

Controlled Synthesis of Hybrid Carbon Allotropes with Tunable Size and Photoluminescent Properties

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Abstract

We report a new class of carbon nanostructures consisting of hemispherical carbon matrices with mixed sp^1 and sp^2 bonding characteristics. These carbon matrices form at elevated temperature through the transformation of organic molecules adsorbed on the surface of colloidal metal nanoparticles, where the metallic core acts simultaneously as a catalyst and a structural template during growth. This synthesis route provides a high degree of control over the morphology of the carbon matrices, as thermally driven Ostwald ripening of the metal nanoparticles enables precise tuning of their diameter. Furthermore, the tendency of the nanoparticles to self-assemble into highly ordered superlattices results in the formation of regular hexagonal arrays of carbon matrices on a variety of substrates. Structural characterisation by aberration-corrected electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and electron energy-loss spectroscopy reveals the coexistence of sp^1 and sp^2 carbon, with residual nitrogen localised at the interface between the carbon matrices and the nitrogen-containing substrate. Spatially resolved EELS reveals that the nitrogen signal is concentrated at these interfaces, while XPS identifies the associated localised N 1s chemical-state contribution, consistent with localised C-N species rather than homogeneous nitrogen incorporation throughout the carbon matrices. Low-loss electron energy-loss mapping demonstrates spatially localised electronic excitations, while quantitative electron energy-loss near-edge structure analysis reveals measurable modifications of the electronic structure associated with the nitrogen-containing interface. Significantly, the carbon matrices exhibit photoluminescence spanning the visible and near-infrared spectral regions, with the emission wavelength showing a dependence on the dimension of the sp^1 -rich carbon domains. The combined structural, vibrational and electronic evidence is consistent with localised one-dimensional sp^1 -rich carbon motifs embedded within a continuous sp^2 carbon framework. Importantly, the synthesis is not restricted to the transmission electron microscope environment but can also be performed in evacuated sealed ampoules under controlled conditions, providing a route toward large-scale preparation of these nanostructures for future fundamental studies and technological applications. These findings establish a versatile platform for tailoring the structural, electronic and optical properties of carbon-based nanomaterials.

Introduction

Carbon—the most versatile element in the Periodic Table—is capable of forming a remarkable variety of stable structures, including diamond, graphite, fullerenes, carbon nanotubes, carbon onions and amorphous carbon, which collectively encompass carbon atoms with sp^1 , sp^2 and sp^3 hybridisation in different proportions [1–7]. For instance, carbon nanotubes and graphene consist predominantly of sp^2 -hybridised carbon, with local deviation from ideal sp^2 bonding occurring at defects, edges and chemically functionalised sites [8–11]. Conversely, nanodiamonds, which are primarily composed of sp^3 -hybridised carbon, often contain sp^2 -hybridised carbon on their surfaces [12]. Furthermore, owing to the pronounced nanoscale curvature of certain carbon nanostructures, deviations from ideal hybridisation can occur, as exemplified by C_{60} fullerene, where curvature induces a non-planar carbon-bonding configuration [13].

Because the electronic, optical and chemical properties of carbon nanomaterials are strongly dependent on the bonding configuration of the carbon atoms, the development of synthetic strategies capable of producing carbon nanostructures with controlled hybridisation remains an important objective in carbon science. Significant advances have been achieved in the synthesis of high-quality graphene, carbon nanotubes and nanodiamonds; however, despite considerable effort, the controlled preparation of sp^1 -hybridised carbon, remains a major challenge. Linear chains of sp^1 carbon atoms have been predicted to represent the ultimate one-dimensional carbon nanowire, exhibiting exceptional mechanical strength [14], high electrical conductivity [15–17], and tunable electronic properties [15–17]. Isolated carbon chains have been shown to be stable in vacuum inside the column of a transmission electron microscope (TEM) or encapsulated within carbon nanotubes [18–20]. However, in bulk, atomic carbon chains are expected to be highly unstable because neighbouring chains readily undergo cross-linking [21], making the controlled synthesis and stabilisation of extended carbyne structures extremely challenging.

