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Formation mechanism of few-layer graphene adjacent to nanoscale zero-valent copper nanoparticles synthesized using kraft lignin as a sustainable aromatic-rich carbon resource

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Few-layer (three- to four-layer) graphene formed adjacent to zero-valent copper nanoparticles (FG-nZVCu) is a promising material for a wide range of applications, including catalysis, environmental remediation, energy storage, and functional composite development. Kraft lignin (KL) has attracted increasing interest as a sustainable and underutilized solid-state carbon precursor for the production of value-added graphitic materials. The effects of five different solvents on the solubility of KL and the dispersion uniformity of Cu²⁺ in the KL–solvent matrices were first investigated, followed by an evaluation of the effect of copper loading (10–40 wt% by KL weight) on the graphene layer number and particle size of FG-nZVCu, and subsequently the effects of *in situ* Cu-catalyzed thermal catalytic graphitization temperature (600–1100 °C) on FG-nZVCu formation. Experimental results show that few-layer turbostratic graphene structures become clearly observable adjacent to nZVCu particles at approximately 800 °C, and their degree of graphitization increases as the temperature increases to 1100 °C. This behavior suggests that the formation mechanism involves Cu-assisted aromatic carbon ring surface rearrangement of aromatic carbon fragments decomposed from KL during thermal treatment. Additionally, the use of the moderately polar solvent tetrahydrofuran (THF) to facilitate KL dissolution enables more uniform dispersion of nZVCu particles within the KL matrix. An optimal Cu loading of 20 wt% results in uniformly distributed nZVCu particles with an average size of 27.3 nm.

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1. Introduction

Graphene–copper hybrid structures are high-performance composites because the intimate interfacial association between graphene layers and zero-valent copper particles (ZVCu) enhances stability, transport behavior, and mechanical performance of the materials. The graphene-encapsulated ZVCu nanoparticles (G-nZVCu) are a typical type of graphene–copper hybrid composite, in which graphene shells encapsulating nZVCu protect the copper cores from oxidation and aggregation, thereby improving durability and thermal stability.^{1–3} In graphene-like carbon/copper composites synthesized by *in situ* chemical vapor deposition (CVD), the thermal conductivity increases by 7.8% at ultralow GLC content, highlighting their potential for high-voltage electrical contact applications.⁴ In addition, G-nZVCu-based composites exhibit

enhanced mechanical properties, with reported improvements in tensile strength and hardness compared with pure copper.^{5–7}

The formation of multilayer graphene-like structures on nanoscale metal particles has been widely reported and is generally interpreted through several growth mechanisms described in the literature. CVD is one of the primary mechanisms by which single-layer or few-layer graphene forms. In this process, gaseous carbon sources such as CH₄, or liquid and solid carbon sources containing aromatic ring structures—such as benzene, toluene, polystyrene (PS), and polycyclic aromatic hydrocarbons (PAHs) (Fig. 1)—decompose on the metal catalyst surface to generate active carbon species. These species may

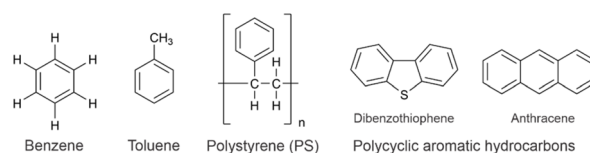


Fig. 1 Fossil-fuel-based aromatic compounds and polymers commonly used as non-renewable hydrocarbon-derived carbon precursors for Cu-catalyzed graphene formation.

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include carbon atoms derived from gaseous hydrocarbon sources such as CH_4 , or carbon-rich aromatic radicals derived from volatile or readily decomposable liquid or solid carbon precursors at relatively low temperatures in the range of 300–550 °C. The resulting active, continuous, and diffusible species subsequently nucleate into graphene domains and grow through diffusion and edge attachment on the surface of catalysts.^{8–11} This mechanism is widely associated with graphene formation on Cu. As a result, carbon species generated from the precursor mainly remain on the Cu surface because of its low carbon solubility. This surface-mediated process promotes relatively self-limited growth and therefore favors the formation of fewer graphitic layers.^{12–15} However, these carbon precursors are non-renewable and may require energy-intensive processing.

In contrast, the dissolution–precipitation mechanism is more commonly associated with metals that have relatively high carbon solubility such as Fe and Ni, in which carbon atoms generated from solid phase carbon such as polymers and biomass as precursors at elevated temperatures first dissolve into the metal catalyst and then precipitate during cooling to form graphitic layers.^{16–18} For instance, using Fe as the metal catalyst, carbon atoms derived from the solid carbon precursor can dissolve into Fe during thermal treatment, promoting phase evolution from zero-valent Fe nanoparticles (nZVFe) to other Fe-based phases such as α -Fe, γ -Fe, or Fe_3C .¹⁹

The final structure of the formed graphene, including the number of layers and morphology (*e.g.*, flat or curved) depends not only on the formation mechanism but also on other factors, such as the carbon solubility and geometry of the catalyst metal used. In the CVD mechanism, flat Cu foil typically favors the formation of flat single- or few-layer graphene,^{20,21} whereas Cu nanoparticles may promote the formation of curved or shell-like graphene layers.²² In the dissolution–precipitation mechanism, metals with high carbon solubility, such as Fe and Ni, are commonly used as catalysts and tend to form multi-layer graphene layers.^{23,24}

Kraft lignin (KL), a sulfur-containing lignin derived as a by-product of the pulping process, is one of the most abundant renewable resources on Earth.^{25–27} It possesses a complex 3D cross-linked and condensed phenolic structure rich in aromatic rings (Fig. 2), with lower molecular weight fragments and

increased phenolic content compared to native lignin²⁸ because the predominant β -O-4 linkages in raw lignin are largely cleaved during pulping. Owing to its chemical structure and high carbon content,²⁹ our previous work proposed using KL as a low-cost and sustainable carbon source for synthesizing graphene-encapsulated zero-valent Fe nanoparticles (G-nZVFe) using Fe as the catalyst.^{19,30–32} The dissolution–precipitation mechanism was used in interpreting the formation of the layered graphene in these studies.^{19,31} Due to the high carbon solubility of Fe, a greater amount of solid carbon species can dissolve into the Fe nanoparticles and subsequently precipitate as thick multilayer graphene shells (>30 layers) that encapsulate the zero-valent Fe cores. Such excessively thick graphitic layers are generally undesirable because they can diminish the unique advantages of metal nanoparticles.

