Oxo dicopper anchored on carbon nitride for selective oxidation of methane

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Selective conversion of methane (CH4) into value-added chemicals represents a grand challenge for the efficient utilization of rising hydrocarbon sources. We report here dimeric copper centers supported on graphitic carbon nitride (denoted as Cu2@C3N4) as advanced catalysts for CH4 partial oxidation. The copper-dimer catalysts demonstrate high selectivity for partial oxidation of methane under both thermo- and photocatalytic reaction conditions, with hydrogen peroxide (H2O2) and oxygen (O2) being used as the oxidizer, respectively. In particular, the photocatalytic oxidation of CH4 with O2 achieves >10% conversion, and >98% selectivity toward methyl oxygenates and a mass-specific activity of 1399.3 mmol g Cu−1 h−1. Mechanistic studies reveal that the high reactivity of Cu2@C3N4 can be ascribed to symphonic mechanisms among the bridging oxygen, the two copper sites and the semi-conducting C3N4 substrate, which do not only facilitate the heterolytic scission of C-H bond, but also promotes H2O2 and O2 activation in thermo- and photocatalysis, respectively.

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Selective conversion of methane to liquid hydrocarbons represents a promising approach toward efficient utilization of natural gas. The present industrial route for such conversions relies on a two-step process by first reforming methane to generate synthesis gas (CO and H₂) at elevated temperatures (>500 °C), and then reacting CO with H₂ to form methanol or other liquid products. However, this process is energy-intensive and economically nonviable for distributed sources such as flare gas. More robust technologies toward direct conversion of methane into condensed energy carriers are thus demanded to facilitate transportation and storage.

Direct, partial oxidation of methane to methyl oxygenates has received intensive attention in recent years. The studies on early days use transition copper exchanged zeolites to catalyze the reaction between CH₄ and O₂ and employ a two-step chemical looping process to subsequentially activate O₂ and desorb the products. Despite the achievement of high selectivities, these reactions are still suffering from the low CH₄ conversions (<1%) and productivities. It thus becomes interesting to facilitate transportation and storage.

The g-C₃N₄ substrate was grown by calcination from O₂ by using selective oxygen reduction catalysts such as Au-Pd containing zeolites. Alternatively, photoexcitation using visible light is proposed to be advantageous with near-room temperature activation of CH₄, mitigating the concern of over oxidation to form CO₂ upon heating. The reported photocatalytic oxidation of methane is still limited by relatively low methane conversions (~1%) and productivities (0.10–1.50 mol g⁻¹ h⁻¹), as the commonly used photocatalysts have quite large bandgaps (e.g., ~3.2 eV for TiO₂ and ~3.6 eV for ZnO) and may only activate methane via the Fenton or homolytic mechanisms that have relatively sluggish kinetics. In this aspect, graphitic carbon nitride (g-C₃N₄) represents a promising photocatalytic substrate with a modest band gap in the range of 2.7–2.9 eV. Its abundant nitrogen sites have been proposed to be advantageous with near-room temperature activation of CH₄, mitigating the concern of over oxidation to form CO₂ upon heating. The reported photocatalytic oxidation of methane is still limited by relatively low methane conversions (~1%) and productivities (0.10–1.50 mol g⁻¹ h⁻¹), as the commonly used photocatalysts have quite large bandgaps (e.g., ~3.2 eV for TiO₂ and ~3.6 eV for ZnO) and may only activate methane via the Fenton or homolytic mechanisms that have relatively sluggish kinetics. In this aspect, graphitic carbon nitride (g-C₃N₄) represents a promising photocatalytic substrate with a modest band gap in the range of 2.7–2.9 eV. Its abundant nitrogen sites have been shown in many reports to be capable of anchor atomically dispersed transition metal sites. It thus becomes interesting to investigate the potential coordination of active Cu sites on g-C₃N₄ and examine their synergies in partial oxidation of methane.

Here we report on Cu₂@C₃N₄ as highly efficient catalysts for partial oxidation of methane. The dimeric copper catalysts were synthesized by supporting an (oxalato)(bipyridine)copper(II) complex, [Cu₂(bpy)₂(μ-ox)]Cl₂, on g-C₃N₄ and then applying a mild thermal treatment in air. The derived catalysts contained dicopper-oxo centers anchoring on g-C₃N₄ via four Cu-N bonds (two for each copper atom), as characterized by using STEM, XPS and XAS, and also confirmed with atomistic simulations. The obtained copper-dimer catalysts were first evaluated for thermal oxidation of methane using H₂O₂ as the oxidizer, and then further applied for photocatalytic oxidation of methane with O₂. Mechanisms governing the observed catalytic enhancements toward selective oxidation of methane were interpreted via combining computational simulation of the reaction pathways, spin-trapping EPR analysis of possible radical intermediates, and in situ XPS measurements under light irradiation.