One possible strategy to improve the stability of linear carbon chains is through periodic structural modulation. Theoretical studies suggest that linear sp^1 carbon fragments separated by periodic sp^2 -bonded kinks reduce the total energy of the system [15, 21–22]. Beyond ideal graphyne structures, theoretical studies also suggest that sp^1 carbon can be incorporated as localised one-dimensional motifs embedded within an sp^2 carbon framework. Such mixed sp^1/sp^2 configurations preserve the conjugated carbon network while introducing localised modifications of the electronic structure consistent with the structural model proposed in the present study. These embedded sp^1 -rich carbon domains provide a chemically plausible structural model for carbon nanostructures exhibiting mixed carbon hybridisation, without requiring the presence of extended free-standing linear carbon chains [23–26]. The coexistence of sp^1 - and sp^2 -hybridised carbon within a common carbon framework is expected to modify the electronic structure by combining the localised electronic states associated with sp^1 -rich carbon domains with the extended π -conjugated network of sp^2 carbon. Such mixed-hybridisation architectures may therefore provide new opportunities for tailoring the structural, electronic, vibrational and optoelectronic properties of carbon nanomaterials.

Electron energy-loss spectroscopy has become one of the most powerful characterisation techniques for investigating the electronic structure and local bonding configuration of carbon nanomaterials. In particular, analysis of the carbon K-edge electron energy-loss near-edge structure enables identification of the π^* and σ states associated with different carbon hybridisation environments, while low-loss electron energy-loss spectroscopy provides complementary information on low-energy electronic excitations, dielectric response and collective electronic phenomena in carbon-based materials. These complementary capabilities make electron energy-loss spectroscopy particularly well suited for correlating the local atomic structure with the electronic properties of complex carbon nanostructures [27–29].

In this study, we report the synthesis and structural evolution of hemispherical carbon nanostructures, hereafter referred to as carbon matrices, which form through the thermally induced transformation of

organic molecules adsorbed on colloidal metal nanoparticles. Using a combination of aberration-corrected electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and electron energy-loss spectroscopy (EELS), we examine their morphology, local bonding configuration, electronic structure and optical properties. Particular attention is devoted to investigating the coexistence of localised one-dimensional sp^1 -rich carbon motifs embedded within an sp^2 carbon framework, together with the structural, electronic and optical characteristics associated with residual nitrogen at the carbon-substrate interfaces. Within this framework, we propose a structurally consistent model in which localised one-dimensional sp^1 -rich carbon domains are incorporated into an sp^2 carbon network, providing a chemically plausible interpretation of the experimental observations while remaining consistent with the current level of structural evidence. Finally, we discuss the implications of the proposed growth mechanism and demonstrate that the formation of these carbon matrices is not restricted to the transmission electron microscope environment, highlighting the feasibility of synthesizing these carbon matrices under controlled vacuum conditions outside the transmission electron microscope.

Results

Few-layer hexagonal boron nitride (FLBN) sheets, with lateral dimensions of 50–200 nm and thickness ranging from one to ten layers, were deposited onto gold or copper TEM finder grids and subsequently annealed in air at 500°C to remove adventitious carbon (Fig. 1a; experimental details are provided in the Methods section). Raman spectroscopy of the cleaned FLBN sheets exhibited a single band at 1363 cm^{-1} , characteristic of the E_{2g} vibrational mode of hexagonal boron nitride (h-BN) (Supplementary Fig. S1b) [27].

Silver nanoparticles (AgNPs), with an average diameter of 7.3 ± 0.7 nm, were synthesised using a modified Kang and Kim method [30]. After coating with a self-assembled monolayer of dodecanethiol, the nanoparticles were deposited onto FLBN sheets supported on either gold TEM grids (CNC1) or copper TEM grids (CNC2). The samples were heated in situ under high vacuum (10^{-5} Pa) to 650°C using a dedicated TEM heating holder (Fig. 1a). Owing to the higher thermal conductivity of copper ($401 \text{ W m}^{-1} \text{ K}^{-1}$), the heating ramp was faster for CNC2 (120 s to reach 650°C) than for CNC1 supported on gold grids (160 s ; $318 \text{ W m}^{-1} \text{ K}^{-1}$). The faster heating rate of the copper-supported samples coincided with more pronounced Ostwald ripening of the silver nanoparticles during the early stages of carbonisation, resulting in the formation of larger carbon matrices in CNC2 than in CNC1.

TEM imaging clearly shows that the gradual disappearance of the AgNP cores during the heating process (Fig. 2a–f and Supplementary Videos 1 and 2), leaving behind carbon "casts" in the form of carbon matrices (CNC1, CNC2; Fig. 1c–d) arranged in a hexagonal array on the FLBN substrate (Fig. 2b–f). These in situ TEM observations provide direct evidence of the structural evolution occurring during heating (Fig. 2a–f and Supplementary Videos 1 and 2), whereas the proposed dehydrogenation and carbonisation mechanism, schematically illustrated in Fig. 1b, is inferred from the combined TEM, Raman, XPS and EELS analyses.

