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Precise and Scalable Synthesis of Dual-Atom Catalysts via Stepwise Microwave-Assisted Atomic Assembly

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Abstract

Dual-atom catalysts (DACs) offer high atom utilization and tunable synergistic interactions, yet scalable synthesis with uniformity and atomic precision remains challenging. Here, we report a stepwise microwave-assisted atomic assembly strategy for constructing dual-atom sites on nitrogen-doped reduced graphene oxide (NG). Cu single-atom sites are first generated by microwave heating of Cu²⁺-anchored amine-functionalized graphene oxide (NH₂-GO). Subsequent microwave irradiation induces localized electron enrichment around Cu sites, enabling adjacent metal ion anchoring (M = Fe, Co, Ni, Cu, and Zn) for DAC construction. This strategy enables gram-scale synthesis, demonstrating its scalability. CuCu-NG exhibits outstanding methane oxidation performance, yielding 8693 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ oxygenates with $\sim 100\%$ selectivity and a Cu-Cu dual-atom site-based turnover frequency of 218 h^{-1} . Mechanistic studies reveal that Cu-Cu coupling induces electronic redistribution and modulates d-band center, promoting H₂O₂ activation and C-H bond cleavage. This stepwise microwave-driven strategy provides a precise and scalable approach for DACs construction via atomic assembly.

Introduction

Dual-atom catalysts (DACs), featuring two adjacent metal atoms with synergistic interactions, offer new opportunities beyond single-atom catalysts (SACs)^{1,2}. By modulating local coordination environments and electronic structures, dual-atom sites can overcome the limitations of isolated active centers³. Nevertheless, the precise, efficient, and scalable construction of DACs remains a critical bottleneck for establishing reliable structure-performance relationships and advancing practical catalytic applications.

Various strategies have been developed for constructing diatomic sites, including pyrolysis, adsorption-impregnation, and ball milling^{4,5,6}. Nevertheless, these approaches generally suffer from limited control over metal distribution, interatomic distances, and atomic dispersion. Conventional pyrolysis requires prolonged high-temperature treatment, entailing high energy consumption and an increased risk of metal aggregation. Atomic layer deposition (ALD) enables precise atomic deposition but relies on expensive equipment and volatile metal precursors, limiting large-scale applications⁷. More recently, macrocyclic ligand-directed synthesis^{8,9}, binuclear metal complex templating^{10,11}, and navigation-and-positioning strategies^{12,13} have improved atomic precision but remain constrained by complicated procedures, prolonged preparation processes and limited scalability. A rapid, universal, and scalable strategy for controllable DAC construction is therefore urgently needed.

Microwave heating, a rapid, non-contact and volumetric heating approach, has emerged as a powerful technique for synthesizing various advanced materials¹⁴. Microwave-assisted methods have also been applied to single-atom catalyst synthesis^{15,16}. Compared with conventional thermal synthesis routes, microwave irradiation enables rapid energy transfer, dramatically shortened processing time, and enhanced energy efficiency. The ultrafast heating process can suppress metal migration and aggregation, thereby favoring the generation of atomically dispersed metal sites with high structural stability. Beyond purely thermal effects, the coupling between microwave electromagnetic fields and free electrons may induce localized surface plasmon resonance (LSPR) effect, generating localized electron-rich highly active regions around metal sites for metal anchoring^{17,18}. Despite these advantages, existing microwave-assisted synthesis of bimetallic or polymetallic catalysts mainly relies on one-pot co-reduction of multiple metal precursors, resulting in uncontrolled structural evolution and the coexistence of isolated atoms, metal clusters, and alloy nanoparticles^{14,19}. A controllable

microwave strategy for stepwise regulation of metal atom incorporation and precise atomic pairing has to be demonstrated.

Herein, we propose a stepwise microwave-assisted atomic assembly strategy for the precise construction of dual-atom sites on nitrogen-doped reduced graphene oxide (NG). Taking Cu-NG SAC as a model, isolated Cu sites are first synthesized by microwave heating of Cu²⁺-containing amine-functionalized graphene oxide (NH₂-GO). In the second step, microwave-induced localized charge enrichment around pre-existing Cu sites enables the preferential capture and anchoring of secondary metal ion (M) adjacent to Cu, forming CuM-NG DACs (M = Fe, Co, Ni, Cu, Zn) and establishing a general platform for DACs synthesis. The catalytic performance of DACs was evaluated in direct selective oxidation of methane (DSOM). The CuCu-NG exhibits an oxygenate yield of 8693 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ and nearly 100% selectivity, with a high TOF_{DAC} of 218 h^{-1} . DFT calculations reveal that Cu-Cu interactions induce electronic redistribution and d-band center modulation, promoting H₂O₂ activation and lowering the energy barriers for C-H bond cleavage.

Results

Synthetic strategy

We developed a stepwise microwave-assisted atomic assembly strategy to precisely construct a series of DACs on NG, including homonuclear CuCu-NG and heteronuclear CuFe-NG, CuCo-NG, CuNi-NG and CuZn-NG (**Fig. 1a and Supplementary Fig. 1**). Taking CuCu-NG as a representative, Cu-NG SACs were first obtained by microwave irradiation of Cu²⁺-anchored NH₂-GO, generating isolated Cu sites while reducing graphene oxide. After adding CuCl₂, subsequent microwave treatment induced localized hotspots and electron enrichment around the pre-existing Cu sites, promoting Cu species capture and anchoring to form Cu-Cu dual-atom pairs. This sequential process helps minimize

random metal distribution during simultaneous nucleation, facilitating controlled DAC formation. Replacing CuCl_2 with Fe, Co, Ni or Zn precursors yielded the corresponding CuM-NG DACs (**Fig. 1b**). Temperature evolution during microwave irradiation was monitored using a colorimetric infrared thermometer based on black-body radiation fitting²⁰. As shown in **Fig. 1c**, the sample rapidly reached an equilibrium temperature of $\sim 1420^\circ\text{C}$ within 2 s under 1000 W and cooled immediately after power removal. The temperature was tunable by microwave power, with equilibrium achieved within 1-2 s across all conditions and exceeded 900°C even at 400 W (**Supplementary Fig. 2**), demonstrating ultrafast microwave heating. A red-hot glow was observed during treatment, while infrared images revealed localized hot regions and thermal distribution evolution (Inset of **Fig. 1c**).

Fig. 1d and Supplementary Table 1 compare reported thermal-treatment conditions and dual-atom pairing fractions for representative DAC synthesis methods. Conventional wet chemical routes operate at mild temperatures ($150\text{--}400^\circ\text{C}$) but require several to tens of hours and often suffer from poor structural stability during annealing^{5,21,22}. Furnace pyrolysis improves atomic stabilization through stronger metal-support interactions but typically requires $900\text{--}1000^\circ\text{C}$ and 2-3 h treatment, resulting in high energy consumption and low efficiency^{4,23,24,25,26}. Ball milling^{27,28,29}, ALD^{7,30,31}, and photoinduced anchoring^{12,13,32} offer faster or milder conditions, but dual-atom pairing ratios remain variable ($\sim 44\text{--}80\%$) and scalability is limited. Microwave-assisted methods shorten treatment times to minutes but often involve liquid phases or additional pyrolysis steps, potentially affecting atomic precision and controllability^{33,34,35}. Joule heating enables ultrafast temperature elevation ($1200\text{--}3000^\circ\text{C}$ within seconds), but suffers from localized heating and limited pairing control^{36,37,38,39}. In contrast, our synthesis strategy achieves $\sim 70\%$ dual-atom pairing within only 25 s, balancing synthesis efficiency and structural precision.

