscale thickness and micrometer-sized edge length (Figure S1). X-ray powder diffraction (XRD) pattern of the C_3N_4 is shown in Figure 2a, in which (100) peak at 13.1° represents the in-planar repeating tris-triazine unit, while the strong (002) peak at 27.4° reflects the characteristic interlayer stacking of conjugated aromatic segments.^[39] The advantages of C_3N_4 nanosheets includes: (1) large surface area of nanosheets facilitates the loading of cocatalysts; (2) low thickness of nanosheets shortens the average distance of photogenerated electrons from semiconductor to cocatalysts; (3) both of the high flexibility of nanosheet and conjugated structure of C_3N_4 guarantee the intimate contact between semiconductor and cocatalysts for high-efficient interfacial charge transfer.

PdCu nanocrystals are then *in situ* grown on C_3N_4 nanosheets through reducing K_2PdCl_4 and $CuCl_2$ in aqueous solution, in which the atomic ratios of Pd to Cu can be tuned by adjusting the concentrations of K_2PdCl_4 and $CuCl_2$ (Figure 1a).

As a result, PdCu nanocrystals with 9:1 and 7:3 Pd-to-Cu atomic ratios are supported by C₃N₄ nanosheets to form C₃N₄-Pd₉Cu₁ and C₃N₄-Pd₇Cu₃ hybrid structures, respectively. As a reference sample, bare Pd nanocrystals are also deposited on C₃N₄ nanosheets to form C₃N₄-Pd structure through the *in-situ* reduction of K_2PdCl_4 (Figure 1a). The strong interaction between Pd atoms and N of g-C₃N₄ is helpful for the high stability of PdCu and Pd nanocrystals on the C₃N₄ as well as the effective photogenerated electron transfer between them.[40-42] As shown in the TEM images (Figure 1b-d, also Figure S2 in low magnification), Pd, Pd₉Cu₁ and Pd₇Cu₃ nanocrystals in truncated cubic profile are uniformly distributed over the surface of C₃N₄ nanosheets. The average edge lengths of Pd, Pd₉Cu₁ and Pd₇Cu₃ nanocrystals are determined to be 6.3, 5.7 and 5.1 nm, respectively (Figure S3). In the XRD patterns of C₃N₄-metal hybrid structures, in addition to the peaks of C₃N₄, other peaks can be indexed to the face-centered cubic (fcc) phase of metal nanocrystals according to the standard XRD peaks of Pd (JCPDS 01-1201) and Cu (JCPDS 01-1241) (Figure 2a). The HRTEM images (inset of Figure 1b-d) of the metal nanocrystals show continuous lattice fringes, indicating the monocrystalline structures of the supported nanocrystals. The Pd, Pd₉Cu₁ and Pd₇Cu₃ nanocrystals have a lattice spacing of 2.23, 2.21 and 2.19 Å, respectively, which can be assigned to the (111) planes of the fcc structures. This result indicates that the incorporation of more Cu atoms into Pd lattice slightly reduces the lattice constant. This statement is also confirmed by the XRD pattern, in which the peaks of metal nanocrystals slightly move to higher angles from C₃N₄-Pd to C₃N₄-Pd₉Cu₁, and then to C₃N₄-Pd₇Cu₃ resulted from the smaller atomic radius of Cu (Figure 2a). With the increase of Cu content, the peaks of PdCu nanocrystals move towards the positions of Cu, confirming the alloying between Pd and Cu. As determined by inductively-coupled plasma mass spectrometry (ICP-MS), the molar loading amounts of Pd, Pd_9Cu_1 and Pd_7Cu_3 nanocrystals on C_3N_4 nanosheets are kept the same to eliminate the influence of loading amount of cocatalysts on the photocatalytic performance (Table S1).