To verify that the formation of the carbon matrices was not induced by electron-beam irradiation, the experiments were repeated outside the TEM column. AgNPs deposited onto FLBN-supported TEM grids were sealed in evacuated glass ampoules and heated under high vacuum using the same thermal protocol employed during the in situ TEM experiments. Carbon matrices with comparable morphology were obtained, demonstrating that their formation is governed by the thermal treatment rather than electron-beam irradiation. Having established that electron-beam irradiation was not required, the synthesis was subsequently scaled up by heating AgNPs deposited on supporting substrates in sealed evacuated glass ampoules using the same thermal protocol (see Methods).

To further investigate the composition and atomic structure of the resulting carbon matrices, electron energy-loss spectroscopy (EELS) (Fig. 3a) and EDX (Fig. 3b and inset) were performed. These analyses indicate that the structures formed during the thermal transformation are predominantly composed of carbon, with only low residual sulfur content (1.2 wt%). Neither EELS nor EDX revealed a detectable oxygen signal in the carbon matrices, indicating that no appreciable oxygen concentration was detected within the detection limits of either technique.

Aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) images reveal a quasi-spherical to hemispherical morphology comprising approximately three to four carbon layers, which is particularly evident in carbon matrices observed in side view at the edges of the FLBN sheets (Supplementary Fig. S5a–d) or when supported on carbon nanofibres (Supplementary Fig. S4). This morphology is consistent with the proposed hollow carbon matrix model, including an open upper surface. Evidence supporting this structural model is provided by aberration-corrected scanning transmission electron microscopy (AC-STEM) images (Supplementary Fig. S5c) and TEM images showing carbon matrices containing partially removed silver cores (Supplementary Fig. S2).

To determine the bonding configuration and the electronic structure of the carbon matrices detailed STEM-EELS analyses were performed. In the high-energy region, the onset of the carbon K-edge is observed at approximately 284.5 eV, within the energy range reported for carbon materials containing significant sp^1 -rich bonding configurations and related one-dimensional carbon motifs [29] (Supplementary Fig. S7). The principal carbon K-edge feature is centred at approximately 292 eV (Figs. 3d–e; Supplementary S7 and S19–S24; Table 1) for carbon matrices grown on both FLBN sheets and carbon supports. A quantitative comparison of the carbon K-edge ELNES reveals measurable differences between carbon matrices grown on carbon supports and those grown on FLBN. The π^* and σ^* resonances shift from 284.50 and 292.10 eV to 284.70 and 292.50 eV, respectively, resulting in an increase of the $\pi^*-\sigma^*$ energy separation from 7.60 to 7.80 eV. The observed shift exceeds the experimental uncertainty, indicating a genuine difference in the electronic structures of the two carbon matrices.

A N-related signal is reproducibly observed in EELS spectra acquired from several carbon matrices grown on carbon nanofibres (CNF@CNC; Supplementary Fig. S7). The signal is localised preferentially at the CNF@CNC interfaces and is not detected throughout the interior of the carbon matrices

(Supplementary Fig. S7). For the FLBN-supported carbon matrices, a nitrogen signal is localised at the carbon-substrate interface and is independently confirmed by XPS (Supplementary Fig. S14), while EDX (Fig. 3b) confirms the elemental composition of the matrices. Because dodecanethiol contains no nitrogen, the observed N-related signal cannot originate from the carbon precursor. The spatial localization of the N signal at the carbon–substrate interface instead indicates that nitrogen is associated with the nitrogen-containing support, with no evidence for appreciable diffusion into the interior of the carbon matrices. We therefore interpret the observed nitrogen signal as a localised interfacial compositional feature rather than as evidence for bulk nitrogen doping of the carbon matrices.

The observed K-edge features can be compared with those reported for diamond (290 eV) and amorphous carbon (295 eV) (Supplementary Figs. S7 and S9). However, the broad shape of the carbon K-edge above 292 eV (Figs. 3e and Supplementary Figs. S7 and S9) differs from that of purely sp²-hybridised carbon and is consistent with the reports of carbon materials containing mixed sp¹/sp² bonding configurations [15, 31–33].