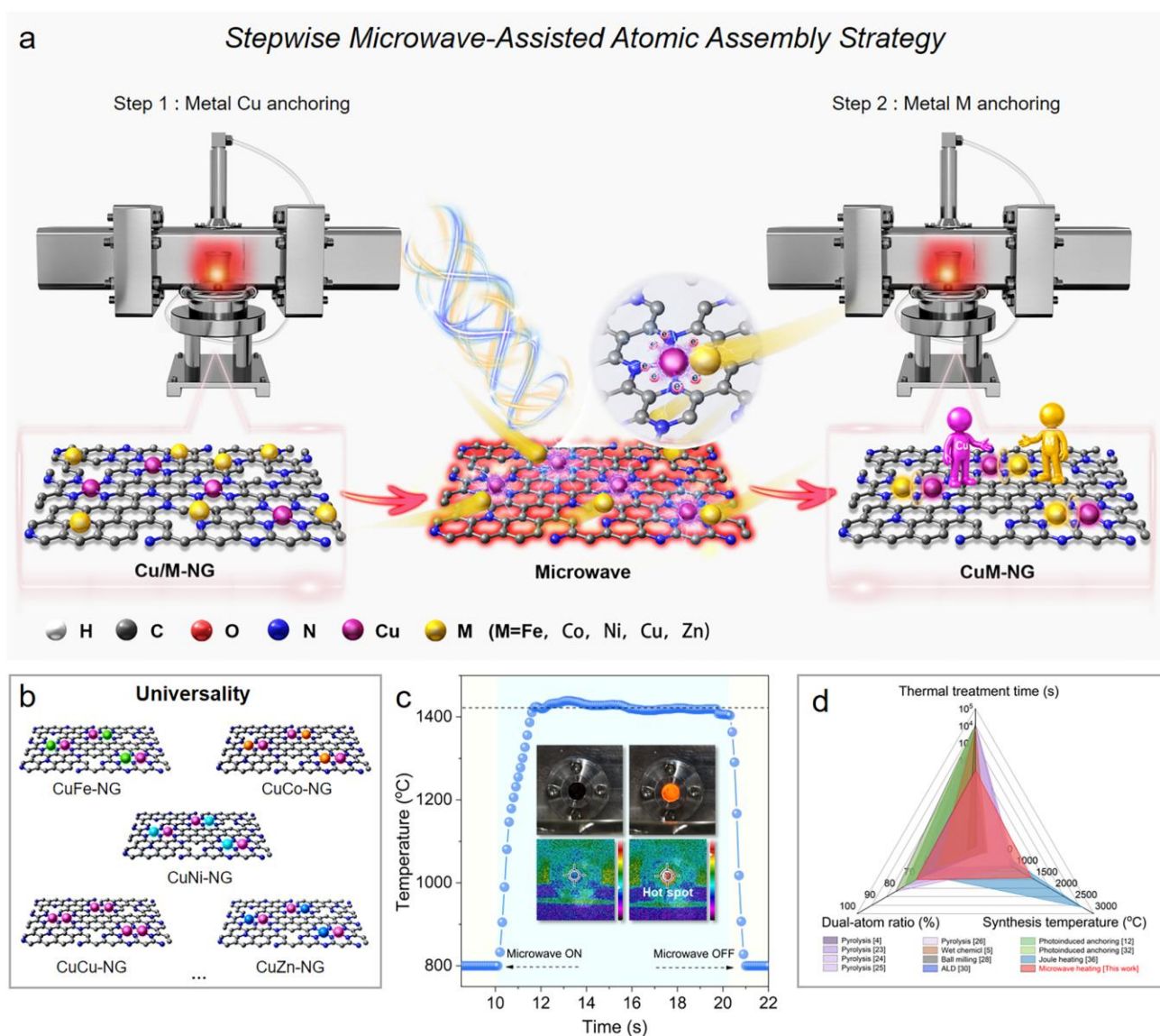


Fig. 1 Stepwise microwave-assisted atomic assembly strategy for DACs synthesis. (a) Schematic illustration of dual-atom construction on NG. (b) The universality of stepwise microwave-assisted atomic assembly strategy for constructing diverse dual-atom configurations. (c) Temperature evolution of the sample during microwave heating. The 800 °C baseline results from the detection limit of the infrared temperature measurement device. Insets: optical images and thermal images recorded through the observation window of the microwave device. (d) Comparison of reported thermal treatment time, temperature, and dual-atom pairing ratio among different DAC synthesis methods.

Structural characterizations

We first characterized the starting materials. Transmission electron microscopy (TEM) images of GO and NH₂-GO show typical two-dimensional layered morphologies with large flat nanosheets (**Supplementary Fig. 3**). Successful amino functionalization was confirmed by Fourier-transform infrared spectroscopy (FT-IR) (**Supplementary Fig. 4**), where a band at 1518 cm⁻¹ is assigned to an N-H bending mode. Upon introducing metal salts, amino and oxygen-containing groups could serve as coordination sites for metal ions. During microwave treatment, amine groups also supplied nitrogen sources for C-N and M-N bonds formation through thermal decomposition and atomic rearrangement. CuCu-NG was selected as a representative homonuclear DAC for structural analysis. TEM and high-resolution TEM (HRTEM) images of Cu-NG and CuCu-NG show no detectable nanoparticles, indicating highly dispersed Cu species (**Fig. 2a,b** and **Supplementary Fig. 5a,b**). Energy-dispersive X-ray spectroscopy (EDS) mapping shows the uniform distribution of C, N and Cu elements (**Fig. 2c** and **Supplementary Fig. 5d**). Aberration-corrected scanning transmission electron microscopy (AC-STEM) image (**Supplementary Fig. 5c**) shows abundant isolated bright spots in Cu-NG, while paired bright spots predominate in CuCu-NG (**Fig. 2d** and **Supplementary Fig. 6**), which are assigned to atomically dispersed Cu species owing to the higher atomic number of Cu than C and N atoms in the NG framework. Three-dimensional (3D) intensity maps reconstructed from the region marked in **Fig. 2d** resolve the spatial distribution of Cu-Cu dual-atom sites (**Fig. 2e**), with representative pairs exhibiting interatomic distances of 0.255 and 0.238 nm (**Fig. 2f**). Statistical analysis gives an average Cu-Cu distance of 0.252 nm and a narrow distribution centered at 0.26 nm (**Fig. 2g,h**), with diatomic pairs accounting for ~69.6% of the total atomic configurations (**Fig. 2i**). N₂ adsorption-desorption isotherms show the specific surface areas of NH₂-GO, Cu-NG, and CuCu-NG are 106.8, 79.9, and 88.7 m² g⁻¹, respectively. BJH analysis reveals similar mesoporous distributions (30-50 nm) among all

samples, derived from graphene nanosheet stacking, which may facilitate mass transport and active-site exposure (**Supplementary Fig. 7**).