In the third step, the as-obtained Pd, Pd₉Cu₁ and Pd₇Cu₃ on C₃N₄ nanosheets are further transformed to the corresponding hydrides through a solvothermal treatment in N,Ndimethylformamide (DMF) (Figure 1a).[43] The as-obtained hybrid structures are named as C_3N_4 -PdH_x, C_3N_4 -Pd₉Cu₁H_x and C_3N_4 -Pd₇Cu₃H_x, respectively (x is not a constant value dependent on the composition of the metal nanocrystals). As revealed by TEM images (Figure 1e-g, also Figure S2 in low magnification), the hydrogenated nanocrystals are still firmly attached to the surface of C_3N_4 . After the treatment, there is a change in the shape of the nanocrystals, and the variation degree increases with the increase of Pd content. For the C₃N₄-PdH_x sample, adjacent nanocubes are fused into irregular nanorods, confirming the serious volume expansion resulted from the interstitial hydrogen atoms (Figure 1e and Figure S2d). Owing to the volume expansion after the hydriding process, the corners of the Pd₉Cu₁H_x nanocubes become more round (Figure 1f and Figure S2e). In contrast, the shapes of Pd₇Cu₃ and Pd₇Cu₃H_x nanocrystals are much similar (Figure 1g and Figure S2f). The more serious lattice expansion with increased content of Pd is also reflected by the average sizes of PdH_x, Pd₉Cu₁H_x and Pd₇Cu₃H_x nanocrystals, which increases by 7.9%, 7.0% and 2.0% after the H doping, respectively (Figure S3). HRTEM images of the metal hydride nanocrystals indicate that the single-crystal structure is not destroyed during the hydriding treatment (inset of Figure 1e-g). The difference is that the lattice spacing of (111) planes increases to 2.29, 2.26, 2.20 Å for PdH_x, Pd₉Cu₁H_x and Pd₇Cu₃H_x, respectively, indicating *ca.* 2.7%, 2.3% and 0.5% lattice expansion after the hydriding process. This statement is in agreement with the XRD results, in which the (111) peaks of nanocrystals shift to lower angle by 1.2°, 1.0° and 0.1° for PdH_x, Pd₉Cu₁H_x and Pd₇Cu₃H_x, respectively (Figure 2a). The lessening of the lattice expansion ratio indicates the declined hydriding degree of the nanocrystals with the increase of Cu content (Figure 1a), which is in agreement with the results of volume expansion (Figure S3). The reason is that the hydriding reaction mainly acts on Pd rather than Cu. It is widely accepted that palladium rather than copper is a hydrogenadsorbing metal that can form stable hydrides.^[44,45] To confirm this, C₃N₄-Cu sample was also synthesized and there was no obvious change in the position of Cu peaks (JCPDS 01-1241) in the XRD patterns before and after the same hydriding treatment (Figure S4). With the lower content of Pd, less amount of H atoms are incorporated into the lattice interstitial sites of PdCu nanocrystals, leading to the weaker lattice expansion. Namely, the value of x decreases with the incremental content of Cu in the PdCuH_x. The nanosheet supported hydrides hybrid structure is further verified by the scanning TEM (STEM) image of C_3N_4 -Pd₉Cu₁H_x and the corresponding energy-dispersive spectroscopy (EDS) mapping (Figure 1h-I). It should be noted that there is some inconsistence in the images of Pd and Cu with the reason that the lower content of Cu in the Pd₉Cu₁H_x results in much weaker Cu signal in comparison with Pd signal in the EDS mapping.^[46] In spite of this, it can be seen clearly that most of Pd and Cu elements are distributed at the same regions, suggesting the Pd and Cu composition of the nanocrystals. After the hydriding process, there is no obvious change in the loading amounts of metal and the Pd : Cu molar ratios in the C₃N₄-based hybrid structures (Table S1).

The chemical structure and composition information of the C_3N_4 based samples are further collected by Fourier transform infrared (FTIR) spectra and X-ray photoelectron spectra (XPS). FTIR spectra of C₃N₄ based samples only exhibit the characteristic peaks of C₃N₄, including the s-triazine ring modes (810 cm⁻¹), aromatic carbon nitride heterocycles (1000–1800 cm⁻ ¹) and N-H stretching (3000–3600 cm⁻¹), indicating that there is no obvious change in the chemical structure of C₃N₄ during the growth of metal nanocrystals as well as the following hydriding process (Figure 2b).^[47] The BET surface areas are measured to be 56, 43, 44, 42, 46, 46 and 41 $m^2 g^{-1}$ for C₃N₄, C₃N₄-Pd, C₃N₄- $PdH_{x},\ C_{3}N_{4}-Pd_{9}Cu_{1},\ C_{3}N_{4}-Pd_{9}Cu_{1}H_{x},\ C_{3}N_{4}-Pd_{7}Cu_{3}\ and\ C_{3}N_{4}-Pd_{7}Cu_{3}$ Pd₇Cu₃H_x, respectively, revealing that the C₃N₄ based composite samples have smaller specific surface areas than that of pure C₃N₄ owing to the loading of metal and metal hydrides, which block some mesopores and space of C_3N_4 (Figure S5).^[48] However, the similar specific surface area of the different

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Figure 3. (a) Average H₂, CO, and CH₄ evolution rates with C₃N₄-based samples as photocatalysts as well as their selectivity in CH₄ production under visible light (420 < λ < 780 nm) irradiation; (b) average CH₄ evolution rates with C₃N₄-Pd₉Cu₁H_x as photocatalyst in four successive cycles under visible light (420 < λ < 780 nm) irradiation.

composites guarantees the approximate ability for CO2 molecules to diffuse into the samples and contact with the surface of metal and metal hydrides for catalytic reactions. With C_3N_4 -Pd₉Cu₁ as a representative sample, survey XPS spectrum indicates the C, N, Pd and Cu elements in the sample (Figure S6a). The highresolution C1s spectrum can be divided into three peaks at 284.5, 285.9 and 287.7 eV, corresponding to the surface adventitious carbon (C-C), residual C-O, and carbon atom in the N-C=N group, respectively (Figure 2c). $^{\left[49\right] }$ In the N1s spectrum, three peaks centered at 398.4, 400.1 and 404.1 eV are attributed to sp²-hybridized nitrogen (C=N-C) involved in the triazine rings, quaternary nitrogen bonded to three carbon atoms in the aromatic rings [N–(C)₃], and π -excitations, respectively (Figure 2d).^[50] In reference to the XPS spectra of bare C_3N_4 , the C1s peak at 287.7 eV and N1s peaks at 398.4 and 400.1 eV are in lower binding energies, suggesting the occurrence of an electronic interaction between C₃N₄ and PdCu in the hybrid structure (Figure S7).^[51,52] As for the high-resolution Pd3d spectrum, the doublet centered at 335.0 (Pd3d_{5/2}) and 340.3 eV (Pd3d_{3/2}) are in agreement with the zero valence of Pd, while trace amounts of Pd (II) are also shown as doublets (336.3/341.6 eV), respectively (Figure 2e).^[26] In comparison with Pd3d, the Cu2p signal is much weaker because of the lower content of Cu. The Cu2p spectrum can also be fitted with four peaks (Figure 2f). Two peaks at 932.5 eV (Cu2p_{3/2}) and 952.5 eV (Cu2 $p_{1/2}$) can be indexed to Cu(0), while the other two peaks centered at 1.3 eV higher binding energy are the characteristic peaks of Cu(I).^[53] The detected peaks of Pd(II) and Cu(I) suggest the surface partial oxidation of PdCu nanocrystals, which is a typical feature of solution-phase synthesized PdCu nanocrystals.^[54] The Pd and Cu signals in C₃N₄-Pd₉Cu₁ are in good agreement with Pd3d spectrum of C₃N₄-Pd and Cu2p spectrum of C₃N₄-Cu, respectively (Figure S8). To further compare the survey XPS spectrum of C₃N₄-Pd₉Cu₁ with that of C_3N_4 -Pd₉Cu₁H_x, it can be found that there is no obvious change in the elements of the sample after the hydriding treatment (Figure S6a). Noting that the doped H atoms can not be detected by the XPS spectra. The high-resolution C1s and N1s signals of C_3N_4 -Pd₉Cu₁ and C_3N_4 -Pd₉Cu₁H_x are also much similar, further confirming the stable composition of C₃N₄ during the hydriding treatment (Figure 2c and 2d). On the contrary, the