Results and discussion
Synthesis and characterization of Cu₂@C₃N₄. The copper-dimer precursor [Cu₂(bpy)₂(μ-ox)]Cl₂ was first prepared by a complexation reaction of copper chloride (CuCl₂), 2,2'-bipyridine and oxalic acid. The g-C₃N₄ substrate was grown by calcination of urea at 550 °C. Cu₂@C₃N₄ catalysts were synthesized by self-assembly of the dimeric copper complex on g-C₃N₄ and then treating the mixture in air at 250 °C to immobilize the copper species. The loading of Cu was determined to be 0.35 wt% by using inductively coupled plasma mass spectrometry (ICP-MS).

The complexation of pyridine, Cu²⁺ and oxalate (C₂O₄²⁻) to form an organometallic compound was confirmed by using Fourier transform infrared spectroscopy (FTIR). The hydroxyl (O-H) and carbonyl (C=O) stretching features around 3450 and 1670 cm⁻¹, respectively, associated with oxalic acid disappeared after the reaction. This was accompanied with the blue shift of the characteristic band (attributed to the asymmetric stretching of the pyridyl ring) of 2,2'-pyridine at ca. 1580 cm⁻¹ to ca. 1650 cm⁻¹, as a consequence of its chelation with Cu²⁺. Correspondingly, the d-d transition of Cu²⁺ at 650–700 nm had a blue shift of 48 nm in the ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS) patterns (Fig. 1c). The FTIR spectra of g-C₃N₄ and Cu₂@C₃N₄ exhibited the stretching vibration modes characteristic of the tri-s-triazine units at 810 cm⁻¹ and the breathing mode of tri-s-triazine units at 1670 cm⁻¹. Comparing to [Cu₂(bpy)₂(μ-ox)]Cl₂, Cu₂@C₃N₄ presented no more infrared features associated with the dimeric copper complex, indicating the complete removal of organic ligands during the immobilization process. This was further confirmed with thermogravimetric analysis (TGA) (Supplementary Fig. 1). The [Cu₂(bpy)₂(μ-ox)]Cl₂/g-C₃N₄ mixture lost ~6% of its initial weight upon annealing in air at up to 250 °C, which is close to the expectation estimated based on the ligand content (~80 wt%) of [Cu₂(bpy)₂(μ-ox)]Cl₂ and its ratio relative to the carbon nitride substrate (~8%) used in the synthesis. X-ray diffraction (XRD) patterns collected for the Cu₂@C₃N₄ catalysts only show the (001) and (002) peaks associated with g-C₃N₄, with the absence of copper metal or oxide features indicating the highly dispersed nature of copper species (Supplementary Fig. 2). Atomic structures of the dimeric copper moieties were resolved by using aberration correction high angle annular dark field scanning transmission electron microscope (HAADF-STEM) imaging (Fig. 1e–g). The collected STEM images exhibit a large number of adjacent, paired bright dots (labeled with red circles, ~0.35 nm in size for each dot) distributed on a substrate of lower contrasts. These small bright dots can be attributed to atomically dispersed Cu considering their much higher Z contrast (M₁₂ or 14). Line-profile scanning for ~100 pairs of such bright dots give an average distance of 2.8 (±0.2 Å) (Fig. 1h). This is much shorter than the value (5.2 Å) for the two copper atoms within [Cu₂(bpy)₂(μ-ox)]Cl₂, again confirming the reconstruction and condensation of the copper-dimer moieties as a result of the removal of organic ligands in the synthesis.

Chemical nature of the Cu dimers in Cu₂@C₃N₄ was probed by using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The Ni L₃ XPS spectrum exhibits a broad feature with the binding energy ranging from 397 to 408 eV (Fig. 2a). This feature can be deconvoluted into four peaks centered at 398.6, 399.4, 401.0, and 404.5 eV, which can be assigned to pyridinic (N<), pyrrolic (N), and uncondensed terminal amine groups in g-C₃N₄, respectively. The Cu 2p spectrum shows two peaks at 932.5 eV and 952.3 eV, which are characteristic of Cu(I) or Cu⁰ (Supplementary Fig. 3). However, the XPS analysis (as well as the corresponding Auger electron spectrum, AES) was unable to explicitly determine the oxidation state of Cu due to the reduced signal-to-noise ratio associated with the low copper content in the catalysts. The copper oxidation state in Cu₂@C₃N₄ was better resolved by using...
X-ray Absorption Near Edge Spectroscopy (XANES) (Fig. 2b).