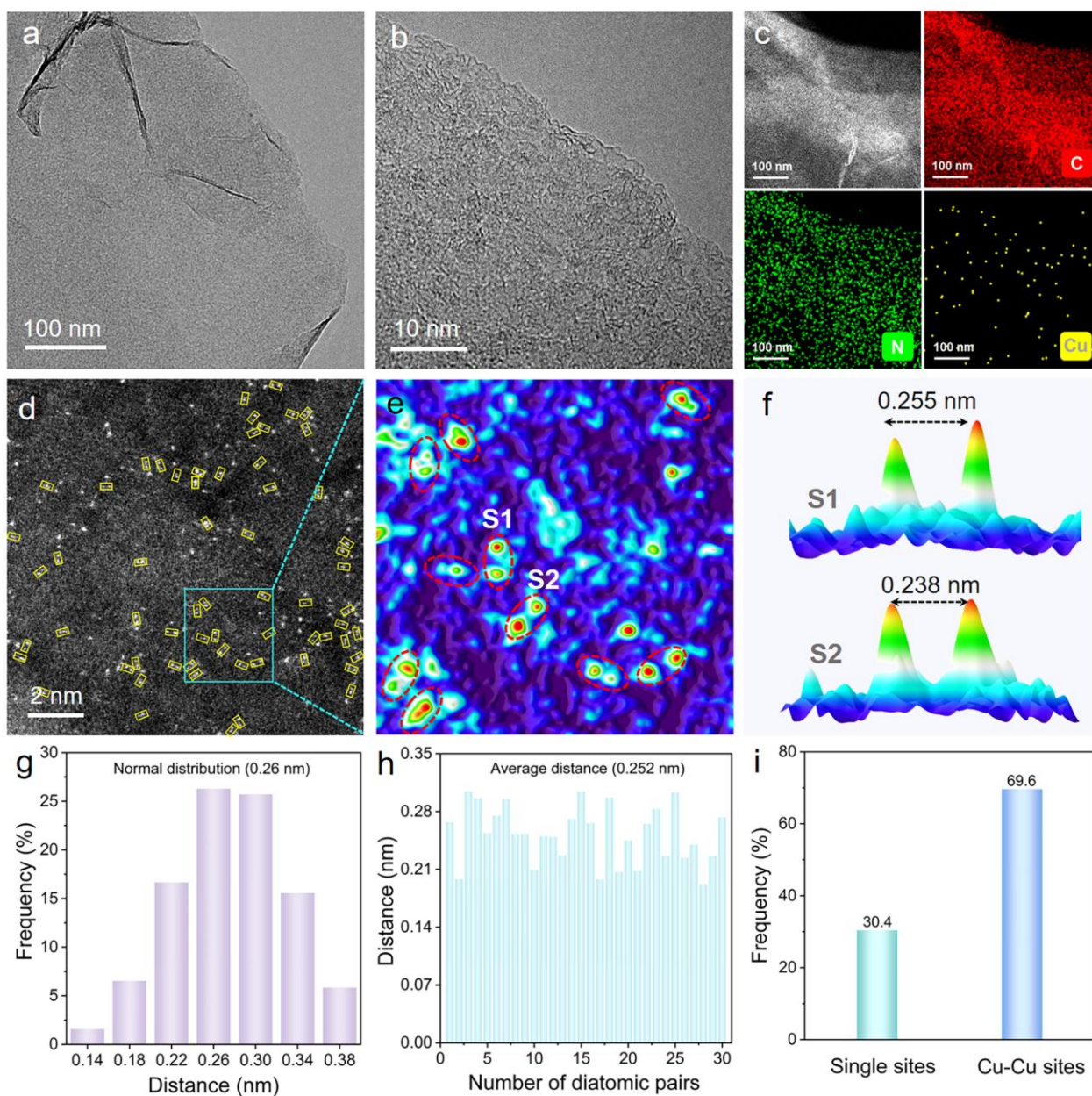


Fig. 2 Structural characterizations of CuCu-NG. (a) TEM, (b) HRTEM, (c) HAADF-STEM and elemental mapping, and (d) AC-STEM images. (e-f) Three-dimensional intensity maps of Cu-Cu sites reconstructed from the region marked in (d). (g) Frequency distribution of interatomic distances between adjacent Cu atoms. (h) Statistical distribution of pair distances and (i) fractions of single Cu sites and Cu-Cu pairs obtained from AC-STEM images.

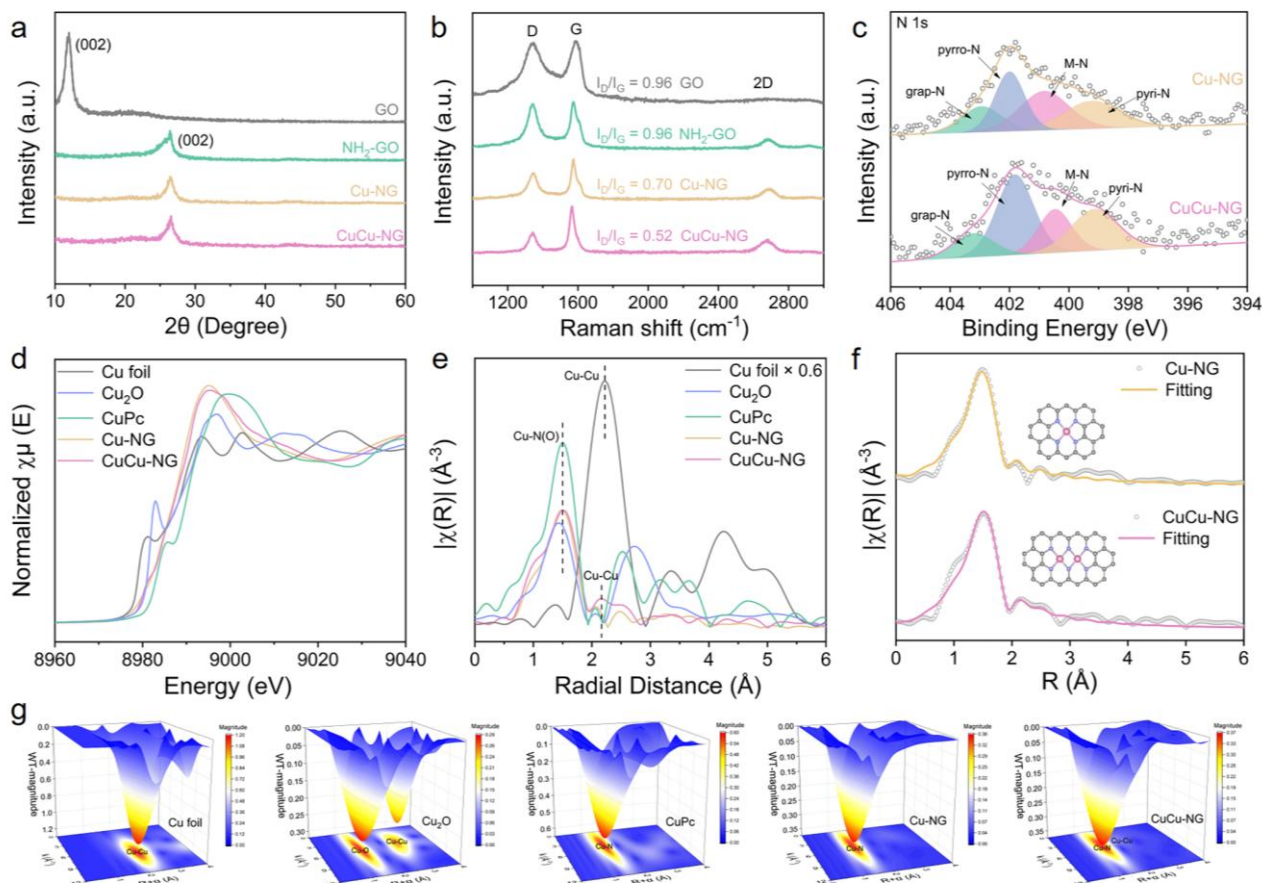


Fig. 3 Structural characterization of samples. (a) XRD patterns and (b) Raman spectra of GO, NH₂-GO, Cu-NG, and CuCu-NG. (c) N 1s XPS spectra of Cu-NG and CuCu-NG. (d) Cu K-edge XANES spectra and (e) Fourier-transformed EXAFS spectra for Cu-NG, CuCu-NG, and reference samples. (f) Cu K-edge EXAFS fitting results of Cu-NG and CuCu-NG in R space. (g) WT-EXAFS spectra of Cu in Cu-NG, CuCu-NG, and reference samples.