high-resolution spectra of Pd3d and Cu2p are different between the two samples. In comparison with C_3N_4 -Pd₉Cu₁H_x exhibits obvious declines in the intensity of Pd(II) and Cu(I) peaks (Figure 2e and 2f), suggesting the reduction of oxidized Cu and Pd on the surface of nanocrystals during the hydriding process.

Photocatalytic performance analysis

15 mg of as-obtained C_3N_4 based samples are then used as photocatalysts in CO_2 reduction reaction, which are irradiated by visible light in the mixed vapor of CO_2 and H_2O , and subsequently the products are measured by gas chromatography. As shown in Figure 3a, C_3N_4 produces large amount of H_2 and small amounts of CO and CH_4 , which is in agreement with previous report.^[55] The selectivity in CH_4 production is determined to be 18.9%, which is calculated according to the average evolution rates of the products as well as the required electrons to generate reduction products using the following equation:

Selectivity(%) = $[8v(CH_4)]/[2v(H_2) + 2v(CO) + 8v(CH_4)] \times 100\%$ With the combination of Pd nanocrystals with C₃N₄, the average production rates of H₂, CO and CH₄ increase by 8.7, 3.8 and 1.5 times, respectively. The high H₂ production rate of 0.129 µmol h⁻¹ contributes to low selectivity (4.0%) of C₃N₄-Pd in CH₄ production. With the alloying of Cu with Pd, the dominant H₂O reduction reaction is effectively eliminated and H₂ product can not be detected. Furthermore, in comparison with C₃N₄-Pd₇Cu₃, C₃N₄-Pd₉Cu₁ realizes a higher average CH₄ production rate but a lower CO production rate, which contributes to the higher selectivity of 96.1% for CH₄ production.

After the hydriding treatment, there is an enhancement of the photocatalytic activities in each sample, which is mainly reflected by the boosted CH₄ production as well as the reduced H₂ and CO production. After the hydriding treatment, the average CH₄ production rate increases by 2.8, 4.0 and 2.6 times for C₃N₄-PdH_x, C₃N₄-Pd₉Cu₁H_x and C₃N₄-Pd₇Cu₃H_x, respectively. Notably, C₃N₄-Pd₉Cu₁H_x achieves the highest performance with a selectivity of 100% and an average rate of 0.018 µmol h⁻¹ for CH₄ production. In contrast, C₃N₄-PdH_x and C₃N₄-Pd₇Cu₃H_x are exhibit relatively lower selectivities of 51.1% and 98.7% as well



Figure 4. (a) UV-vis-NIR diffuse reflectance spectra of C_3N_4 based photocatalysts; (b,c) photocurrent vs. time (I-t) curves (b) and EIS Nyquist plots (c) of C_3N_4 based photocatalysts at 0.2 V vs. Ag/AgCl under visible light (420 < λ < 780 nm) irradiation; (d) PL spectra of C_3N_4 based photocatalysts excited at 390 nm.

as production rates of 0.004 and 0.010 $\mu mol~h^{\text{-1}}$ for CH_4 production, respectively. The excellent photocataytic activity of C_3N_4 -Pd₉Cu₁H_x is further confirmed by its superior selectivity and average production rate for CH₄ production in comparison with those of previously reported C₃N₄-metal hybrid photocatalysts and the $C_3N_4\mbox{-}Cu$ synthesized by us (Table S2). $^{[21,23,49,55,56]}$ In addition to the photocatalytic activity, the C_3N_4 -Pd₉Cu₁H_x also realizes an excellent photocatalytic stability. As indicated by Figure 3b, the C_3N_4 -Pd₉Cu₁H_x photocatalyst shows high durability in four 4 h cycles, which can be ascribed to the wellmaintained $Pd_9Cu_1H_x$ nanocrystals on the C_3N_4 nanosheets. From the TEM image of C₃N₄-Pd₉Cu₁H_x after the photocatalytic cycles, it can be seen that $Pd_9Cu_1H_x$ nanocrystals are still firmly attached to the C₃N₄ nanosheets without any change in the shape (Figure S9a). Moreover, the same positions of the XRD peaks show that there is no obvious change in the structure of Pd₉Cu₁H_x after the photocatalytic cycles (Figure S9b). Noting that O₂ as oxidation product is also detected in the photocatalytic reaction, suggesting the occurrence of $H_2O + 2h^+ \rightarrow 1/2O_2 + 2H^+$. Meanwhile, no liquid products of CO2 reduction are detected in the photocatalytic system.