The Cu K edge spectrum exhibits a pre-edge transition at 8984 eV, which falls between the peaks associated with Cu$_2$O (8983 eV) and CuO (8986 eV). This indicates an intermediate oxidation state between $^{+1}$ and $^{+2}$ for Cu in Cu$_2$@C$_3$N$_4$. Noticeably, our results do not support the picture with a mixture of Cu(I) and Cu(II), as the $1s$ $\rightarrow$ $3d$ transition at 8977 eV, a feature characteristic of Cu$^{2+}$ (as shown for the references CuO and copper tetraphenylporphyrin (Cu-TPP) in Supplementary Fig. 4)\textsuperscript{35}, is absent in the spectrum of Cu$_2$@C$_3$N$_4$. The partial oxidation state (between $^{+1}$ and $^{+2}$) of Cu within the copper dimers supported on g-C$_3$N$_4$ can be viewed as a result of the semiconducting nature of the substrate. This is distinct from the cases for extensively studied copper exchanged zeolites, in which the dicopper-oxo centers ([Cu-O-Cu]$^{2+}$) anchor on the Al sites with localized negative charges and have an oxidation state of $^{+2}$ for both Cu atoms\textsuperscript{9,36,37}.

The atomic structure of the Cu dimers was resolved by combining extended X-ray absorption fine structure (EXAFS) analysis and atomistic modeling based on DFT calculations. Figure 2c compares the k$^2$-weighted Cu K edge EXAFS spectra for Cu$_2$@C$_3$N$_4$, Cu foil, Cu$_2$O, CuO, and Cu-TPP (with single-atom Cu$^{2+}$ coordinating to four pyrrolic N, Supplementary Fig. 4). The Cu$_2$@C$_3$N$_4$ catalyst exhibits first-shell scattering at 1.62 Å in R space (prior to phase correction), which is proximate to the values, 1.59 and 1.55 Å, found for Cu-TPP and CuO, respectively. This is distinct from the cases for Cu$_2$O and Cu, the first-shell scattering of which locates at 1.50 and 2.30 Å, respectively. From these observations, we tentatively assign the primary scattering pair at 1.62 Å in the R-space spectrum of Cu$_2$@C$_3$N$_4$ to be Cu-N or Cu-O bonding. To fit the EXAFS spectrum, a total of 9 possible Cu-dimer configurations was postulated, based on which DFT calculations were performed to relax the structures and determine bonding distances and angles (Supplementary Fig. 5 and Table 1). Considering the presence of minor Cu monomers observed in the STEM images (Fig. 1e–g), we have applied a linear combination of Cu monomers and dimers to fit the EXAFS spectrum. Various possible Cu-dimer configurations have been considered, with the corresponding EXAFS spectra compared to the experimental results to identify the best fit (Fig. 2d, e; also see Supplementary Figs. 6–7). It is estimated that 72.4% of the Cu atoms are in the dimeric configuration, close to the value (~70%) derived from statistical analysis of the STEM images. The determined copper-dimer structure comprises two Cu atoms bridged by an O atom, with the Cu-O bonds having lengths of 1.76 Å and 1.79 Å and an included angle ($\angle$Cu-O-Cu) of 99.6° (Fig. 2f, Table 1). Each Cu atom is coordinated to two N atoms on
the C₃N₄ framework, with the bonding distance varying from 1.90 to 1.99 Å and the bonding angle (∠N-Cu-N) being 82° for Cuα and 110° for Cuβ (Fig. 2f). Noticeably, the identified configuration with best fitting to the EXAFS spectrum also has the lowest (most negative) formation energy among the various configurations, in line with the expectation for stable atomic structures in the real catalysts (Supplementary Table 1). Our combined EXAFS analysis and DFT calculations resolved the Cu-Cu distance in the Cu dimers to be ~2.71 Å (Table 1), which is in agreement with the average Cu-Cu distance measured from the STEM images (Fig. 1h). It is noted that this value is much smaller than the Cu-Cu distance (4.10 Å) associated with the dicopper-oxo center ([Cu-O-Cu]²⁺) in Cu-ZSM-5. Furthermore, Bader charge analysis based on DFT calculation shows that the Cu atoms in the Cu dimers have oxidation states of +1.63 and +1.72 (Supplementary Fig. 7), resembling the results derived from XANES spectra (see the above discussion for Fig. 2b).

From the above discussion, we can see that the dimeric copper centers in Cu₂@C₃N₄ have distinct atomic structures and electronic chemical properties form their counterparts confined in zeolites. We hypothesize that their non-integer oxidation state (intermediate between +1 and +2) and reduced cluster size (smaller Cu-Cu distance as compared to Cu-ZSM-5) would lend them exquisite catalytic performance for selective oxidation of methane.