Leng *et al.*^{34,35} reported the graphene structure formed in the KL–Cu system at 400–500 °C using the dissolution–precipitation mechanism; however, no evidence of Cu phase evolution was documented to support this interpretation. The formation of graphene structures in the KL–Cu system reported in the Leng *et al.* study is unlikely to follow a typical CVD mechanism, where a continuous gas-phase carbon source can diffuse to the Cu surface; instead, KL served as a solid, macromolecular biomass-derived precursor. Although KL pyrolysis may generate some carbon-containing volatile fragments, only a small amount of CH_4 gas was detected at 250 °C during the heating study of KL up to 1000 °C.³⁶ Although the dissolution–precipitation mechanism may still occur, it is unlikely to be the dominant pathway because Cu has very limited carbon solubility, making the dissolution of carbon species into Cu unfavorable.

These studies open up the idea for exploring aromatic-rich biomass-derived precursors for graphene synthesis using Cu as the catalyst: lignin is a naturally abundant, aromatic-rich biomass precursor that also contains abundant phenylpropane-based aromatic units. Although lignin has a more complex, three-dimensional, and irregular macromolecular structure than fossil-fuel-based aromatic compounds and polymers, it might offer a sustainable alternative route for producing few-layer graphene-like structures rather than thick multilayer graphitic shells. Based on this proposed idea, the solvent environment, Cu loading, and graphitization temperature are expected to be the key synthesis parameters controlling few-layer (three- to four-layer) graphene formed adjacent to zero-valent copper nanoparticles (FG-nZVCu) formation. The solvent used during precursor preparation affects the dissolution behavior of KL and the homogeneity of KL/ Cu^{2+} mixtures, which in turn affects the dispersion of catalytic Cu species during thermal treatment. A molecular simulation study³⁷ suggested that no single suitable organic solvent is universally optimal for lignin dissolution. Effective solubility therefore requires solvent selection that considers both hydrophilic and hydrophobic molecular interactions of lignin, including those associated with its aliphatic and phenolic groups.^{38,39} Cu loading governs the extent of interaction between Cu^{2+} and the KL matrix, thereby influencing both the dispersion of the resulting FG-nZVCu within the matrix, and the catalytic

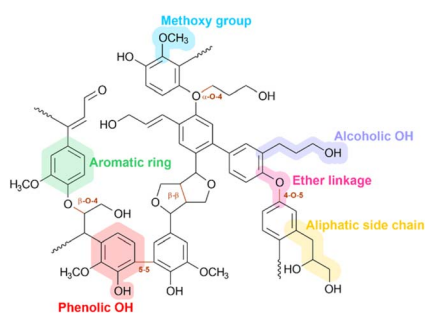


Fig. 2 Schematic illustration of the primary interunit linkages present in softwood lignin. The structure was redrawn and adapted based on the information reported in the literature.³³

performance of nZVCu in the formation of graphene-like structures. Theoretically, the higher the catalyst loading, the greater the contact between metal ions and lignin active sites, resulting in better catalytic capacity for graphene formation,^{40–42} but excessive metal loading may cause aggregation issues.^{43,44} In our previous study, the use of Fe as the catalyst was limited by its tendency to agglomerate when the loading exceeds 10% because of the high surface energy of metal species formed at elevated temperature,⁴³ which negatively impacted the uniformity of metallic catalyst dispersion in the KL matrix.

Therefore, the specific objectives of this study were to systematically investigate the effects of solvent selection for KL dissolution, Cu loading, and graphitization temperature on the formation of FG-nZVCu within the KL matrix by measuring and quantifying dispersion uniformity, graphene layer number, and particle size distribution. The ultimate goal is to elucidate the formation mechanism of graphene structures within the KL matrix, thereby paving the way for more cost-efficient and sustainable graphene production.

2. Experimental

2.1. Materials

Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) powder, ethanol, tetrahydrofuran (THF), ethyl acetate, and acetone were purchased from Sigma-Aldrich (St Louis, MO, USA). KL (BioChoice) was supplied by Domtar Inc. (Plymouth, NC, USA). Fig. 1 presents the primary interunit linkages commonly found in softwood lignin, illustrating the representative chemical structure of KL used in this study. Elemental analysis of KL shows that it contains approximately 60% carbon, 5–6% hydrogen, 0.5–1% ash, and 30% oxygen.⁴⁵ Table 1 summarizes the reported chemical structures, molecular weights, dielectric constants, and Hansen solubility parameter (HSP) values of the solvents used in this study.

2.2. Methods

2.2.1. Experimental design. Experiment I was a one-way factorial design with one replicate per combination, conducted to evaluate the effect of solvent type (deionized (DI) water, ethanol, ethyl acetate, THF, and acetone) on the solubility of KL and the dispersion uniformity of Cu^{2+} in the KL-solvent matrices at a fixed Cu loading of 20 wt%. The target

graphitization temperature was fixed at 1000 °C. The pre-graphitization sticky mixture and post-graphitization solids were labeled X-KL/Cu-20% and 1000-X-KL/Cu-20%, respectively, where X denotes W, E, EA, THF, and A, corresponding to DI water, ethanol, ethyl acetate, THF, and acetone, respectively.

Experiment II was one-way factorial design with one replicate per combination, conducted to evaluate the effect of Cu loading (10, 20, 30, and 40 wt% relative to KL weight) on the formation of graphene layer number and particle size of FG-nZVCu. The target graphitization temperature was fixed at 1000 °C. The pre-graphitization sticky mixture and post-graphitization solids were labeled THF-KL/Cu-Y% and 1000-THF-KL/Cu-Y%, respectively, where Y denotes the Cu loading (10%, 20%, 30%, and 40%).

Experiment III was a one-way factorial design with one replicate per combination, conducted to evaluate the effect of temperature (600, 700, 800, 900, 1000, and 1100 °C) on the formation of FG-nZVCu in graphitized solids labeled T-THF-KL/Cu-20%, where T denotes the graphitization temperature (600, 700, 800, 900, 1000, and 1100 °C).