Photocatalytic mechanism study

To further analyze the possible mechanism of the photocatalytic results, the charge kinetics of C_3N_4 based samples are then investigated considering the generation and transfer of photogenerated electrons greatly influence the ultimate photocatalytic activity. The UV-vis-NIR diffuse reflectance

spectra are firstly collected to reveal the light absorption abilities of C₃N₄ based samples (Figure 4a). Bare C₃N₄ exhibits light absorption in visible region with an absorption edge of ca. 460 eV, which can be ascribed to the intrinsic bandgap of $C_3N_4.^{\left[57\right]}$ The absorption edge of C₃N₄ does not change after the introduction of metal nanocrystals. But the background absorption in the longer wavelength region is greatly augmented after the loading of nanocrystals, which is in agreement with the color of the samples changing from yellow to gray (Figure S10). The broad background absorption is attributed to the absorbance of Pd and PdCu nanocrystals through exciting the bound electrons to high energy levels via interband transitions.^{[58]} In spite of this, C_3N_4 is still the light-harvesting component, because Pd and PdCu are nonplasmonic metal in visible region and can not be excited to produce hot electrons.^[59] As shown in Figure S11, the suspensions of bare Pd and PdCu nanoparticles exhibit black color with only a weak plasmonic absorption band in the UV region. More importantly, all the C₃N₄ based hybrid structures before and after the hydriding process show comparable light absorption, which is in accordance with their same color and guarantees their equivalent abilities in generating electron-hole pairs (Figure S10). From the UV-vis-NIR diffuse reflectance spectra (Figure 4a) and valence-band XPS spectra (Figure S6b), the same bandgap and valance band position of C₃N₄ between C₃N₄-Pd₉Cu₁ and C₃N₄-Pd₉Cu₁H_x suggest that the electronic structure of C₃N₄ is not altered during the hydriding transversion.

With the comparable capability in generating charge carriers, the electron-hole separation abilities of the C_3N_4 based samples



Figure 5. (a) XRD pattern of TiO₂ based photocatalysts; (b) average H₂, CO and CH₄ evolution rates with TiO₂ based samples as photocatalysts under UV light ($\lambda < 420 \text{ nm}$) irradiation.

are revealed by photocurrent response (Figure 4b). C₃N₄ exhibits obvious photocurrent density under visible light irradiation, demonstrating that it is photo-excited to produce electron-hole pairs. Then the photocurrent density of C₃N₄ is significantly boosted with the loading of metal nanocrystals, confirming the cocatalyst role of the nanocrystals in trapping electrons from C_3N_4 . In detail, photogenerated electrons in C_3N_4 can transfer to metal nanocrystals through the formation of which Schottky junction, reduces the electron-hole recombination in C₃N₄. The photocurrent responses are found to be in the sequence of C_3N_4 -Pd $> C_3N_4$ -Pd₉Cu₁ $> C_3N_4$ -Pd₇Cu₃. It is widely recognized that the electron trapping ability of metal cocatalyst is greatly determined by its work function. The work function of Pd (≈5.1 eV) is larger than that of Cu (≈4.7 eV).^[60] Thus the higher content of Pd contributes to the stronger electron trapping ability of cocatalysts. Furthermore, both of the work functions of Pd and Cu are larger than that of C_3N_4 (≈4.3 eV), ensuring the transfer of photogenerated electrons from C₃N₄ to both of Pd and PdCu nanocrystals.^[23] The different electron trapping abilities of Pd and PdCu nanocrystals are confirmed by the electrochemical impedance further spectroscopy (EIS) and photoluminescence (PL) emission spectra (Figure 4c and 4d). With the increase of Cu content, the enlarged radii of semicircular Nyquist plots suggest the poorer interfacial electron transfer from C₃N₄ to cocatalysts. Also the PL intensity of C₃N₄ significantly decreases with the addition of metal nanocrystals, indicating that the radiative electron-hole recombination inducing PL in C_3N_4 is effectively suppressed by the cocatalysts. The order of PL quenching degree is C_3N_4 -Pd C_3N_4 -Pd₉Cu₁ > C_3N_4 -Pd₇Cu₃, matching well with the >photoelectrochemical results.

The high electron trapping ability of the cocatalysts may facilitate the 8-electron reduction of CO₂ to CH₄ as compared with 2-electron reactions in producing CO and H₂. However, the charge kinetics behaviors are not in agreement with the photocatalytic results, in which C_3N_4 -Pd realizes the highest electron trapping ability but the lowest photocatalytic activity and selectivity for CH₄ production among the three C_3N_4 -metal samples. This contradiction reveals that the ultimate photocatalytic activity is not only determined by the charge

transfer behaviors, but also the reactive kinetics on the surface of cocatalysts. The large amount of H_2 generated in C_3N_4 -Pd derives from the high adsorption and activation abilities of H₂O molecules on the surface of Pd.^[61,62] In sharp contrast, Cu is a highly active sites for the adsorption and activation of CO₂ molecules.[63-65] Especially, the isolation of Cu atoms in Pd lattice can form the paired Cu-Pd sites for improved CO2 adsorption and elevate the d-band center of Cu sites for improved CO₂ activation.^[27] As a result, the H₂ evolution reaction is inhibited on the surface of PdCu cocatalysts. Furthermore, the rate-limiting H reduction of adsorbed CO to CH₄ occurs following the reduction of CO₂ to CO at Cu sites.^[4,66] When the content of Cu is too high, surface Pd atoms can not offer enough adsorbed H atoms in reduction of CO. As a result, Pd₇Cu₃ exhibits a higher average CO production rate in comparison with Pd₉Cu₁, giving rise to the lower selectivity in CH₄ production. Therefore, Pd₉Cu₁ cocatalyst with medium electron trapping ability but superior surface reactivity realizes the highest photocatalytic activity and selectivity in CH4 production among the three samples. To further confirm this statement, we have employed TiO₂ nanosheets as UV excitable semiconductor to integrate with Pd and PdCu cocatalysts (Figure 5a and Figure S12). The loading amounts of the cocatalysts on TiO_2 are also kept the same in the TiO_2 based samples, which are lower than those on C₃N₄ owing to the smaller specific surface area of thicker TiO₂ nanosheets. As shown in Figure 5b, both of the UV photocatalytic activity and selectivity of TiO₂-Pd₉Cu₁ in reduction of CO₂ to CH₄ are higher than those of TiO2-Pd and TiO2-Pd7Cu3 despite the different semiconductor supporters and different loading amounts of cocatalysts under different light excitation wavelengths.