Thermocatalytic oxidation of methane with H₂O₂. The Cu₂@C₃N₄ catalysts were first evaluated for the thermocatalytic oxidation of CH₄ (Supplementary Figs. 8–12). This was conducted using a continuous stirred-tank reactor (CSTR) filled with 0.2 mM of H₂O₂ and 0.1 MPa of CH₄ (see Experimental Methods in the Supplementary Materials). Methyl oxygenates (CH₃OH and CH₃OOH) were found to be the primary products, with the yield achieving 0.14% within 30 min of reaction at 30 °C (Fig. 3a). As previously reported, the generated CH₃OOH can be facilely reduced to CH₃OH under ambient conditions (Supplementary Fig. 12). The yield of methyl oxygenates increased to 0.37% at 70 °C, corresponding to the increase of productivity from 51.6 to 129.7 mmol gCu⁻¹ h⁻¹. Albeit the increase of reaction rate, the rise of reaction temperature is accompanied with the increase of CO₂ selectivity from 0.8% at 30 °C to 5.0% at 70 °C (Supplementary Fig. 13). Similarly, elongated operations also led to the yield of more CO₂ (Supplementary Fig. 13). The cyclability tests showed that the Cu₂@C₃N₄ catalyst was stable throughout the methane oxidation reaction with H₂O₂ in five consecutive measurements by refilling CH₄ and H₂O₂, the Cu₂@C₃N₄ catalyst exhibited indiscernible change in reactivity and product distribution, with the productivity of methyl oxygenates found to be consistent at ~70 mmol gCu⁻¹ h⁻¹ at 50 °C (Supplementary Fig. 14). Furthermore, the atomic structure of dicopper-oxo centers was confirmed to remain intact after reaction by performing HADDF-STEM imaging and EXAFS analysis on the spent Cu₂@C₃N₄ catalyst after 6 h of reaction (Supplementary Fig. 15 and Supplementary Table 2).
Considering that the bare g-C₃N₄ substrate is inactive for CH₄ oxidation (Supplementary Fig. 16), the dicopper-oxo centers can be identified as the active sites in Cu₂@C₃N₄. Considering that monomeric Cu in copper exchanged zeolites ³⁰,³⁹,⁴⁰ or metal–organic frameworks ⁴¹ has also been discussed to be active for CH₄ oxidation, we have performed comparative studies on a single-atom control (Cu₁@C₃N₄) using the same g-C₃N₄ substrate. This catalyst was prepared by using a vapor-migration strategy ⁴² with the Cu loading controlled to be also at ~0.35 wt%, with the single-atom dispersion confirmed by using XAS (Supplementary Fig. 17). Catalytic studies showed that Cu₁@C₃N₄ was merely active for methane oxidation, delivering a...
yield of only 0.03% (versus 0.2% by Cu2@C3N4) for methyl oxygenates at 50 °C (Fig. 3b). The low reactivity of Cu1@C3N4 indicates that Cu monomers, if present in the Cu2@C3N4 catalysts, would not make significant contributions to the observed high methane partial oxidation activity, and also underlines the necessity of having dicopper-oxo centers for catalyzing the partial oxidation of methane. The activity of Cu2@C3N4 is also substantially enhanced as compared to copper exchanged zeolites. A comparative study of Cu-ZSM5 with a Si/Al ratio of 11.5 and full exchange (Cu/Al ~ 0.51) using similar reaction conditions only delivered a productivity of 25.5 mmol \( g_{\text{Cu}} \cdot h^{-1} \) for methyl oxygenates at 50 °C, as compared to 74.4 mmol \( g_{\text{Cu}} \cdot h^{-1} \) for Cu3@C3N4 at this temperature (Fig. 3b). Note that the copper species in this Cu-ZSM-5 catalyst is also predominantly present in the form of dicopper-oxo centers36, similar to that identified in Cu3@C3N4 (as shown in Fig. 2f). These results thus indicate that the dimeric Cu supported on carbon nitride is much more reactive for the oxidation of methane with \( \text{H}_2\text{O}_2 \) than their counterparts confined in zeolites.

The partial oxidation of methane with \( \text{H}_2\text{O}_2 \), the efficiency of utilizing the peroxide oxidizer (instead of producing \( \text{O}_2 \) through a disproportionation reaction) is an important metric for evaluating the performance of catalysts19,43. This is usually assessed by comparing the “gain factor” that is defined as the molar ratio between the produced methyl oxygenates (\( \text{CH}_3\text{OH} \) and \( \text{CH}_3\text{OOH} \)) and the consumed \( \text{H}_2\text{O}_2 \). Post-reaction titration of the concentration of residual hydrogen peroxide using cerium sulfate44 (Supplementary Fig. 18) showed that the Cu2@C3N4 catalyst had a gain factor of 0.19 (Fig. 3c and Supplementary Fig. 19). In comparison, the gain factor was determined to be only 0.03 and 0.06 for Cu1@C3N4 and Cu-ZSM5-11.5, respectively. It is interesting that the gain factor exhibited dependence on the copper loading in the dimer catalyst. A Cu2@C3N4 catalyst of reduced loading (0.25 wt%) had a gain factor of 0.12, which is lower than that for the normal catalyst with 0.35 wt% of copper. Moreover, correlation between the productivity of methyl oxygenates and the gain factor gives rise to a linear relationship, underscoring its meaning of describing the reactivity between methane and \( \text{H}_2\text{O}_2 \) on a given catalyst (Fig. 3c)19,45.