2.2.2. KL-Cu mixture preparation. In experiment I, an X-KL sticky mixture was first prepared by dispersing 100 g of KL in 150 mL of one of five solvents. A copper nitrate solution with a fixed Cu loading of 20 wt% was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DI water until completely dissolved. The copper nitrate solution was then added to one of five X-KL sticky mixtures in separate 2000 mL beakers, followed by stirring on a hot plate at 80 °C for 1 h, which evaporated most of the solvent. The X-KL/Cu-20% mixtures then were dried to evaporate the rest of the solution in a vacuum oven at 70 °C overnight.

In experiment II, a THF-KL sticky mixture was prepared by dispersing 100 g of KL in 150 mL of THF. A copper nitrate solution with one of four target Cu loadings was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in DI water until completely dissolved. The copper nitrate solution was then added to each of the four THF-KL mixtures in separate 2000 mL beakers, followed by stirring on a hot plate at 80 °C for 1 h. The THF-KL/Cu-Y% mixtures then were dried in a vacuum oven at 70 °C overnight before catalytic graphitization.

In experiment III, six pre-graphitization T-THF-KL/Cu-20% mixtures were prepared using the procedure described in experiment II.

Table 1 Properties of solvents for dissolving KL,⁴⁶ including Hansen solubility parameter values^{47–50} ^a

Solvents	Molecular weight (g mol ⁻¹)	Dielectric constant	δ_{D} (MPa ^{1/2})	δ_{P}	δ_{H}	$\delta_{\text{P}} + \delta_{\text{H}}$
DI water	18	~80	15.5	16.0	42.4	58.4
Ethanol	46	~24	15.8	8.8	19.4	28.2
THF	72	~7.6	16.8	5.7	8	13.7
Acetone	58	~20.7	15.5	10.4	7	17.4
Ethyl acetate	88	~6	15.8	5.3	7.2	12.5

^a Note: δ_{D} , δ_{P} , and δ_{H} represent the dispersion force, polar interaction, and hydrogen-bonding components of the Hansen solubility parameters, respectively. $\delta_{\text{P}} + \delta_{\text{H}}$ represents the combined contribution from polar and hydrogen-bonding interactions. The corresponding chemical structures of these solvents are provided in Table S1.

2.2.3. Catalytic graphitization. Fig. 3 illustrates the major steps of the copper-assisted thermal catalytic graphitization using a vertical tube furnace setup. For each graphitization run, 15 g of oven-dry X-KL/Cu-20%, THF-KL/Cu-Y%, or T-THF-KL/Cu-20% mixtures were packed into a muffle oven with an inert atmosphere. The temperature was ramped to 300 °C at 10 °C min⁻¹ and held for 30 minutes to achieve stabilization. After cooling, the solids were milled at 300 rpm for 15 minutes per cycle, for a total of six cycles, to reduce particle size. The resulting solids were separately packed into a metal tubular reactor for graphitization. Argon gas was introduced at a flow rate of 50 mL min⁻¹ to maintain an inert atmosphere. The temperature was ramped to the target level at a constant heating rate of 10 °C min⁻¹ and held for 1 hour upon reaching the setpoint. After graphitization, the temperature was reduced to 400 °C, followed by steam oxidation at 400 °C for 1 hour. The furnace was then allowed to cool naturally to room temperature. The graphitized solids were collected, weighed, and labeled accordingly.

2.2.4. Characterization. Fourier-transform infrared spectroscopy (FTIR) spectra were obtained to determine structural changes in the KL/Cu mixture using a PerkinElmer attenuated total reflection (ATR) spectrometer (PerkinElmer, Waltham, MA, USA) with a resolution of 4 cm⁻¹ over 128 scans, covering the range of 450 to 4000 cm⁻¹. Scanning Electron Microscopy (SEM) analysis was performed on the graphitized solids at an accelerating voltage of 5 kV and a working distance (WD) of 10 mm. Prior to imaging, the solids were coated with a 15 nm platinum (Pt) layer and examined. High-resolution Transmission Electron Microscopy (HRTEM) was performed on the graphitized solids using a JEOL JEM-100CX II (JEOL, Peabody, MA). The physical size distribution of the copper-based particles was subsequently determined from HRTEM images using ImageJ. Prior to analysis, the solids were sonicated in an aqueous solution for 1 minute and then transferred onto carbon-coated copper grids. X-ray diffraction (XRD) analysis was conducted on the graphitized solids using an Ultima3 diffractometer (Rigaku, Japan) with Cu K α radiation ($\lambda = 1.5406$ Å). Diffraction patterns were recorded over a 2θ range of 15–80° in step-scan mode, with a step size of 0.02° and a counting time of

1 s per step. The refinement results were obtained using the whole-pattern fitting (WPF) function in Jade 2010 software using ICDD's PDF-4 database (Materials Data, Inc. (MDI)), and are therefore interpreted as semi-quantitative indicators of phase-evolution trends. The grain sizes (nm) of Cu, CuO, and Cu₂O were calculated using the Scherrer formula below for comparative analysis among samples, and the resulting values were plotted as a function of Cu loading:

$$L = \frac{0.9\lambda}{B_M \cos \theta} \quad (1)$$

where L is the apparent crystallite size, λ represents the wavelength of the CuK α radiation (1.5406 Å), B_M is the full width at half maximum (FWHM) of the fitted peak, and θ is the peak centroid of the fitted peak.

3. Results and discussion

3.1. Precursor design: effects of solvent and Cu loading

3.1.1. Solvent type effects. Based on the Hansen solubility parameters, the solvents exhibit comparable dispersive forces δ_D but differ significantly in their δ_P and δ_H (Table 1). Because KL contains both hydrophobic aromatic regions and oxygen-containing polar functional groups, the solvent effect should be interpreted based on the combined contribution of the three Hansen solubility components rather than total solubility alone. The dispersion component (δ_D) is mainly associated with interactions involving the aromatic carbon structure of KL, whereas the polar component (δ_P) and hydrogen-bonding component (δ_H) are more closely related to interactions with oxygen-containing groups, including hydroxyl, methoxy, carbonyl, and carboxyl groups.