X-ray diffraction (XRD) patterns of Cu-NG and CuCu-NG exhibit only graphene diffraction peaks without detectable crystalline Cu or Cu oxide phases, confirming the absence of noticeable metal aggregation (**Fig. 3a**). Microwave reduction removes oxygen-containing groups and decreases the interlayer spacing from 0.78 nm in GO ($2\theta = 11.3^\circ$) to 0.34 nm in Cu-NG and CuCu-NG ($2\theta = 26.5^\circ$)¹⁵. The (002) diffraction peak in NH₂-GO originates from pre-annealing before amination to enhance conductivity and microwave absorption. Raman spectra show increased graphitization after

microwave treatment (**Fig. 3b**). Compared with GO, Cu-NG and CuCu-NG display enhanced G and 2D bands, with the I_D/I_G ratio decreasing from 0.96 to 0.70 and 0.52, respectively, indicating progressive defect healing and enhanced graphitization of the NG framework⁴⁰.

X-ray photoelectron spectroscopy (XPS) was conducted to analyze the elemental composition and electronic states of the samples. Survey spectra show C and O signals in all samples, with weak N signals due to its low content (**Supplementary Fig. 8a**). The increased C/O ratio from 12.39 (NH₂-GO) to 19.45 (Cu-NG) and 41.92 (CuCu-NG), together with enhanced sp² C=C signals in C 1s spectra (**Supplementary Fig. 8b**), demonstrates the progressive oxygen-containing groups removal after microwave treatment. N 1s spectra of GO and NH₂-GO can be deconvoluted into pyridinic, pyrrolic, and graphitic N (**Supplementary Fig. 8c,d**), while an additional peak at 400.4 eV after metal incorporation is assigned to metal-coordinated N (**Fig. 3c**). These N-containing coordination environments can stabilize dispersed metal sites and may contribute to catalytic activity. The Cu 2p_{3/2} and Cu 2p_{1/2} peaks of CuCu-NG (932.8 and 952.8 eV) shift negatively compared with Cu-NG (934.1 and 953.7 eV), suggesting electron redistribution induced by Cu-Cu interactions (**Supplementary Fig. 8e,f**)¹⁶. Metal loadings determined by inductively coupled plasma optical emission spectrometry (ICP-OES) are listed in **Supplementary Table 2**.

The coordination environment and electronic structure of Cu were further investigated by Cu K-edge X-ray absorption fine structure (XAFS) spectroscopy, including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses. As shown in **Fig. 3d**, the Cu K-edge XANES spectra of Cu-NG and CuCu-NG are located between those of Cu foil and Cu₂O references⁴¹, with spectral profiles closer to Cu₂O, suggesting a predominantly positive Cu state close to +1³⁶. Fourier-transform EXAFS spectra (k²-weighted) of Cu-NG and CuCu-NG show a

dominant peak at 1.49 Å, corresponding to Cu-N coordination based on CuPc reference (**Fig. 3e**)^{42,43}. CuCu-NG additionally shows a weak contribution at 2.15 Å, close to the Cu-Cu scattering distance of Cu foil (2.22 Å), implying the presence of short-range Cu-Cu interactions. EXAFS fitting results (**Fig. 3f** and **Supplementary Figs. 9-10**) agree well with the experimental spectra, and structural parameters are summarized in **Supplementary Table 3**. The fitted Cu-N coordination numbers are 3.9 for Cu-NG and 4.4 for CuCu-NG, with corresponding bond distances of 1.97 and 2.00 Å. CuCu-NG contains an additional Cu-Cu scattering with a coordination number of 0.8 and a bond distance of 2.39 Å, consistent with the analysis from HAADF-STEM (**Fig. 2g,h**). Structural models derived from these results are shown in the inset of **Fig. 3f**. Wavelet transform (WT) EXAFS analysis was further performed to distinguish backscattered atoms (**Fig. 3g**). Cu-NG displays a dominant feature at ~4.52 Å⁻¹, consistent with Cu-N coordination. CuCu-NG retains this Cu-N feature (4.36 Å⁻¹) and exhibits additional intensity at higher k values, resembling the Cu-Cu scattering in Cu foil. These results further support the coexistence of Cu-N coordination and Cu-Cu interactions in CuCu-NG, consistent with the EXAFS fitting analysis^{41,42,43}.

Having established the structure of homonuclear CuCu-NG, we extended the stepwise microwave-assisted atomic assembly strategy to construct heteronuclear CuM-NG DACs (M = Fe, Co, Ni, and Zn). XRD patterns show no detectable crystalline metal phases, confirming highly dispersed metal species on the NG (**Supplementary Fig. 11a**). Raman spectra exhibit low I_D/I_G ratios (0.47-0.51), indicating well-defined graphitic crystallinity after microwave treatment (**Supplementary Fig. 11b**). XPS further reveals increased C/O ratios and M-N coordination features (**Supplementary Figs. 11c** and **12**). CuFe-NG was selected as a representative heteronuclear DAC for structural analysis. HRTEM images reveal no detectable nanoparticles or clusters (**Supplementary Fig. 13a,b**), while AC-STEM

images show abundant paired atomic sites assigned to Cu-Fe dual atoms based on Z-dependent contrast and atomic-scale correlation (**Fig. 4a** and **Supplementary Fig. 13c**). 3D intensity profiles further distinguish Cu and Fe atomic signals from the NG framework (**Supplementary Fig. 13e**). Elemental mapping confirms uniform distribution of C, N, Cu, and Fe across the NG framework (**Fig. 4c**). Within the analysed images, the Cu-Fe pair distance distribution centers at ~ 0.22 nm, with an average value of 0.220 nm. Paired atomic features accounted for $\sim 71.1\%$ of the observed metal sites, while the remaining sites exist as isolated atoms (**Fig. 4b** and **Supplementary Fig. 13d**). Fe K-edge XAFS spectroscopy was performed to investigate the local coordination environment of CuFe-NG. The XANES spectrum indicates Fe oxidation states between +2 and +3 (**Supplementary Fig. 14a**). FT-EXAFS analysis reveals a dominant peak at ~ 1.47 Å assigned to Fe-N coordination, with fitted coordination number of ~ 4.7 and bond distance of ~ 2.00 Å (**Fig. 4d** and **Supplementary Table 3**). The absence of Fe-Fe scattering excludes detectable Fe aggregation, while a weak feature at ~ 2.5 Å is attributed to short-range Cu-Fe interaction, with a coordination number of ~ 0.8 and distance of ~ 2.53 Å. EXAFS fitting in *R*-space shows good agreement between experimental and fitted curves (**Fig. 4d inset**). WT-EXAFS further identifies Fe-N coordination and additional Fe-Cu scattering contribution (**Supplementary Fig. 15**). Similar structural characterizations of CuCo-NG, CuNi-NG, and CuZn-NG collectively demonstrate the generality of this microwave-enabled atomic assembly strategy for constructing diverse heteronuclear DACs (**Fig. 4** and **Supplementary Figs. 16-24**).