To further demonstrate the contribution of H doping to the enhanced photocatalytic performance, the photoelectrochemical properties of C_3N_4 -hydrides photocatalysts are also measured. After the hydriding treatment, both of the augment of photocurrent response and the decrease of arc radii are observed for the three samples, suggesting the incremental electron trapping abilities of the hydride cocatalysts. In view of the lattice H is more electronegative than those of Pd and Cu in the metal hydrides, the formed new H-induced energy states are

below the bottom of Pd and PdCu-derived d-bands, thus improving the ability to accept electrons.^[30] The enhanced electron trapping ability is also confirmed by the PL spectra, in which the PL quenching degrees of C_3N_4 -hydrides are larger than those of corresponding C_3N_4 -metal samples. The relationship between the hydriding degree and electron acceptability of cocatalysts can also be confirmed by the less improved electron trapping ability of Pd₇Cu₃H_x with lower hydriding degree.

In addition to the electron trapping ability, H doping also contributes to the enhanced reactive kinetics on the surface of cocatalysts. In comparison with the photocurrent response, the effect of hydrogenation on the photocatalytic activity in CH4 production appears to be larger. As the rate-limiting process of CH₄ production, the reduction of CO on the Cu sites is greatly influenced by the amount of H adsorbed on the Pd atoms. Though Pd based metal cocatalysts can adsorb H atoms during the photocatalytic reaction, the limited adsorption amount can not maintain the continuous conversion of CO to CH₄. Consequently, CO can also be produced on the surface of metal cocatalysts. On the contrary, metal hydride is a reservoir of atomic hydrogen, and a higher concentration of hydrogen atoms leads to a higher flux of atomic hydrogen from the bulk to the surface.^[67] The higher availability of hydrogen atoms in the chemisorbed state at the surface of cocatalysts accelerates the reduction of CO and formation of CH₄, which contributes to the decrease or absence of CO production on the metal hydride cocatalysts. Meanwhile, the expanded lattice of metal hydride also facilitates the diffusion of H atoms into the lattice of cocatalysts during the photocatalytic reaction, which further prevents the H₂ evolution in the photocatalytic reaction. And the successive hydrogen cycle guarantees the metal hydride cocatalysts in long-term use with high catalytic stability. To confirm the proposed photocatalytic mechanism, isotopic labeling experiments are performed on C₃N₄-Pd₉Cu₁H_x using D_2O instead of H_2O . The mass spectra of CH_xD_{4-x} (m/z = 17 and 18) suggest that the H atoms in the CH₄ product originate from both H₂O and lattice H in PdCuH_x (Figure S13a). Moreover, C¹³labeled isotopic experiments are performed on C₃N₄-Pd₉Cu₁H_x using ¹³CO₂ in place of ¹²CO₂. The mass spectra of ¹³CH₄ (m/z = 17) suggest that the CH₄ product originates from the added CO₂ molecules (Figure S13b).^[68,69]

Based on the above discussion, three effects are believed to contribute to the enhanced photocatalytic performance of PdCuH_x cocatalysts in conversion of CO₂ to CH₄ (Figure 6). Firstly, the doping of H atoms into the lattice of PdCu significantly improves the electron trapping abilities of the cocatalysts. Secondly, Cu atoms in Pd lattice act as highly active catalytic sites in reduction of CO₂ to CO as well as the following reduction of CO to CH₄. Thirdly, H atoms in Pd lattice participate in the rate-limiting process in reduction of CO to CH₄. The above three effects can be used to explain the highest photocatalytic activity and selectivity of C_3N_4 -Pd₉Cu₁H_x in CH₄ production among the C₃N₄ based samples. On one hand, high content of Pd not only ensures the large work function of Pd₉Cu₁ cocatalysts in electron trapping, but also facilitates the incorporation of more H atoms into Pd₉Cu₁ lattice in conversion

of CO to CH₄. On the other hand, the incorporation of trace Cu atoms in Pd matrix can form pairings of Pd-H sites with adjacent Cu sites, which not only facilitate the adsorption and activation of CO₂ molecules, but also enhance the reduction of Cu-bound CO to CH₄. As for the Pd₇Cu₃H_x, higher content of Cu not only decreases the electron trapping ability of cocatalysts, but also leads to the formation of Cu-Cu pairs, in which the synergistic reactivity interplay between Pd-H sites and neighboring Cu sites in CH₄ production can not be realized. The designed Pd₉Cu₁H_x as ideal cocatalysts is further confirmed by the excellent photocatalytic activity of TiO₂-Pd₉Cu₁H_x (0.330 µmol h⁻¹ of average CH₄ production rate using 15 mg of catalysts with 100% selectivity) in comparison with those of TiO₂-Pd, TiO₂-Pd₉Cu₁, TiO_2 -Pd₇Cu₃, TiO_2 -PdH_x and TiO_2 -Pd₇Cu₃H_x under UV light irradiation (Figure 5b).