The FTIR spectra (Fig. 4a and b) of the X-KL/Cu-20% mixtures and raw KL show that the peaks in the 1300–1000 cm⁻¹ region, attributed to C–O stretching vibrations of phenolic, alcoholic, and ether groups in KL, are reduced after Cu incorporation. The reduction in peak intensity was most pronounced for bands associated with phenolic C–O stretching, likely due to their electron-rich environment, followed by those associated with alcoholic and ether groups. Across the five tested solvents, the extent of intensity reduction follows the order A-KL/Cu-20% > THF-KL/Cu-20% > EA-KL/Cu-20% > E-KL/Cu-20% > W-KL/Cu-20%. This suggests that DI water and ethanol are less effective at promoting interactions between KL and Cu²⁺ ions, as their high polarity and strong hydrogen-bonding capacity limit compatibility with the hydrophobic aromatic regions of KL. One explanation is that these solvents have relatively high hydrogen-bonding parameters ($\delta_H = 42.4$ and 19.4 MPa^{1/2}, respectively), favoring their interactions with the hydrophilic functional groups of KL (e.g., –OH and CO) but limiting their compatibility with the hydrophobic aromatic regions that constitute a large portion of the KL structure. In contrast, the peak at ~2935 cm⁻¹ (Fig. 4a), corresponding to aliphatic C–H stretching of methyl groups on side chains in all five X-KL/Cu-20% mixtures, shows only minor change relative to raw KL (Fig. 4b). This indicates that coordination with Cu ions occurs primarily at

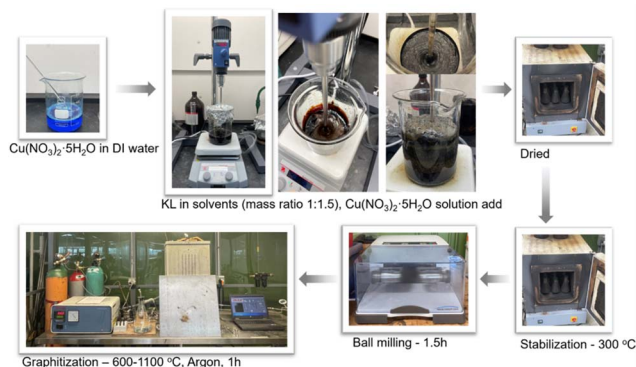


Fig. 3 Schematic representation of the major steps in preparing and synthesizing KL-derived graphene.

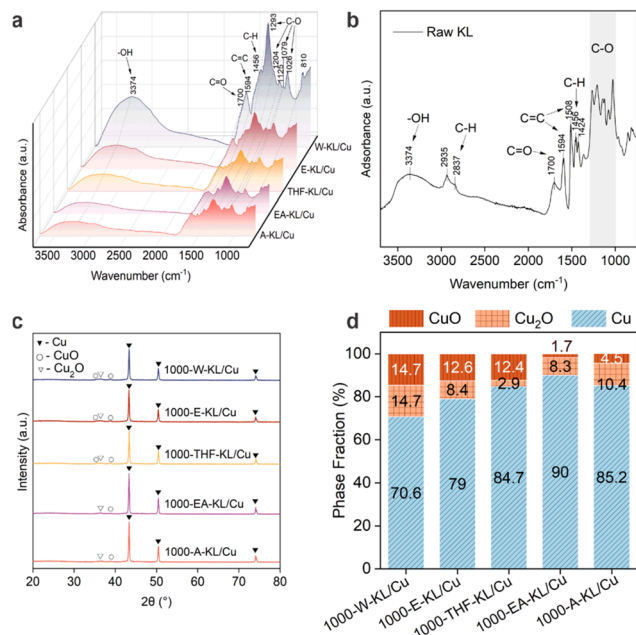
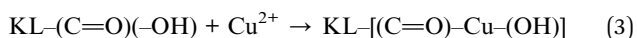
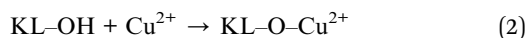


Fig. 4 FTIR patterns of (a) oven-dry X-KL/Cu-20% mixtures in the range of 3600–800 cm⁻¹, indicating solvent effects and (b) raw KL; (c) XRD spectra, and (d) fractions of Cu, CuO, and Cu₂O in 1000-X-KL/Cu-20%.

oxygen-containing functional groups such as C=O and –OH rather than aliphatic groups in KL.

All these results suggest the formation of coordination interactions between oxygen-functional groups in KL and Cu²⁺ ions. Both the coordination interaction (2) between phenolic hydroxyl groups in KL and Cu²⁺ and the chelation reaction (3), in which adjacent carbonyl and hydroxyl groups cooperatively bind Cu²⁺, contribute to stabilizing Cu²⁺ within the KL matrix:



XRD analysis of the 1000-X-KL/Cu-20% solids (Fig. 4c) revealed strong diffraction peaks corresponding to metallic Cu (which is the technical term used in XRD for nZVCu formed in this study) which appeared at 40–45° (111), 50–55° (200), and 70–75° (220). The relative peak intensities, ranked by solvent, follow the order 1000-EA-KL/Cu-20% > 1000-A-KL/Cu-20% > 1000-THF-KL/Cu-20% > 1000-E-KL/Cu-20% > 1000-W-KL/Cu-20%. This trend is consistent with the XRD-derived phase evolution shown in Fig. 4d, where the refined metallic Cu fractions decreased from 90 to 70.6%. These results indicate that Cu ions were more extensively reduced to nZVCu in three solvents—ethyl acetate, acetone, and THF—than in DI water and ethanol, following the order ethyl acetate > acetone > THF. This order differs from that observed for the C–O stretching intensity, where acetone precedes ethyl acetate. Nevertheless, ethyl acetate, acetone, and THF consistently fall within the same group, ranking above DI water and ethanol in both cases.