Scalable synthesis is essential for practical applications of DACs. Building on our previously developed automated microwave reaction platform²⁰, we extended our strategy to gram-scale DAC synthesis. Specifically, 40 g of NH₂-GO was used as the precursor, with 0.32 g of CuCl₂·2H₂O introduced during the first impregnation step. After freeze-drying and microwave reduction, Cu-NG

SACs were obtained and further converted into CuCu-NG DACs through a second $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ incorporation and microwave treatment, while maintaining structural stability and dual-atom configurations (Supplementary Figs. 25-26). Notably, the 40 g-scale synthesis could be accomplished through only five consecutive microwave cycles, highlighting the excellent scalability and practical feasibility of this microwave-driven DAC construction strategy.

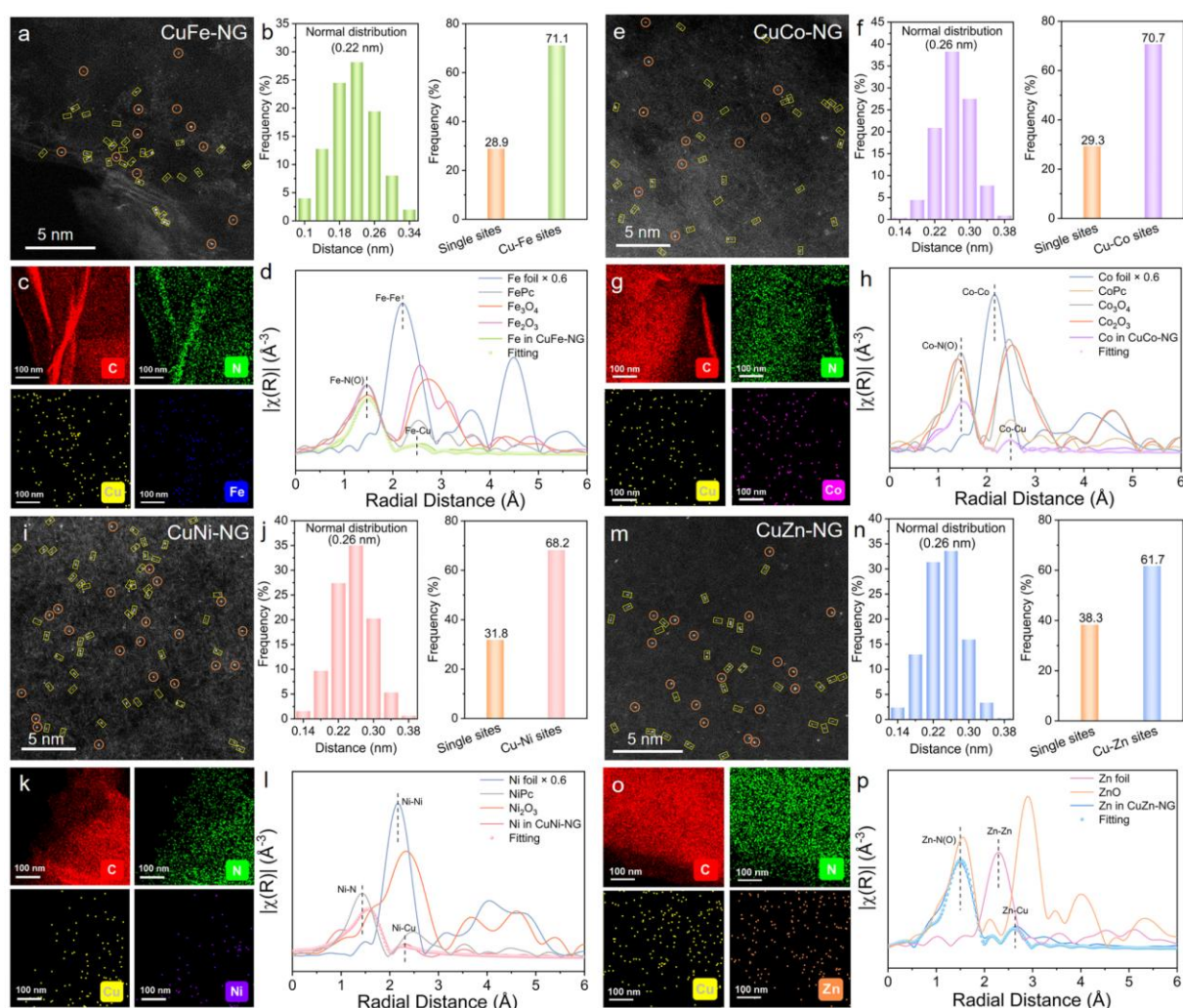


Fig. 4 Structural characterization of CuM-NG (M = Fe, Co, Ni, and Zn). (a, e, i, m) AC-STEM images of CuFe-NG, CuCo-NG, CuNi-NG, and CuZn-NG, respectively. (b, f, j, n) Pair-distance distributions and fractions of single and paired sites derived from AC-STEM images. (c, g, k, o) Elemental mapping images of the corresponding DAC. (d, h, l, p) Fourier-transformed EXAFS spectra in R space and corresponding fitting results.