Figure 6. Schematic illustrating the photocatalytic mechanism in the reduction of CO_2 to CH_4 with C_3N_4 -PdCuH_x as catalyst.

Conclusions

In summary, lattice engineering is performed on the metal cocatalysts for improved photocatalytic performance in conversion of CO2 to CH4, which is achieved through the simultaneous incorporation of Cu and H atoms into the lattice of Pd cocatalysts. It is found that the substitutional Cu atoms in the Pd lattice act as highly active catalytic sites in reduction of CO₂ to CO intermediates as well as the following conversion of CO to CH₄ in addition to prevent the side reaction in reduction of H₂O to H₂. Meanwhile, the interstitial H atoms in the Pd lattices not only enhance the electron trapping ability of cocatalysts, but also participate in the rate-limiting process in reduction of CO to CH₄. Remarkably, the synergistic effect between Cu and H atoms in Pd lattice is maximized through the formation of paired Pd-H-Cu sites in optimizing the rate-limiting Pd-H reduction of Cu-bound CO. As a result, Pd₉CuH_x cocatalysts integrated with C₃N₄ have achieved a high selectivity of 100% for CH₄ production with an average rate of 0.018 µmol h⁻¹ under visible light irradiation. The designed Pd₉Cu₁H_x as ideal cocatalyst is further confirmed by the highest photocatalytic activity (0.330 μ mol h⁻¹) and selectivity (100%) of TiO₂-Pd₉Cu₁H_x in CH₄ production under UV light irradiation among the TiO₂ based samples. This work demonstrates the importance in the design of cocatalysts for

solar-driven \mbox{CO}_2 conversion through lattice engineering at atomic precision.

Experimental Section

Synthesis of C₃N₄-PdCu. In a typical synthesis of C₃N₄-PdCu, 20 mg of C₃N₄ nanosheets were dispersed in 8 mL of water to form an aqueous suspension with probe sonication (Scientz-IID, China) for 1 h in a 50 mL glass vial. Subsequently, 105 mg of polyvinylpyrrolidone (PVP), 120 mg of ascorbic acid, and 300 mg of KBr were added into the glass vial under magnetic stirring, which were then transferred to a 50-mL three-neck flask, and pre-heated under magnetic stirring at 80 °C for 10 min in an oil bath. Then 3.0 mL of an aqueous solution containing certain amounts of K₂PdCl₄ and CuCl₂·2H₂O was added into the flask, and the reaction was proceed at 80 °C for 3 h. 0.054 mmol of K₂PdCl₄ and 0.006 mmol of CuCl₂·2H₂O were used in the synthesis of C₃N₄-Pd₇Cu₃, 0.042 mmol of K₂PdCl₄ and 0.018 mmol of CuCl₂·2H₂O were used. The resultant product was separated by centrifugation, washed with acetone once and water three times, and dried at 45 °C in a vacuum.

Synthesis of C₃N₄-PdCuH_x. In the conversion of C₃N₄-PdCu into C₃N₄-PdCuH_x, 40 mg of as-synthesized C₃N₄-PdCu was re-dispersed in 20 mL of N,N-dimethylformamide (DMF) in a 50-mL Teflon-lined stainless-steel autoclave, which was then heated at 160 °C for 16 h. The resultant product was separated by centrifugation, washed with acetone once and water three times, and dried at 45 °C in a vacuum.

Photocatalytic CO₂ reduction measurement. CO₂ photocatalytic reduction reaction was conducted in a 100 mL reactor purchased from Perfect Light Company (China, Beijing). To remove possible trace organic contaminants, all the samples were treated at 160 °C for 3 h in air. In a typical measurement, 15 mg of photocatalyst was dispersed on the flat glass plate on the bottom of the reactor. And 1 mL H₂O was added and surrounded the plate. The reactor loaded with photocatalysts was first purged with high purity CO2 for 30 min. Then the light-irradiation experiment was performed by using a 300 W Xe lamp with visible light as the illumination source. The power density of visible light (780 nm $> \lambda$ > 420 nm) was measured to be 50 mW cm⁻² with an irradiatometer (FZ-A, Photoelectric Instrument Factory, Beijing Normal University). The photocatalytic reaction was typically performed for 4 h. During the irradiation, 1 mL gas was sampled from the glass chamber. And the amount of products involved were determined using gas chromatography (GC-2014, Shimadzu) with Ar as carrier gas. $\,H_2$ and O_2 were determined using a thermal conductivity detector (TCD). CH₄ was measured by flame ionization detector (FID), and CO was converted to CH_4 by a methanation reactor and then analyzed by FID. The possible liquid products were also analyzed by a FID using gas chromatography (GC-2010 Plus, Shimadzu). During the stability test, the photocatalysts were collected after each run and then reused for the photocatalytic reaction. In the activity measurement of TiO₂ based photocatalysts, UV light (λ < 420 nm) with a power density of 10 mW cm⁻² was used instead of visible light with other experimental conditions unchanged.