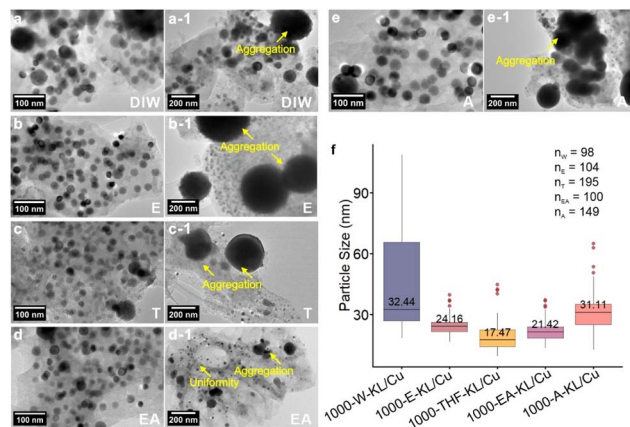


Fig. 5 TEM images showing copper-based particle size distribution of uniformity (a)–(e) and aggregation behavior (a1)–(e1) in 1000-X-KL/Cu-20% mixtures, together with the corresponding particle size distributions (f).

The physical size distributions (Fig. 5f) of the copper-based particles formed in the five solvents were analyzed using HRTEM (Fig. 5a–e), including possible individual nZVCu, CuO and Cu₂O particles, as well as particles composed of different combinations of these three Cu species. The results showed median particle sizes within the nanoscale range, following the order 32.4 nm (W) > 31.1 nm (A) > 24.2 nm (E) > 21.9 nm (EA) > 17.7 nm (THF). This reduction in particle size suggests that THF and ethyl acetate solvents promote better dispersion of Cu ions in the KL matrix compared to the other three solvents. This improved dispersion in THF- and ethyl acetate-dissolved KL can be attributed to their combined polarity and hydrogen-bonding characteristics (Table 1), as reflected by their relatively low ($\delta_P + \delta_H$) values of 13.7 and 12.5 MPa^{1/2}, respectively. This is also because KL is structurally heterogeneous and contains both polar fractions and less polar aromatic fractions. Ethyl acetate and THF have intermediate polarity and moderate hydrogen-bonding capacity, allowing them to interact with polar groups such as hydroxyl and carbonyl functionalities while also maintaining affinity for the aromatic backbone through dispersive interactions. Therefore, these solvents of lower ($\delta_P + \delta_H$) values can penetrate different KL regions more uniformly, leading to better overall dissolution and a more uniform distribution of Cu²⁺ ions within the KL matrix, promoting the subsequent reduction of Cu²⁺ to nZVCu during thermal treatment. However, acetone, which has a relatively high δ_P (10.4 MPa^{1/2}), together with a higher dielectric constant (~20.7) and smaller molecular weight (58 g mol⁻¹) than THF and ethyl acetate, may facilitate greater Cu mobility during graphitization, thereby increasing the possibility of particle migration and aggregation, resulting in relatively larger particle sizes in 1000-A-KL/Cu (Fig. 5).

In addition, the smallest median particle size and the narrowest size distribution of copper-based particles formed in the 1000-THF-KL/Cu-20% solid can be attributed to the balanced solvent properties of THF. Specifically, THF contains an ether oxygen that acts as a hydrogen-bond acceptor³⁷ ($\delta_H = 8$), enabling interactions within hydroxyl groups in KL. In addition,

THF has moderate polarity ($\delta_p = 5.7$) and a cyclic ether structure. Although THF is not aromatic, its compact ring structure allows it to exhibit better compatibility with the aromatic regions of KL. These characteristics enable stronger interactions between THF molecules and KL chains, thereby improving lignin dissolution and promoting a more homogeneous distribution of Cu ions throughout the KL matrix. Although the relative ranking of ethyl acetate, acetone, and THF varies across FTIR, XRD, and particle size analyses, they consistently fall within the same performance group, all outperforming DI water and ethanol.

The solvent is used to improve KL dissolution and to facilitate the penetration and distribution of Cu^{2+} within the KL matrix. After drying, the solvent is largely removed before graphitization. THF improves KL dissolution and Cu^{2+} dispersion, leading to more uniformly distributed nZVCu particles during thermal treatment, increasing the amount of local contact between KL and Cu, therefore helping the formation of localized few-layer graphitic regions.

3.1.2. Copper loading effects. SEM images (Fig. 6a) reveal the fluffy morphology of the 1000-THF-KL/Cu-Y% solids, along with HRTEM images showing the corresponding copper-based particle size distributions at different Cu loadings. At 20% Cu loading, the copper-based particles exhibit the most uniform distribution, with the smallest mean particle size of 27.3 nm and a coefficient of variation (COV) of 19.19%. The copper-based particles become larger and more irregularly dispersed at 30% Cu loading, with the mean particle size increasing to 89.27 nm (COV = 44.74%). At 40% Cu loading, the mean particle size further increases to 142.21 nm (COV = 49.65%), indicating greater size variability and a higher degree of clustering.

The XRD patterns and their refinement results of the 1000-THF-KL/Cu-Y% solids reveal that the proportion of the refined metallic Cu (nZVCu) phase increases from 72.6% at 10% Cu loading to 93.3% at 40% Cu loading (Fig. 6b–c). In contrast, the proportion of refined tenorite (CuO) decreases from 25.2% to 1.6% over the same loading range. The proportion of refined cuprite (Cu_2O), an intermediate phase, initially increases from 2.2% at 10% Cu loading to 6.7% at 30% Cu loading, and then slightly decreases at 40% Cu loading. These trends suggest that increasing Cu loading promoted the production of higher nZVCu content.

Fig. 6d presents the grain sizes (*i.e.*, XRD-derived crystallite sizes) of the crystalline phases of nZVCu, CuO , and Cu_2O , calculated from their corresponding XRD peaks using the Scherrer equation, as a function of Cu loading. The grain sizes of nZVCu and Cu_2O remain relatively stable across the Cu loading range, varying only slightly between 30 and 35 nm. However, the grain size of CuO shows a slight decrease from 10 to 20% Cu loading, followed by a significant increase at 40% Cu loading, indicative of aggregation. This behavior is attributed to the increased grain sizes of CuO at higher loadings, which promotes incomplete reduction due to mass and heat transfer limitation, as well as oxidation during steam oxidation treatment. Consequently, the larger particles observed in HRTEM at higher loadings are primarily assigned to CuO .