Direct selective oxidation of methane with H₂O₂

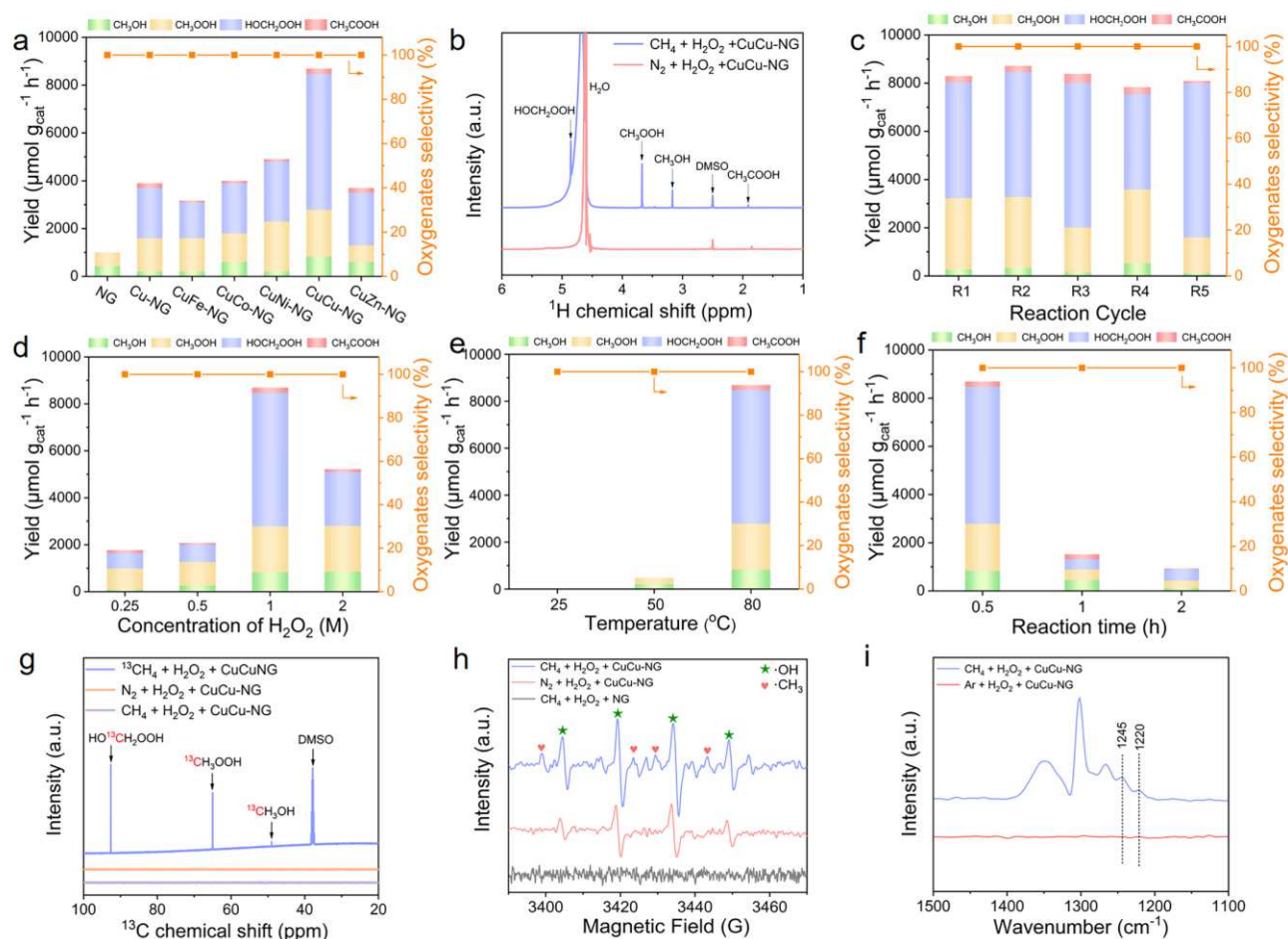


Fig. 5 Catalytic performance of catalysts for the direct selective oxidation of methane. (a) Catalytic performance of samples in DSOM. (b) ¹H NMR spectra of the liquid-phase products over CuCu-NG under CH₄ or N₂. (c) Recycle stability of the CuCu-NG for methane oxidation. Catalytic reactions were conducted in 10 mL H₂O₂ aqueous solution (1 M) with 3 MPa CH₄ at 80 °C for 0.5 h. Effects of (d) H₂O₂ concentrations, (e) reaction temperature and (f) time on DSOM over CuCu-NG. (g) ¹³C NMR spectra of the liquid-phase products obtained with ¹³CH₄, CH₄, and pure N₂. (h) EPR spectra of DMPO-trapped radicals generated over CuCu-NG. (i) In situ DRIFTS spectra on the CuCu-NG at 80 °C under different reaction conditions.

The synergistic catalytic effect of DACs was evidenced in the direct selective oxidation of methane (DSOM) under mild conditions using aqueous H₂O₂ as the solvent. To provide a comparable single-

site reference, Cu-NG SAC was synthesized using the same Cu precursor input (0.6 wt%) as CuCu-NG (**Supplementary Fig. 27**). Cu-NG exhibited an oxygenate yield of $3900 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$, whereas CuCu-NG achieved $8693 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ with nearly 100% selectivity, 2.2 times that of Cu-NG. The corresponding Cu mass activity was $1530 \text{ mmol g}_{\text{Cu}}^{-1} \text{h}^{-1}$ and the TOF_{DAC} reached 218 h^{-1} , which are comparable to those of leading catalysts reported previously (**Fig. 5a**, **Supplementary Fig. 28** and **Supplementary Table 4**). ^1H NMR spectroscopy identified CH_3OH , CH_3OOH , HOCH_2OOH , and CH_3COOH as liquid products. No oxygenates were detected when methane was replaced by nitrogen, supporting methane as the carbon source (**Fig. 5b**). Moreover, CuCu-NG demonstrated excellent catalytic stability, maintaining an oxygenate yield of $8300 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ and nearly unchanged selectivity after repeated cycles (**Fig. 5c**). HRTEM, AC-STEM, XRD, Raman, and XPS analyses confirmed the preservation of the graphene framework and stable Cu-Cu dual-atom structure after cycling (**Supplementary Fig. 29**).

The effects of reaction parameters on DSOM performance were further investigated. The oxygenate yield showed a volcano-shaped dependence on H_2O_2 concentration, while maintaining nearly 100% liquid-product selectivity (**Fig. 5d**). This trend may arise from excessive H_2O_2 competitively occupying Cu-Cu sites, suppressing the secondary conversion of $\text{CH}_3\text{OH}/\text{CH}_3\text{OOH}$ and C-C coupling rather than their initial formation. Temperature-dependent experiments showed negligible methane oxidation at 25°C , whereas the yield increased significantly to $8693 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ at 80°C (**Fig. 5e**). **Fig. 5f** revealed rapid oxygenate formation at the initial stage, followed by a gradual decrease in liquid-phase yield while maintaining high selectivity, likely due to reduced methane availability, continuous H_2O_2 consumption⁴⁴, and product inhibition at Cu-Cu sites⁴⁵.

^{13}C -labeling experiments confirmed methane as the carbon source of oxygenates (**Fig. 5g**). Acetic

acid was not resolved due to its low concentration. Electron paramagnetic resonance (EPR) spectroscopy revealed negligible $\cdot\text{OH}$ signals over pristine NG but distinct $\cdot\text{OH}$ generation over CuCu-NG under $\text{N}_2 + \text{H}_2\text{O}_2$ conditions, indicating Cu-site-assisted H_2O_2 activation. The enhanced $\cdot\text{OH}$ intensity and emergence of $\cdot\text{CH}_3$ signals after CH_4 introduction support a radical pathway for methane activation (**Fig. 5h**). In situ DRIFTS spectroscopy showed new bands at 1220 and 1245 cm^{-1} after introducing CH_4 and H_2O_2 , assigned to CH_x -containing intermediates and oxygenated species formation during methane oxidation (**Fig. 5i**).

To understand the synergistic effect of Cu-Cu dual-atom sites, comparative DFT calculations were performed using CuCu-NG and Cu-NG models to investigate electronic modulation and methane oxidation mechanisms (**Supplementary Fig. 30**). Differential charge density analysis (**Fig. 6a**) reveals distinct electronic characteristics between Cu-NG and CuCu-NG. Cu-NG exhibits localized charge accumulation along Cu-N coordination directions, characteristic of isolated single-atom sites. In contrast, CuCu-NG shows charge depletion between the Cu atoms and enhanced accumulation in the surrounding coordination environment, indicating strong Cu-Cu electronic coupling and charge redistribution. The projected density of states (PDOS) analysis (**Fig. 6b**) further shows broadened Cu 3d bands and enhanced density near the Fermi level in CuCu-NG, indicating increased electron delocalization. Although Cu-NG exhibits a d-band center closer to the Fermi level, generally associated with stronger adsorbate binding, excessive adsorption strength may hinder subsequent intermediate conversion and desorption^{36,46,47}. The moderated d-band position of CuCu-NG may provide an optimal adsorption-desorption balance. Cu-Cu interaction also induces N 2p state redistribution, enhancing p-d hybridization and ligand-environment reconstruction (**Fig. 6c**).