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- S. N. Habisreutinger, L. Schmidt-Mende, J. K. Stolarczyk, Angew. Chem. Int. Ed. 2013, 52, 7372.
- [2] W. Tu, Y. Zhou, Z. Zou, Adv. Mater. 2014, 26, 4607.
- [3] J. L. White, M. F. Baruch, J. E. Pander III, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* 2015, *115*, 12888.
- [4] S. C. Roy, O. K. Varghese, M. Paulose, C. A. Grimes, ACS Nano 2010, 4, 1259.
- [5] T. Inoue, A. Fujishima, K. Honda, Nature 1979, 277, 637.
- [6] J. Yu, J. Low, W. Xiao, P. Zhou, M. Jaroniec, J. Am. Chem. Soc. 2014, 136, 8839.
- [7] L. Liu, H. Zhao, J. M. Andino, Y. Li, ACS Catal. 2012, 2, 1817.
- [8] Q. Liu, Y. Zhou, J. Kou, X. Chen, Z. Tian, J. Gao, S. Yan, Z. Zou, J. Am. Chem. Soc. 2010, 132, 14385.
- [9] S. Yan, S. Ouyang, J. Gao, M. Yang, J. Feng, X. Fan, L. Wan, Z. Li, J. Ye, Y. Zhou, Z. Zou, *Angew. Chem. Int. Ed.* 2010, *49*, 6400.
- [10] R. Kuriki, K. Sekizawa, O. Ishitani, K. Maeda, Angew. Chem. Int. Ed. 2015, 54, 2406.
- [11] H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, Adv. Mater. 2012, 24, 229.
- [12] S. Bai, J. Jiang, Q. Zhang, Y. Xiong, Chem. Soc. Rev. 2015, 44, 2893.
- [13] C. Guo, J. Ran, A. Vasileff and S. Z. Qiao, *Energy Environ. Sci.* 2018, 11, 45.
- [14] M. Z. Rahman, K. Davey and S. Z. Qiao, J. Mater. Chem. A 2018, 6, 1305.
- [15] J. Yang, D. Wang, H. Han, C. Li, Acc. Chem. Res. 2013, 46, 1900.
- [16] J. Ran, J. Zhang, J. Yu, M. Jaroniec, S. Z. Qiao, Chem. Soc. Rev. 2014, 43, 7787.
- [17] S. Bai, W. Yin, L. Wang, Z. Li, Y. Xiong, RSC Adv. 2016, 6, 57446.
- [18] J. Ran, M. Jaroniec, S. Z. Qiao, Adv. Mater. 2018, 30, 1704649.
- [19] J. Ran, B. Zhu, S. Z. Qiao, Angew. Chem. Int. Ed. 2017, 56, 10373.
- [20] W. N. Wang, W. J. An, B. Ramalingam, S. Mukherjee, D. M. Niedzwiedzki, S. Gangopadhyay, P. Biswas, J. Am. Chem. Soc. 2012, 134, 11276.
- [21] J. Yu, K. Wang, W. Xiao, B. Cheng, Phys. Chem. Chem. Phys. 2014, 16, 11492.
- [22] Y. Zhu, Z. Xu, W. Jiang, S. Zhong, L. Zhao, S. Bai, J. Mater. Chem. A 2017, 5, 2619.
- [23] S. Bai, X. Wang, C. Hu, M. Xie, J. Jiang, Y. Xiong, Chem. Commun. 2014, 50, 6094.
- [24] K. lizuka, T. Wato, Y. Miseki, K. Saito, A. Kudo, J. Am. Chem. Soc. 2011, 133, 20863.
- [25] P. Kar, S. Farsinezhad, N. Mahdi, Y. Zhang, U. Obuekwe, H. Sharma, J. Shen, N. Semagina, K. Shankar, *Nano Res.* 2016, 9, 3478.
- [26] Y. Zhu, Z. Xu, Q. Lang, W. Jiang, Q. Yin, S. Zhong, S. Bai, *Appl. Catal. B: Environ.* 2017, 206, 282.
- [27] R. Long, Y. Li, Y. Liu, S. Chen, X. Zheng, C. Gao, C. He, N. Chen, Z. Qi, L. Song, J. Jiang, J. Zhu, Y. Xiong, J. Am. Chem. Soc. 2017, 139, 4486.
- [28] Q. Lang, Y. Yang, Y. Zhu, W. Hu, W. Jiang, S. Zhong, P. Gong, B. Teng, L. Zhao, S. Bai, *J. Mater. Chem. A* 2017, 5, 6686.
- [29] Q. Kang, T. Wang, P. Li, L. Liu, K. Chang, M. Li, J. Ye, Angew. Chem. Int. Ed. 2015, 54, 841.
- [30] Y. Zhu, C. Gao, S. Bai, S. Chen, R. Long, L. Song, Z. Li, Y. Xiong, *Nano Res.* 2017, 10, 3396.
- [31] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, *8*, 76.
- [32] P. Niu, L. Zhang, G. Liu, H. M. Cheng, Adv. Funct. Mater. 2012, 22, 4763.
- [33] P. Yang, H. Ou, Y. Fang, X. Wang, Angew. Chem. Int. Ed. 2017, 56, 3992.