To understand the enhanced reactivity of Cu2@C3N4 for methane partial oxidation, we have performed DFT calculations to simulate the reaction pathways on the dicopper-oxo centers (Figs. 3d, e; also see Supplementary Fig. 20 and Supplementary Table 3). It is predicted that the reaction starts with sequential activation of two \( \text{H}_2\text{O}_2 \) molecules on the copper-dimer centers through radical mechanisms24,46,47. The first hydrogen peroxyde molecule is dissociated via \( \text{H}_2\text{O}_2 \rightarrow \text{OOH} + \cdot \text{H} \), where the hydrogen adsorbs on the bridging oxygen and the \( \cdot \text{OOH} \) radical migrates onto Cu4 to become a peroxyl (\( \cdot \text{OOH} \)) adsorbate. The second hydrogen peroxyde undergoes \( \text{H}_2\text{O}_2 \rightarrow \text{OH} + \cdot \text{O} \) with the hydroxyl group adsorbing on Cu4 and the \( \cdot \text{OH} \) radical recombines with the \( \cdot \text{H} \) on the bridging oxygen site to form a \( \cdot \text{HO} \) molecule. The involvement of \( \cdot \text{OOH} \) and \( \cdot \text{OH} \) in \( \text{H}_2\text{O}_2 \) activation was corroborated by the observation of these radicals in the electron paramagnetic resonance (EPR) spectroscopic studies by using 5,5′-Dimethyl-1-pyrroline-N-oxide (DMPO) as the radical trap (Supplementary Fig. 21)48. The generation of radicals is the rate limiting factor in both cases of \( \text{H}_2\text{O}_2 \) activation, which is predicted to have a kinetic barrier of 0.17 (for \( \cdot \text{OOH} \)) or 0.56 (for \( \cdot \text{OH} \)) eV. Noticeably, these barriers are substantially lower than the corresponding values found for the single-atom Cu sites (1.3 and 1.5 eV, Supplementary Fig. 22) and the dicopper-oxo centers confined in zeolites (0.58 and 0.81 eV in Cu-ZSM-5)49, in line with the higher gain factor and enhanced utilization of \( \text{H}_2\text{O}_2 \) as observed on the Cu2@C3N4 catalysts (Fig. 3c). The enhanced \( \text{H}_2\text{O}_2 \) activation on Cu2@C3N4 could be ascribed to the π-conjugated heterocyclic rings and the semiconducting nature of the C3N4 substrate, which is known for accommodation of charge transfer and able to supply electrons to the dicopper-oxo center for stabilization of the oxygenated adsorbates30,33. The C3N4 supported Cu dimers are thus believed to be more advantageous than their zeolitic counterparts for catalyzing the redox chemistries being examined here.

Following the activation of \( \text{H}_2\text{O}_2 \), methane is introduced to the dicopper-oxo center with one of the C-H bond attacked by the bridging oxygen (Fig. 3d, e). This C-H bond dissociation has a modest energy barrier of 0.61 eV (vs. ~0.71 eV in the case of Cu-ZSM-5)10,39,46. While the generated \( \cdot \text{H} \) adsorbs on the bridging oxygen, the methyl group migrates on to the adjacent Cu sites. Hereby the C-H bond dissociation is believed to be heterolytic instead of homolytic or the Fenton type, as no \( \cdot \text{CH}_3 \) radicals were observed using EPR (Supplementary Fig. 23)19,24,38. The heterolytic dissociation of C-H bond is believed to be essential for partial oxidation of methane at high selectivities, as the other two activation mechanisms via \( \cdot \text{CH}_3 \) radicals are typically accompanied with over oxidation to form substantial amounts of \( \text{CO}_2 \). Compared to the case in Cu-ZSM-537, the Cu dimers supported on g-C3N4 have shorter Cu-O bond length (1.77 Å vs 1.88 Å) and smaller Cu-O-Cu (99.6° vs 135°), which are believed to sterically favor the heterolytic cleavage of the C-H bond and facilitate the transfer of the -CH3 group. Noticeably, the -CH3 group can adsorb on either Cu4 or Cu6, where the reaction bifurcates into two possible pathways. On the one hand, \( \cdot \text{CH}_3 \) on Cu4 recombines with the \( \cdot \text{OOH} \) on this site to form \( \text{CH}_3\text{OOH} \). On the other hand, it can also recombine with \( \cdot \text{OH} \) on Cu6 to form \( \text{CH}_3\text{OH} \). Desorption of these adsorbates gives rise to the corresponding methyl oxygenates. While the rate is limited by the \( \text{CH}_3 + \cdot \text{OH} \rightarrow \cdot \text{CH}_2\text{OH} \) recombination on Cu6 (with a barrier of 0.72 eV), the highest barrier for the \( \text{CH}_3\text{OOH} \) pathway is found to be the desorption of \( \cdot \text{CH}_2\text{OH} \) (0.52 eV). Overall, the \( \text{CH}_3\text{OH} \) pathway associated with Cu4 is energetically more favorable than the \( \text{CH}_2\text{OH} \) pathway with Cu6, explaining the experimentally observed much higher yield of \( \text{CH}_3\text{OOH} \) than \( \text{CH}_3\text{OH} \). The pathways as revealed in Fig. 3d emphasizes the synergy among the two Cu atoms and the bridging O in catalyzing the complex reaction involving multiple molecules (e.g., \( \text{CH}_4 + 2\text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{OOH} + 2\text{H}_2\text{O} \)), which is a unique feature of the carbon nitride supported dimeric copper centers. An analogous reaction mechanism was also proposed in the partial oxidation of methane with \( \text{H}_2\text{O}_2 \) catalyzed by Au-Pd colloids19.