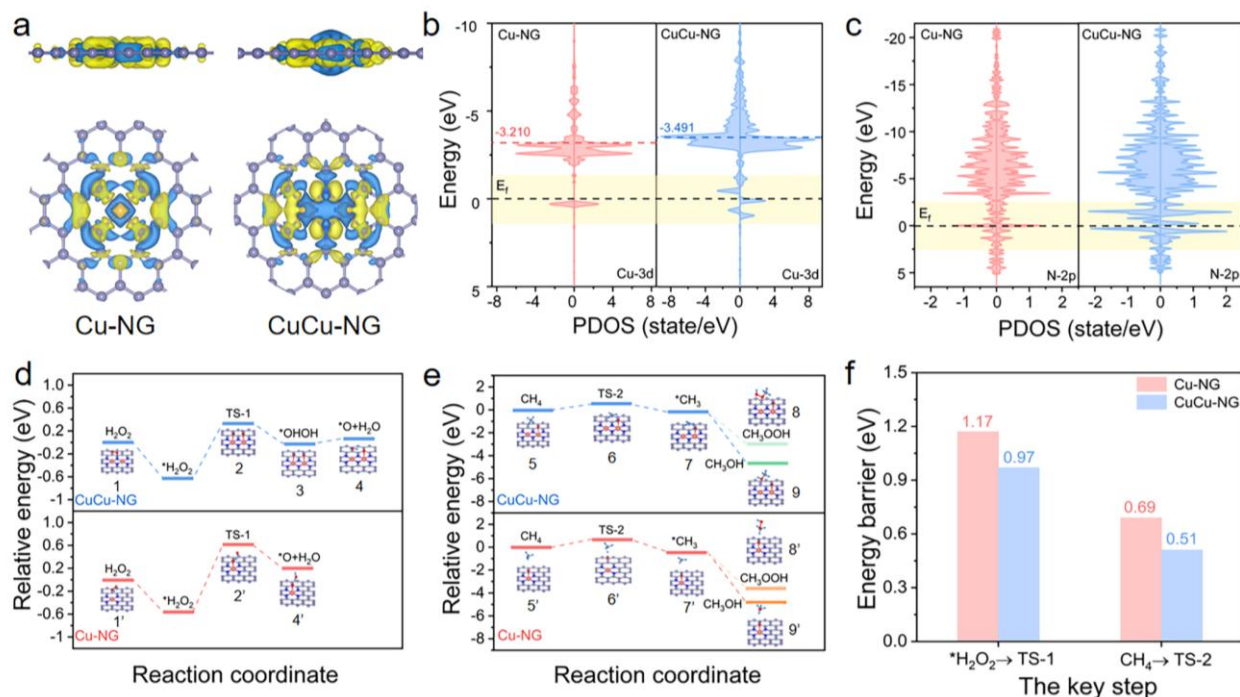


Fig. 6 Theoretical analysis of DSOM on CuCu-NG. (a) Differential charge-density maps of Cu-NG and CuCu-NG. Yellow and blue regions represent charge accumulation and depletion, respectively. Projected density of states of (b) Cu 3d and (c) N 2p. Relative electronic energy profiles for (d) H₂O₂ activation and (e) methane catalytic oxidation toward primary oxygenated products (CH₃OH and CH₃OOH) on Cu-NG and CuCu-NG. (f) Energy barriers of the key reaction steps. Colour scheme: light blue, H; red, O; blue, N; bluish-purple, C; pink, Cu.

The synergistic catalytic roles of Cu-Cu sites were further investigated through relative electronic energy calculations for H₂O₂ activation (**Fig. 6d**) and CH₄ conversion to primary oxygenates (**Fig. 6e**). The optimized configurations of intermediates and transition states are shown in **Supplementary Figs. 31-32**. H₂O₂ first adsorbs on Cu sites (1) and undergoes O-O bond cleavage via first transition state (TS-1) to generate hydroxyl species in CuCu-NG (3). Compared with Cu-NG, where H₂O₂ dissociation favors Cu-O species and H₂O formation (4'), CuCu-NG stabilizes the reaction intermediate 3 with a lower reaction energy (-0.02 eV versus 0.20 eV) and H₂O₂ activation energy barrier (0.97 eV) (**Fig.**

6f). Subsequently, proton reshuffling generates active O and weakly adsorbed H₂O (4) through a water-assisted H transfer pathway⁴⁸. After oxidant activation, CH₄ adsorbs on Cu sites (5 and 5') and undergoes the first C-H bond cleavage via TS-2 (6 and 6') to form *CH₃ and Cu-OH species (7 and 7'). CuCu-NG significantly lowers the activation barrier to 0.51 eV compared with Cu-NG (0.69 eV), indicating enhanced C-H activation via Cu-Cu electronic coupling. The resulting *CH₃ intermediate reacts with oxygen radicals ($\cdot$ OH or $\cdot$ OOH) to generate primary oxygenates (CH₃OH and CH₃OOH). The favorable energy profile of CuCu-NG promotes oxygenate formation through Cu-Cu interaction-induced electronic reconstruction, which facilitates oxidant activation and C-H cleavage.

Discussion

In summary, we have developed a universal stepwise microwave-assisted atomic assembly strategy for the precise and rapid construction of DACs via stepwise atomic assembly. The approach exploits microwave-induced electronic accumulation at pre-formed Cu single-atom sites to direct the selective anchoring of a second metal ion in close proximity, leading to the formation of homonuclear CuCu-NG as well as a series of heteronuclear CuM-NG (M = Fe, Co, Ni, Zn) DACs with dual-atom pairing ratios up to ~70%. The microwave-assisted process was further extended to gram-level synthesis, demonstrating its potential for practical catalyst production. Among them, CuCu-NG exhibits outstanding performance for direct selective oxidation of methane, achieving an oxygenate yield of 8693 $\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$ with nearly 100% selectivity, corresponding to a Cu mass activity of 1530 $\text{mmol g}_{\text{Cu}}^{-1} \text{h}^{-1}$ and a TOF of 218 h^{-1} . Experimental and theoretical investigations reveal that the Cu-Cu interaction-induced electronic redistribution and modulation of the d-band center promote oxidant activation and C-H bond cleavage by lowering the associated energy barriers. This stepwise assembly concept can be extended to a broader range of metal combinations and provides significant insights

into the synergistic catalytic process of diatomic cooperation.

Methods

Synthesis of Cu-NG SAC and CuM-NG DACs (M = Fe, Co, Ni, Cu and Zn)

NH₂-GO was synthesized according to a previously reported method with slight modifications¹⁵. In a typical procedure, NH₄OH solution (14 mL, 30%) was added dropwise into GO aqueous suspension (140 mL, 2 mg mL⁻¹) under continuous stirring for 1 h. The resulting suspension was then transferred into a Teflon-lined autoclave and heated at 80 °C for 5 h. After cooling to room temperature, excess NH₄OH was removed by heating and stirring the suspension overnight at 50 °C. The purified NH₂-GO was subsequently obtained by freeze-drying. Before the amination treatment, GO was pre-annealed at 300 °C (5 °C min⁻¹) for 30 min under an Ar atmosphere to enhance its electrical conductivity and microwave responsiveness.