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- H. Ou, P. Yang, L. Lin, M. Anpo, X. Wang, Angew. Chem. Int. Ed. 2017, 56. 10905.
- X. Wang, S. Blechert, M. Antonietti, ACS Catal. 2012, 2, 1596. [35]
- [36] M. Zhou, P. Yang, R. Yuan, A. M. Asiri, M. Wakeel, X. Wang, ChemSusChem 2017, 10, 4451.
- [37] G. Liu, P. Niu, C. Sun, S, C. Smith, Z. Chen, G. Q. Lu, H. M. Cheng, J. Am. Chem. Soc. 2010, 132, 11642.
- [38] Z. Wang, W. Guan, Y. Sun, F. Dong, Y. Zhou, W. K. Ho, Nanoscale 2015. 7. 2471.
- [39] Q. Xiang, J. Yu, M. Jaroniec, J. Phys. Chem. C 2011, 115, 7355.
- J. H. Lee, J. Ryu, J. Y. Kim, S. Nam, J. H. Han, T. Lim, S. Gautam, K. H. [40] Chae, C. W. Yoon, J. Mater. Chem. A 2014, 2, 9490.
- [41] R. Arrigo, M. E. Schuster, Z. Xie, Y. Yi, G. Wowsnick, L. L. Sun, K. E. Hermann, M. Friedrich, P. Kast, M. Havecker, A. Knop-Gericke, R. Schlogl, ACS Catal. 2015, 5, 2740.
- X. Su, A. Vinu, S. S. Aldeyab, L. Zhong, Catal. Lett. 2015, 145, 1388. [42]
- Z. Zhao, X. Q. Huang, M. Li, G. Wang, C. Lee, E. Zhu, X. Duan, Y. [43] Huang, J. Am. Chem. Soc. 2015, 137, 15672.
- [44] W. Kong, Q. Wang, J. Zhu, Angew. Chem. Int. Ed. 2017, 56, 3987.
- [45] I. D. Hills, G. C. Fu, J. Am. Chem. Soc. 2004, 126, 13178
- Y. Ge, Z. H. Shah, X. Lin, R. Lu, Z. Liao, S. Zhang, ACS Sustainable [46] Chem. Eng. 2017, 5, 1675.
- Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu, X. Wang, Phys. Chem. Chem. [47] Phys. 2012, 14, 1455.
- B. Zhu, P. Xia, Y. Li, W. Ho, J. Yu, Appl. Surf. Sci. 2017, 391, 175. [48]
- Q. Lang, W. Hu, P. Zhou, T. Huang, S. Zhong, L. Yang, J. Chen, S. Bai, [49] Nanotechnology 2017, 28, 484003.
- H. Xu, J. Yan, X. She, L. Xu, J. Xia, Y. Xu, Y. Song, L. Huang, H. Li, [50] Nanoscale 2014, 6, 1406.
- [51] W. J. Ong, L. L. Tan, S. P. Chai, S. T. Yong, Dalton Trans. 2015, 44, 1249.

- M. H. Vu, M. Sakar, C. C. Nguyen, T. O. Do, ACS Sustainable Chem. [52] Eng. 2018. 6. 4194.
- S. Zhao, H. Yue, Y. Zhao, B. Wang, Y. Geng, J. Lv, S. Wang, J. Gong, [53] X. Ma, J. Catal. 2013, 297, 142.
- [54] K. Jiang, P. Wang, S. Guo, X. Zhang, X. Shen, G. Lu, D. Su, X. Huang, Angew. Chem. Int. Ed. 2016, 55, 9030.
- F. Ye, F. Wang, C. Meng, L. Bai, J. Li, P. Xing, B. Teng, L. Zhao, S. Bai, [55] Appl. Catal. B: Environ. 2018, 230, 145.
- [56] Z. Ni, F. Dong, H. Huang and Y. Zhang, Catal. Sci. Technol. 2016, 6, 6448
- J. Chen, S. Shen, P. Guo, M. Wang, P. Wu, X. Wang and L. Guo, Appl. [57] Catal. B: Environ. 2014, 152-153, 335.
- [58] H. Sakamoto, T. Ohara, N. Yasumoto, Y. Shiraishi, S. Ichikawa, S. Tanaka and T. Hirai, J. Am. Chem. Soc. 2015, 137, 9324.
- [59] S. Sarina, H. Y. Zhu, Q. Xiao, E. Jaatinen, J. Jia, Y. Huang, Z. Zheng, H. Wu, Angew. Chem. Int. Ed. 2014, 53, 2935.
- [60] H. B. Michaelson, J. Appl. Phys. 1977, 48, 4729.

[61]

- B. Weng, Q. Quan, Y. J. Xu, J. Mater. Chem. A 2016, 4, 18366.
- [62] Y. Zhu, Z. Xu, W. Jiang, W. Yin, S. Zhong, P. Gong, R. Qiao, Z. Li, S. Bai, RSC Adv. 2016, 6, 56800.
- [63] C. W. Li, M. W. Kanan, J. Am. Chem. Soc. 2012, 134, 7231.
- [64] D. Raciti, K. J. Livi, C. Wang, Nano Lett. 2015, 15, 6829.
- [65] I. Shown, H. C. Hsu, Y. C. Chang, C. H. Lin, P. K. Roy, A. Ganguly, C. H. Wang, J. K. Chang, C. I. Wu, L. C. Chen, K. H. Chen, Nano Lett. 2014. 14. 6097.
- [66] S. Zhang, P. Kang, M. Bakir, A. M. Lapides, C. J. Dares, T. J. Meyer, Proc. Natl. Acad. Sci. USA 2015, 112, 15809.
- [67] S. Kato, S. K. Matam, P. Kerger, L. Bernard, C. Battaglia, D. Vogel, M. Rohwerder, A. Zuttel, Angew. Chem. Int. Ed. 2016, 55, 6028.
- [68] S. Wang, Z. Ding and X. Wang, Chem. Commun. 2015, 51, 1517. [69] S. Wang, Y. Hou and X. Wang, ACS Appl. Mater. Interfaces 2015, 7, 4327

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100% selectivity: The photocatalytic reduction of CO_2 to CH_4 with high production rate and 100% selectivity was realized through the simultaneous incorporation of substitutional Cu and interstitial H atoms in the lattice of Pd cocatalysts. The excellent performance can be explained by the synergistic interplay between Pd-H and Cu-CO sites in promoting the rate-limiting reaction in conversion of CO to CH₄.



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