**Photocatalytic oxidation of methane with O2.** Despite the selective oxidation of methane obtained with Cu2@C3N4, the thermocatalytic reaction still relies on the use of \( \text{H}_2\text{O}_2 \) as oxidant, which is not a readily available feeding in industry. Moreover, the low \( \text{CH}_4 \) conversions (<1%) also limits the potential of this process for practical implementations. Considering that g-C3N4 is a semiconductor (with a bandgap of 2.7–2.9 eV25,26, with demonstrated photocatalytic applications37, we have turned to photocatalysis to overcome the limitation of thermocatalytic reactions. Photocatalytic oxidation of methane was carried out at 50 °C by applying near-edge excitation (300 W Xenon lamp equipped with a 420 nm bandpass filter) and using \( \text{O}_2 \) as the oxidant (Supplementary Fig. 24). It is hypothesized that photo-excitation can efficiently activate \( \text{O}_2 \) and generate the oxygenates (\( \cdot \text{OOH} \) and \( \cdot \text{OH} \)), mimicking and improving the role that \( \text{H}_2\text{O}_2 \) played in the reaction21,22,54.

The photocatalytic reaction gave much higher conversions of methane than the thermocatalytic process, reaching 1.3% at 1 h (Fig. 4a). The methane conversion increases with time, reaching...
The photocatalytic oxidation of CH4 with O2 catalyzed by Cu2@C3N4. The values were obtained by raising the partial pressure of methane (PCH4). As PCH4 increased from 0.1 to 1 MPa (at P02 = 0.1 MPa, while the total pressure was kept constant at 3 MPa), the productivity escalated from 184.3 to 709.8 mmol gCu−1 h−1, albeit with the methane conversion reducing from 13.1 to 5.1 (at 6 h, Fig. 4b and Supplementary Fig. 26). The improvement of productivity at higher PCH4 can be ascribed to the increased concentration of dissolved methane in the aqueous solution. The low conversion of methane at high PCH4 was likely limited by the inadequacy of oxygen. At P02 = 0.5 MPa and PCH4 = 1 MPa, a methane conversion of 10.1% was obtained with >98% selectivity toward methyl oxygenates, corresponding to an even higher productivity of 1399.3 mmol gCu−1 h−1. A comprehensive comparison to the literature results under similar reaction conditions indicate that this represents the highest activity for partial oxidation of methane, with improvement factors of at least >10 (Supplementary Table 4).

The photocatalytic oxidation of methane with O2 was confirmed by conducting control experiments under various conditions (Supplementary Table 5). In particular, the Cu2@C3N4 catalyst was found to be inactive in darkness (while the other conditions were kept the same), ruling out the involvement of thermocatalytic reaction between CH4 and O2 in the photocatalytic studies. The photocatalytic activity of bare g-C3N4 was also nearly negligible, underlining the role of Cu dimers in catalyzing the related molecular transformations. The generation of active peroxide species in situ during the photocatalytic reaction was confirmed by performing EPR spectroscopic studies by also using DMPO as the radical trapping agent (Fig. 4c). The spectra recorded under visible light irradiation, in both cases with and without methane, show the fingerprints of ‧OOH radicals, which can be assigned to the spin of unpaired electrons on oxygen21,45,54. Similar to the findings from photocatalytic studies, such signals were not observed from the controls in the absence of O2, Cu2@C3N4, or light. These ‧OOH radicals are likely derived from the thermal activation of H2O2 (as observed in the thermocatalytic studies, Supplementary Fig. 21), which was produced from photocatalytic reduction of O2 in situ55-57. It thus becomes evident that Cu2@C3N4 is not only a good thermocatalyst for partial oxidation of methane with H2O2, but also an exceptional photocatalyst when the oxidant is replaced by O2.