3.2. Temperature effects

The XRD patterns (Fig. 7a) of T-THF-KL/Cu-20% solids show that all three nZVCu peaks increased as the temperature increased from 600 to 1100 °C. No additional Cu-containing crystalline phases associated with carbon dissolution were detected by XRD. Together with the low carbon solubility of Cu, the above results suggest that the formation of few-layer

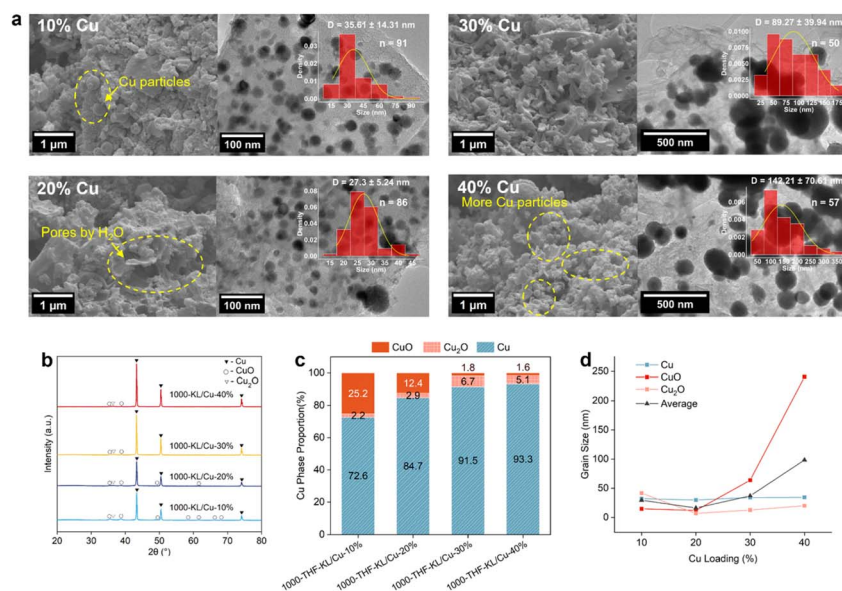


Fig. 6 (a) SEM and HRTEM images and the corresponding nZVCu particle size distribution of 1000-THF-KL/Cu-Y% solids; (b) XRD spectra and (c) phase distribution of nZVCu, Cu_2O , and CuO , and (d) the relationship between Cu loading and grain size for nZVCu, Cu_2O , and CuO in 1000-THF-KL/Cu-Y%.

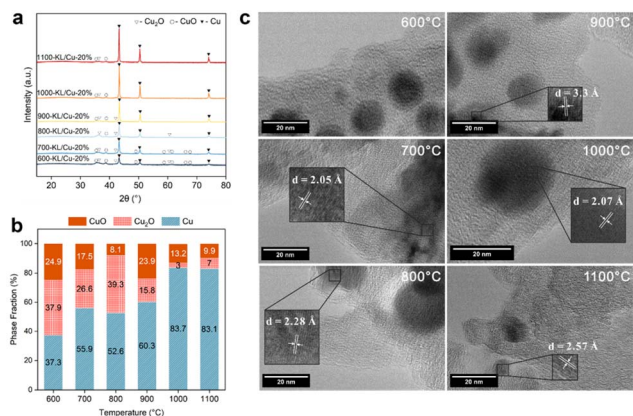


Fig. 7 (a) XRD patterns of T-THF-KL/Cu-20% solids and (b) phase fraction variations of nZVCu, CuO, and Cu₂O; (c) TEM images of T-KL/Cu-20% solids, showing lattice spacing variations at different graphitization temperatures from 600 to 1100 °C.

graphene adjacent to nZVCu is not the dissolution-precipitation mechanism. Fig. 7b shows that as the temperature increased from 600 to 1100 °C, the increases in the nZVCu fraction from 37.3 to 83.1% could be attributed to the continuing reduction behavior of the CuO phase to nZVCu. Conversely, the CuO fraction decreased from 600 to 800 °C, and then briefly increased at 900 °C, before dropping at 1100 °C. The Cu₂O phase exhibited a similar non-linear trend, with an initial decrease from 600 to 700 °C, followed by an increase at 800 °C and a gradual reduction at higher temperatures to 3–7%. These phase changes indicate that the reduction of CuO and Cu₂O to nZVCu was favored at higher temperatures because of the thermal decomposition of lignin and the reduction of copper oxide phases.

Fig. 7c shows that the measured *d*-spacing of 2.05 Å (0.205 nm) in 700-THF-KL/Cu-20% closely matches the characteristic interplanar spacing of metallic Cu (111). This observation is consistent with the phase fraction analysis shown in Fig. 7b, confirming that nZVCu had already formed within the carbon matrix at lower temperatures of 600 and 700 °C. At higher temperatures (800–1100 °C), the mixed lattice fringes exhibit the *d*-spacings of 2.07 Å (0.207 nm), 2.28 Å (0.228 nm), 2.57 Å (0.257 nm), and 3.3 Å (0.33 nm). These values correspond closely to metallic Cu (0.208 nm for the (111) plane), CuO (0.232 nm for the (111) and (002) planes; 0.252 nm for the (110) plane), and Cu₂O (0.301 nm for the (111) plane), suggesting the coexistence of metallic Cu and copper oxide phases. At 600 and 700 °C (Fig. 8a and b), the carbon matrix exhibits a highly disordered morphology with diffuse contrast, which means only amorphous carbon was observed in the KL matrix. As few clear and well-defined layers, turbostratic graphene structures were first clearly observed beginning at 800 °C adjacent to nZVCu (Fig. 8c), showing small pieces and domains of 3 to 4 layers (Fig. 8g). This suggests that the graphene formation in the KL-Cu system does not follow a CVD mechanism because there are no continuous volatile carbon sources, such as CH₄ or diffusible carbon-containing volatile fragments generated during heating of KL at 800 °C,³⁶ that could serve as continuous carbon

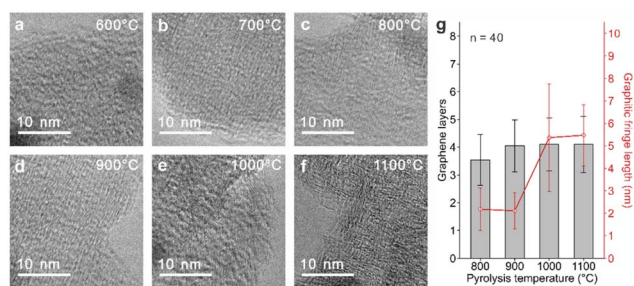


Fig. 8 (a)–(f) HRTEM images of T-KL/Cu-20% solids show graphitic structures and (g) comparison of graphene layers and graphitic fringe lengths at different graphitization temperatures from 600 to 1100 °C.

precursors for the CVD growth of graphene layers. As the temperature increases from 800 to 1100 °C, the degree of graphitization was enhanced, and the graphene-like domains became larger and more clearly defined. The graphitic fringe length increased from approximately 2 nm at 800–900 °C to about 4–5 nm at 1000–1100 °C. This improvement was associated with the increased formation of nZVCu, which served as an active catalyst.