A certain amount of CuCl₂·2H₂O was dissolved in an NH₂-GO aqueous suspension and stirred for 1 h to obtain samples with nominal Cu loadings of 0.3 and 0.6 wt%. After freeze-drying, 100 mg of CuCl₂-loaded NH₂-GO (Cu-NH₂-GO) was placed into a quartz crucible and subjected to microwave irradiation in a laboratory-built automated microwave reactor (2.45 GHz) at 1200 W for 15 s under a continuous Ar flow (1000 cm³ min⁻¹)²⁰. After cooling for 10 min under Ar, Cu-NG samples were obtained.

100 mg of Cu-NG (nominal Cu loading of 0.3 wt%) was ultrasonically dispersed in 20 mL of deionized water for 10 min, followed by the dropwise addition of CuCl₂·2H₂O aqueous solution (100 µL, 8.0 mg mL⁻¹) under continuous stirring. The resulting suspension was freeze-dried to obtain a CuCl₂-containing Cu-NG precursor. Subsequently, the precursor was transferred into a quartz

crucible and treated in a microwave reactor (2.45 GHz) at 1000 W for 10 s under continuous Ar purging ($1000\text{ cm}^3\text{ min}^{-1}$). After cooling for 10 min under an Ar atmosphere, CuCu-NG was collected for further characterization and catalytic evaluation. The preparation procedures for CuFe-NG, CuCo-NG, CuNi-NG, and CuZn-NG were similar to that of CuCu-NG, except that different secondary metal precursors (Fe, Co, Ni, and Zn) were introduced. The feeding amount of secondary metal precursors was controlled to maintain a nominal metal content of 0.3 wt%.

Activity measurements for direct selective oxidation of methane

Catalytic activity tests for direct selective oxidation of methane (DSOM) were performed in a 25 mL stainless-steel autoclave. Typically, 10 mg of catalyst was dispersed in 10 mL of 1 M H_2O_2 aqueous solution, followed by sealing and CH_4 purging. The reactor was then charged with CH_4 to an initial pressure of 3 MPa and maintained at $80\text{ }^\circ\text{C}$ under vigorous stirring (900 rpm). After 0.5 h of reaction, the autoclave was rapidly cooled to $5\text{ }^\circ\text{C}$ in an ice bath. Gaseous products from the reactor outlet were collected in a gas sampling bag (MBT62-1, Dalian Haide Technology Co., Ltd.) and analyzed by GC (SP-3420A) equipped with a flame ionization detector (FID). A TDX-1 column connected to FID was used to separate CO, CH_4 and CO_2 . Meanwhile, the equipped Ni catalyst converter could quantitatively convert CO and CO_2 into CH_4 . Prior to gas collection, the sampling bag was purged with N_2 , leak-tested, and evacuated. A miniature vacuum pump connected to the GC inlet was employed to withdraw gas for 30 s, ensuring a constant injection volume. CO, CH_4 , and CO_2 were quantified based on calibration curves generated from certified standard gases. Liquid products were analyzed by ^1H NMR spectroscopy using a 600 MHz Bruker AVANCE III spectrometer. D_2O was used as the solvent, and dimethyl sulfoxide (DMSO) was added as an internal standard. Typically, 500 μL of reaction solution and 10 μL of DMSO were mixed for NMR analysis.

The yield of products ($\mu\text{mol/g}_{\text{cat}}/\text{h}$) and oxygenates selectivity (%) were calculated using the following equations (1-2):

$$\text{Yield of products } (\mu\text{mol/g}_{\text{cat}}/\text{h}) = \frac{n(\text{Oxygenated products})}{m(\text{g}) \times t(\text{h})} \quad (1)$$

where $n(\text{Oxygenated products})$ represents the number of moles of oxygenated products, including CH_3OH , CH_3OOH , HOCH_2OOH , and CH_3COOH , m is the number of grams of the catalyst, and t is the reaction time.

$$\text{Oxygenates selectivity } (\%) = \frac{n(\text{Oxygenated products})}{n(\text{Total products})} \times 100 \quad (2)$$

where $n(\text{Oxygenated products})$ represents the number of moles of oxygenated products, including CH_3OH , CH_3OOH , HOCH_2OOH , and CH_3COOH , $n(\text{Total products})$ is the total number of moles of all products, including both liquid-phase and gas-phase products.

The contribution of Cu-Cu dual-atom sites was estimated based on the experimentally determined fractions of dual-atom and single-atom Cu sites from AC-STEM analysis. The average turnover frequency (TOF_{avg}) was first calculated based on the total number of Cu atoms according to:

$$\text{TOF}_{\text{avg}} (\text{h}^{-1}) = \frac{n(\text{Oxygenated products})}{n(\text{Cu}) \times t(\text{h})} \quad (3)$$

where $n(\text{Oxygenated products})$ represents the number of moles of oxygenated products, including CH_3OH , CH_3OOH , HOCH_2OOH , and CH_3COOH , $n(\text{Cu})$ represents the number of moles of Cu atom, and t is the reaction time. The TOF_{avg} is calculated to be 97 h^{-1} .

Based on AC-STEM statistical analysis, the Cu-Cu dual-atom site fraction (f_{DAC}) and isolated Cu single-atom site fraction (f_{SAC}) were determined to be 69.6% and 30.4%, respectively. Considering that each Cu-Cu dual-atom site contains two Cu atoms, the relationship between the TOF_{avg} and the Cu-Cu dual-atom site-based TOF (TOF_{DAC}) and Cu single-atom site-based TOF (TOF_{SAC}) can be expressed as:

$$\text{TOF}_{\text{avg}} (\text{h}^{-1}) = \frac{f_{\text{DAC}} \text{TOF}_{\text{DAC}} + f_{\text{SAC}} \text{TOF}_{\text{SAC}}}{2f_{\text{DAC}} + f_{\text{SAC}}} \quad (4)$$

where TOF_{DAC} represents the TOF of one Cu-Cu dual-atom site, and TOF_{SAC} represents the TOF of one isolated Cu single-atom site. Using $f_{\text{DAC}}=0.696$, $f_{\text{SAC}}=0.304$, and $\text{TOF}_{\text{SAC}}=41.6 \text{ h}^{-1}$, the TOF_{DAC} was calculated as 218 h^{-1} .

DFT calculations

All density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP)⁴⁹. The exchange-correlation potential was treated within the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA)⁵⁰. The electron-ion interactions were described using the projector augmented wave (PAW) method. A plane-wave cutoff energy of 450 eV was employed, and Brillouin zone sampling was carried out using a $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh centered at the Γ point. The convergence criteria for energy and forces were set to 10^{-5} eV and $0.03 \text{ eV } \text{\AA}^{-1}$, respectively. Van der Waals interactions were included using the DFT-D3 correction⁵¹. Transition states were determined using the climbing-image nudged elastic band (CI-NEB) method. The activation energy barrier was calculated as $\Delta E_{\text{a}} = E_{\text{TS}} - E_{\text{IS}}$, where E_{TS} and E_{IS} represent the energies of the transition and initial states, respectively.

Data availability

The data that substantiate the study's findings and contribute to the assessment of the paper's conclusions can be accessed within the paper and its Supplementary Information.

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Author contributions

Z. G. and W. T. conceived of the idea and designed the present work. W. T. carried out the materials synthesis and characterization experiments. X. W. and H. S. carried out the catalysis analysis on the direct selective oxidation of methane. Z. L., N. J. and J. L. assisted with additional characterization experiments. Z. L. conducted the temperature measurements using an infrared thermal imaging thermometer (CSASCIT T0830). W. T. wrote most of the paper. J. Z., Z. G., Z. X. and W. L. supervised the project. All authors discussed the results and commented on the manuscript.

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