In addition to the reduction of O2 to peroxides, the photon excitation is also believed to enhance the methane activation. This was revealed by using in situ irradiation X-ray photoelectron spectroscopy (ISI-XPS)58 to examine charge transfer between the dimeric copper center and the C3N4 substrate (see the Experimental Methods in the Supplementary Materials). As shown in Fig. 4d, the XPS spectra collected on hydrated Cu2@C3N4 in darkness exhibited two O 1s peaks at ca. 533.0 and 531.7 eV, which can be assigned to the oxygen binding to Cu, i.e., -Cu-OH and -Cu-O-Cu-, respectively59,60. Under light irradiation (400–500 nm), both of these two peaks had a blue shift of ~0.5 eV. Similar observations were obtained at the Cu 2p edge (Supplementary Fig. 27). Meanwhile, a red shift of the N 1s peak associated with C3N4 was observed, from 398.8 eV in darkness to 398.2 eV under light irradiation (Fig. 4e). Such phenomena consistently point to the transfer of holes (rather than electrons) from the g-C3N4 substrate to the dicopper-oxo center, where CH4 is activated and oxidized to form CH3O. Meanwhile, the excited electrons in the g-C3N4 substrate lead to the reduction of O2 and

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2\text{O}_2 \]

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O} \]

\[ \text{CH}_3\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{OOH} + \text{H}_2\text{O} \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} \]

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

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\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

\[ \text{CH}_3\text{OOH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}_2\text{O}_2 \]

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formation of H₂O₂, which then migrates or diffuses onto the dicopper-oxo center and gets activated to form *OH or *OH. In the following, these oxygen species recombine with *CH₃ to form methyl oxygenates, as in the case of thermocatalytic reactions (Fig. 4f and Supplementary Figs. 28–29). Similar phenomena of charge transfer induced catalytic enhancements have previously been reported in photocatalysis using TiO₂-based photocatalysts.⁶¹–⁶³

In conclusion, we have developed new dimeric copper catalysts for partial oxidation of methane. These catalysts were synthesized by immobilization of a copper-dimer organometallic complex on graphitic carbon nitride, and dicopper-oxo centers were characterized to anchor on this substrate via Cu-N bonding. The derived Cu₄@g-C₃N₄ catalysts were first examined for thermocatalytic oxidation of methane with H₂O₂, and then studied for photocatalytic reactions with O₂ being used as the oxidant. Enhanced catalytic activities were demonstrated in both cases as compared to the other reported catalysts under similar reaction conditions, achieving improvement factors of more than an order of magnitude. Synergy activities were demonstrated in both cases as compared to the other catalysts. Cu₂@C₃N₄ substrate has been revealed to promote H₂O₂ and O₂ activation and the heterolytic scission of CH₄. Our work highlights the great potential of carbon nitride supported dimeric copper centers in catalyzing redox chemical reactions.

Methods

Materials and Chemicals. The following chemicals were purchased and used as received without further purification: Copper(II) chloride dihydrate (CuCl₂·2H₂O, ACS grade, Sigma Aldrich), 2,2’-bipyridine (Cu(acac)₂, ACS reagent, Sigma Aldrich), oleylamine (CH₃(CH₂)₇CH₂NH₂, ≥ 98%, Sigma Aldrich), dicarboxylmethylamine (NH₂C(CH₂)₇COOH, reagent grade, Sigma Aldrich), dicyandiamide (NH₂C≡N, ≥ 98%, Sigma Aldrich), ethanol (C₂H₅OH, HPLC grade, Fisher Scientific), methanol (CH₃OH, HPLC grade, Fisher Scientific), deionized water (18.2 MΩ) was collected from an ELGA PURELAB flex apparatus.

Synthesis of copper dimer complex. Solutions A, B, and C were prepared by ultrasonically dispersion method, respectively. The detailed preparation process was as follows: Solution A: 1.6 mmol 272 mg CuCl₂·2H₂O was ultrasonically dispersed in 20 mL deionized water; Solution B: 1.6 mmol 248 mg 2,2’-bipyridine was ultrasonically dispersed in 10 mL methanol; Solution C: 0.8 mmol 100 mg oxalic acid was ultrasonically dispersed in 10 mL deionized water. Subsequently, Adding solution B and solution C to solution A drop by drop respectively and kept stirring for 1 h. Finally, the light-blue solid was obtained. The obtained product was centrifuged, washing with water and methanol for three times and drying in vacuum⁶⁹.

Synthesis of g-C₃N₄. 20 g of urea was placed to an alumina crucible (100 mL). Subsequently, the crucible was sealed with multiple layers of tin foil and put into a muffle furnace with the heating program from 250 °C to 550 °C for 2 h at the rate of 20 °C min⁻¹. The obtained powder was further repeated the above calcination operation, the difference was that the heating rate was kept at 5 °C min⁻¹ and the retention time at 550 °C was 3 h. Finally, the yellowish-white powder was obtained.