In addition, nZVCus was already embedded in the KL matrix at 600 and 700 °C (Fig. 7c), but no clear graphitic edges could be observed in Fig. 8a and b. This indicates that nZVCu formation is a necessary catalytic condition but is not sufficient by itself for the development of graphene-like structures. Temperature governs both catalyst evolution and carbon ring surface rearrangement, making it the dominant factor controlling the development and observable clarity of graphene-like structures in the KL-Cu system.

3.3. Proposed formation mechanism and its implications

Clear and well-defined few-layer and turbostratic graphene structures were observed from 800 °C. This temperature is important because previous gas-phase analysis of KL pyrolysis showed no continuous or sufficient gaseous carbon sources, such as CH₄ or carbon-containing volatile fragments generated during heating of KL at 800 °C to support CVD-type graphene growth.³⁶ Although some previous studies have reported graphene formation through low-temperature routes in the range of 300–550 °C,^{8–10,51} systems generally used volatile, readily decomposable, or ring-containing carbon feedstocks that could continuously supply active carbon-containing species to the catalyst surface during CVD growth.

The present KL/Cu system in this study is different from these low-temperature CVD routes in several important aspects. First, the entire pyrolysis was conducted under an inert Ar atmosphere without introducing any external carbon source. Second, KL is a solid-state macromolecular aromatic-rich biomass precursor, rather than a volatile molecular feedstock that continuously supplies mobile carbon species. Third, H₂ is commonly used in low-temperature CVD routes to reduce and clean the pre-existing set-up metal catalyst surface and suppress residual oxidizing species. In our study, Ar was used as the atmosphere, and nZVCu was formed *in situ* through the

Table 2 Comparison of reported graphene formation routes using different carbon precursors and metal catalysts with the present KL/Cu system

Feedstock	Precursor state	Catalyst	Growth environment and temperature	Graphene properties	Ref.
PMMA, polystyrene, and benzene	Solid/liquid carbon sources, readily decomposed at ~140–260 °C to supply carbon-containing species	Cu foil	H ₂ ; begin as low as 300 °C for benzene	Monolayer graphene films	Li <i>et al.</i> ⁸
Benzene PAHs	Liquid aromatic precursor Solid aromatic molecular precursors, sublimed and decomposed on the Cu surface under high vacuum	Cu foil Cu foil	Ar/H ₂ ; ~300 °C Ar/H ₂ ; 550–1000 °C	Monolayer graphene films Large-area graphene sheets	Jang <i>et al.</i> ⁹ Wan <i>et al.</i> ¹⁰
Camphor	Readily decomposable at 200 °C to supply mobile carbon species	Ni foam	550 °C	3D graphene network; 6–16 layers	Zheng <i>et al.</i> ⁵¹
Kraft lignin	Solid-state macromolecular aromatic-rich biomass precursor	nZVCu	Ar; was observed to begin at ~800 °C	Turbostratic, 3–5 layers, fringe length of 4–5 nm	This study

reduction of Cu species during pyrolysis. Therefore, the catalyst evolution occurred simultaneously with the carbon rearrangement, rather than through graphene growth on an external metal catalyst surface.

In addition, the morphology of resulting graphitic structures further distinguishes the present system from reported lower-temperature CVD routes. The HRTEM observations show localized few-layer turbostratic graphene regions formed adjacent to nZVCu particles, rather than continuous flat graphene layers typically obtained from CVD routes. Therefore, it is unlikely that the formation of few-layer graphene structures in the KL–Cu system follows the CVD mechanism, because carbon species such as CH₄ are required as carbon precursors for the CVD growth of graphene layers adjacent to the Cu catalyst. Instead, the formation of few-layer turbostratic graphene structures in this study is proposed to proceed mainly through a mechanism termed Cu-assisted aromatic carbon ring surface rearrangement. A comparison of reported graphene formation routes using different carbon precursors with the present KL/Cu system is provided in Table 2.

It should also be noted that the present KL/Cu system differs from other non-conventional graphene synthesis strategies, such as ion-implantation-assisted growth.⁵² Ion implantation can directly tune graphene thickness by controlling the implanted carbon dose, making it suitable for layer-controlled graphene films on substrates. However, it requires specialized equipment, controlled metal substrates. In contrast, the KL/Cu method in this study uses kraft lignin as a renewable macromolecular aromatic carbon precursor and relies on Cu²⁺ dispersion followed by tube furnace *in situ* reduction and graphitization. This method is not intended to achieve atomic-level layer-number control or high-quality graphene films. Instead, it provides a simple and potentially scalable biomass-derived route for producing localized few-layer turbostratic graphene with expected stacking, edge defects, and disorder associated with lignin-derived carbon ring arrangement.

This proposed mechanism is supported by a meta-analysis study,⁵³ which validated a catalyst surface-assisted rearrangement mechanism of graphitic carbon formation from solid carbon precursors, including resorcinol–formaldehyde forms, sawdust, saccharides, and related materials. *In situ* TEM observations⁵³ showed that graphene layers can form adjacent to metal nanoparticles at approximately 500 °C, while XRD results indicated the development of graphitic ordering at

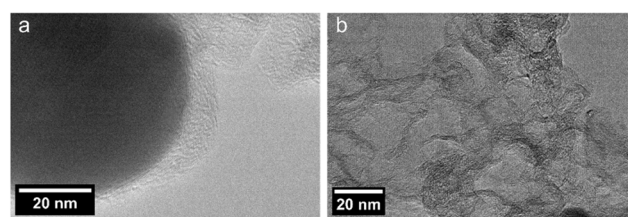


Fig. 9 HRTEM images of three- to four-layer turbostratic graphene structures: (a) a magnified view of the surface of nZVCu, and (b) overlapped and wrinkled sheets adjacent to the nZVCu particles.

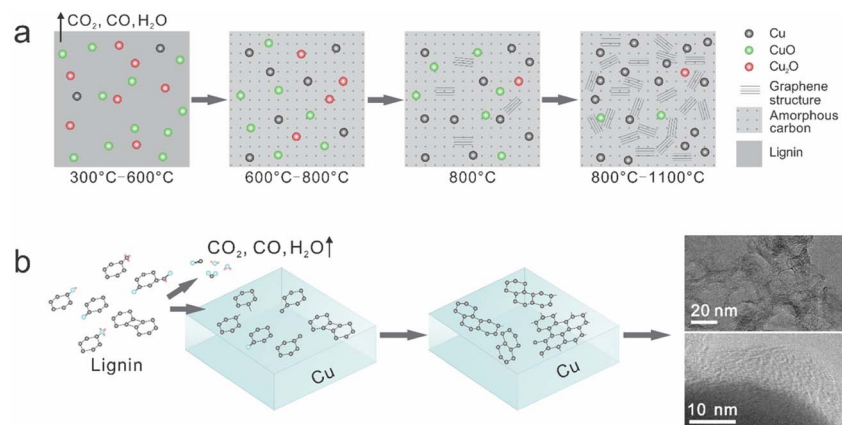


Fig. 10 Conceptual diagram illustrating (a) the temperature effect on copper phase evolution, the carbon graphitization process, and (b) the Cu-assisted aromatic carbon ring surface rearrangement mechanism in the formation of few-layer turbostratic graphene structures using KL as a solid-state carbon source.

around 700 °C when solid carbon precursors were treated with Fe, Ni, or Co catalysts. These findings are consistent with our TEM results, in which graphitization was observed starting at 800 °C. Collectively, these observations suggest that graphitic layers can develop adjacent to metal nanoparticles rather than through the two conventional mechanisms of CVD or dissolution–precipitation.

KL has abundant aromatic ring structures, which provide potential as solid-state carbon precursors for synthesizing few-layer graphene through Cu-assisted aromatic carbon ring surface rearrangement and localized graphitization. In this process, Cu²⁺ is first dispersed within the KL matrix through interactions with oxygen-containing functional groups, followed by reduction to nZVCu during high-temperature treatment. Meanwhile, KL undergoes decomposition and deoxygenation, generating lignin-derived aromatic carbon fragments adjacent to nZVCu. The low carbon solubility of Cu may limit excessive aromatic carbon activation, while nZVCu as catalyst particles can guide the rearrangement of carbon layers to form few-layer, turbostratic, and curved graphene-like structures with 3–5 layers adjacent to nZVCu particles (FG-nZVCu) (Fig. 9). This structure is attributed to the combination effects of solvent-assisted Cu dispersion, the low carbon solubility of Cu, nanoscaled catalyst geometry, Cu loading, and temperature-driven carbon ring rearrangement.

A conceptual diagram (Fig. 10) illustrates the effect of temperature on copper phase evolution and the carbon graphitization process evaluated in this study when KL is used as a solid-state carbon source. Initially, at temperatures below 300 °C, Cu²⁺ ions coordinate with lignin functional groups, while lignin partially decomposes and releases volatile species such as CO₂, CO, CH₄, and H₂. As the temperature increases from 600 to 800 °C, copper species such as CuO and Cu₂O are partially reduced to uniformly dispersed nZVCu particles within the carbon matrix, while lignin gradually decomposes into smaller aromatic carbon fragments. Above 800 °C, CuO and Cu₂O are further reduced to nZVCu particles, which catalyze the deoxygenation and dehydrogenation of lignin-derived aromatic carbon fragments. These fragments rearrange adjacent to the

nZVCu particles, forming graphene-like carbon structures that evolve into three- to four-layered turbostratic graphene at higher temperatures.

4. Conclusions

A staged Cu-assisted aromatic carbon ring surface rearrangement mechanism for the formation of few-layer turbostratic graphene structures using KL as a solid-state carbon source was proposed. This route provides a biomass-derived strategy, distinct from conventional CVD, dissolution–precipitation, and substrate-based thickness-control methods.

This process begins with solvent-controlled KL dissolution and Cu²⁺ dispersion, where moderately polar solvents of THF enable the most uniform dispersion of Cu²⁺ into the KL matrix through interactions with oxygen-containing functional groups among the five solvents evaluated. During thermal treatment, copper oxides (CuO and Cu₂O) are first formed and subsequently reduced to nZVCu particles, while lignin-derived aromatic carbon fragments interact with the evolving nZVCu particles. At 600 °C, both nZVCu and copper oxide phases are present, and with increasing temperature, the proportion of metallic Cu increases. Cu²⁺ ions disperse effectively in the KL matrix using THF, resulting in uniformly distributed nZVCu particle size with an average size of 27.3 nm at a loading of 20% after thermal catalytic graphitization. These well-dispersed nZVCu particles promote the Cu-assisted aromatic carbon ring surface rearrangement of aromatic carbon fragments decomposed from KL, leading to the formation of few-layer, turbostratic graphene-like structures. The formation of graphene-like structures and sheets adjacent to Cu-based particles is observed to begin at approximately 800 °C, and the degree of graphitization increases as the temperature increases to 1100 °C.

Author contributions

SG: conceptualization, investigation, methodology, data curation, formal analysis, visualization, writing – original draft,

writing – review and editing. QY: conceptualization, investigation, methodology, funding acquisition, supervision. YK: funding acquisition, resources, supervision, scientific discussion. TM: resources, supervision, scientific discussion. JTS: resources, supervision, scientific discussion. ZC: resources, funding acquisition, supervision, scientific discussion. JZ: conceptualization, methodology, investigation, formal analysis, funding acquisition, project administration, supervision, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the findings of this study are included in the article and its supplementary information (SI). Additional raw data are available from the corresponding author upon reasonable request.

Supplementary information: solvent properties and Hansen solubility parameters (Table S1); quantitative phase fractions of Cu, Cu₂O, and CuO under different solvent, Cu loading, and graphitization temperature (Tables S2–S4); and the calculation of particle size distributions (Table S5). See DOI: <https://doi.org/10.1039/d6ta04482d>.

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