Synthesis of Cu₄@g-C₃N₄. Solution A: 0.5 g g-C₃N₄ was ultrasonically dispersed in 50 mL methanol solution; Solution B: 42 mg copper dimer was ultrasonically dispersed in 5 mL methanol solution; Solution B was drop-wise added to solution A and was stirred at room temperature for 24 h, and the obtained solid was calcined in muffle furnace with the heating program from 30 °C to 250 °C for 10 h at the rate of 2 °C min⁻¹. Finally, the blue-yellow solid was got.

Synthesis of Cu₄@g-C₃N₄. 340 mg CuCl₂·2H₂O were grounded to be-well mixed, then spread in an alumina crucible (100 mL) with a cap covered. The crucibles were placed in a muffle furnace, and gradually heated to 550 °C for 8 h with the ramping rate of 5 °C min⁻¹ and then cool down.

Material characterization. X-Ray Diffraction (XRD) patterns were obtained from a PANalytical X’Pert X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5406 Å). Nitrogen adsorption measurements were measured on a Micromeritics ASAP 2010 instrument with the samples degassed under vacuum at 300 °C for 4 h. Specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller (BET) theory. The Cu contents were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a PerkinElmer Elman DRC II Quadrupole ICP-MS after dissolution of the samples in aqua regia. High angle annular dark field (HAADF) STEM images were acquired using a JEOL TEM/STEM ARM 200FG (equipped with an Oxford X-max 100TLE windowless X-ray detector) at a 22 mrad probe convergence angle and a 90 mrad inner-detector angle. The analysis of surface elements was performed on X-ray photoelectron spectroscopy (XPS), Thermo Fisher Scientific Escalab 250Xi spectrometer with Al Kα radiation as the excitation source. Fourier Transform Infrared spectroscopy were carried out on ThermoNicolet Nexus 670. Diffuse reflectance ultraviolet-visible (UV-Vis) spectra were collected on a Shimadzu UV-2450 spectrometer equipped with an integrating sphere attachment using BaSO₄ as the reference. FTIR Spectrometer Ultraviolet photoelectron spectroscopy (UPS) measurements were performed on an ESCALAB 250 UPS instrument with a He I gas discharge lamp operating at 21.22 eV and a total instrumental energy resolution of 90–120 meV.

XAS experiments were performed at the 10-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. Samples were pressed into a stainless-steel sample holder. All measurements were performed at the Cu K edge (8.973 eV) on transmission mode in fast scan from 250 eV below the edge to 800 eV above the edge. Spectra processing, including background removal and normalization were performed on ATHENA module in Demeter package. The extraction of structural parameters and fitting of the DFT optimized models of fresh and spent Cu₄@g-C₃N₄ samples were performed on ARTEMIS module. For the optimized structure, EXAFS data were fit from k = 2.7 to 10 Å⁻¹ (dk = 2) and R = 1–3.2 Å with a Hanning window.

Electron Paramagnetic Resonance (EPR) measurements were performed on a Bruker EMX EPR spectrometer at X-band frequency (9.46 GHz). 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was used as the spin-trapping agent, which can capture the radicals of •OH and •O₂⁻. As for the detection of •OH and •O₂⁻, methanol and DI H₂O were used respectively, due to the DMPO-OOH is not stable in H₂O, it would be quickly converted to DMPO-OH.

The in-situ irradiation X-Ray photoelectron spectroscopy (ISI-XPS) was carried out on an AXIS SUPRA (Kratos Analytical Inc, Shimadzu) coupled with a continuous tunable wavelength dispersive optical fiber (PLS-EM 150, Beijing Perfectlight Co. Ltd.). The wavelength of irradiation light was set at 400–500 nm to mimicking the visible light. The measurement setup is developed to monitor the photoelectron transfer process. Before measurement, the hydrated Cu₄@g-C₃N₄ was obtained by pretreatment of fresh Cu₄@g-C₃N₄ by water.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information file. The data generated in this study for main manuscript are provided in the Source Data file. Other raw data of the presented figures and tables are available from the corresponding authors upon request. Source data are provided with this paper.

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Author contributions
C.W. and P.X. contributed to the idea and experimental design. P.X., J.D., and J.Z. conducted the synthesis of control samples, catalytic evaluation. T. Pa performed spectroscopic analysis. N.Z.-F, H.Z., and S.D. conducted the EPR characterization and NMR analysis. C.W., Z.H. and R. S-Y, performed the high resolution microscopy. Z.Y. and S.D. contributed to the simulation analysis. P.Z. conducted the in-situ irradiation X-Ray photoelectron spectroscopy characterization. C.W. and P.X. wrote the paper and all authors commented on the final manuscript.

Competing interests
The authors declare no competing interests.

Additional information
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