To further investigate the low-energy electronic excitations of the carbon matrices, low-loss STEM-EELS analysis was performed (Supplementary Fig. S6). The normalized spectra acquired from several independent regions exhibited good reproducibility, supporting the assignment of the measured low-loss electronic excitations to the carbon matrices rather than to the supporting substrate or electron- beam irradiation. Spatial intensity maps generated over the 0.9–1.1 eV, 5.0–5.4 eV and 7.3–8.3 eV energy-loss windows revealed distinct variations in the spatial distribution of the low-loss signal. The 0.9–1.1 eV excitation is predominantly localised in the central region of the carbon matrix (Supplementary Fig. S6), whereas the higher-energy excitations exhibit a broader distribution across the nanostructure. The surrounding vacuum showed negligible intensity, supporting the assignment of the measured electronic excitations to the carbon matrix rather than to the surrounding vacuum or the supporting substrate. To further assess the reproducibility of the low-loss EELS response, spectra were acquired from multiple independent sampling positions at both room temperature (RT) and after in situ heating to 360°C. Representative spectra obtained at room temperature are presented in Supplementary Figs. S25–S28, while the corresponding measurements acquired after thermal treatment are shown in Supplementary Figs. S29–S33. In all cases, the low-loss electronic excitations were reproducibly observed across independent sampling positions, confirming that the measured spectral features are intrinsic to the carbon matrices and remain preserved following thermal treatment. These observations further demonstrate the robustness of the electronic structure of the carbon matrices.

Further information was obtained from the low-loss region (0–40 eV), corresponding to both single-particle electronic excitations and collective (plasmon) excitations [15, 35]. The spectra exhibit an inter-band transition at approximately 5.2 eV, together with a broad $\pi + \sigma$ plasmon centred at 23.6 eV (Fig. 3c). This plasmon energy differs from those reported for graphitic carbon (27.0 eV), four-layer graphene (18.0 eV), amorphous carbon (20.3 eV) and diamond (34.0 eV) [15]. Collectively, the high and low-energy EELS measurements support the presence of an electronic structure distinct from those of graphene, graphite,

amorphous carbon and diamond, consistent with the proposed mixed sp^1/sp^2 carbon framework [15, 31–34]. These observations are supported by complementary ELNES, XPS and EDX analyses. Although further theoretical and spectroscopic investigations would be valuable to elucidate the local bonding configuration, the present results support the conclusion that the carbon matrices constitute distinct nanoscale carbon architecture. In addition, EDX analysis detected approximately 1.2 wt% sulfur, which may be associated with the edges of the carbon matrices, as reported for sulfur nanoribbons by Chuvilin [35], or alternatively located between neighbouring carbon chains, where sulfur has previously been proposed to contribute to the stabilisation of carbon films [15].

To evaluate the reproducibility of the ELNES measurements, six independent carbon matrices were analysed. The fitted π and σ peak positions and integrated peak areas are summarised in Table 1. As summarized in Table 1, the variation of the fitted peak positions between independent measurements is considerably smaller than the systematic shift observed between carbon matrices grown on carbon and those synthesised on FLBN, confirming that the observed shift reflects a genuine difference in the electronic structure rather than experimental variability (Supplementary Fig. S11).

Table 1: Quantitative analysis of the carbon K-edge ELNES spectra acquired from carbon matrices grown on FLBN. Six independent regions (9.3, 9.4, 9.5, 10.4, 11.4 and 11.5), with three measurements for each region except for region 9.5, for which four measurements were analysed, giving a total of 19 measurements. The measurements were used to evaluate the reproducibility of the ELNES measurements. The corresponding spectra are presented in Supplementary Figs. S19–S24, respectively. Reported values include the fitted π^* and σ^* peak positions, integrated peak areas and the resulting sp^2 ratio.

Area	π^* peak (eV)	σ^* peak (eV)	π^* area ($\times 10^3$ counts)	σ^* area ($\times 10^3$ counts)	sp^2 ratio [$\pi^*/(\pi^* + \sigma^*)$]
9.3	284.5 $\pm$ 0.2	292.1 $\pm$ 0.3	2.26 $\pm$ 0.11	4.88 $\pm$ 0.18	0.32 $\pm$ 0.03
9.3	284.5 $\pm$ 0.2	292.1 $\pm$ 0.3	9.39 $\pm$ 0.28	15.55 $\pm$ 0.47	0.38 $\pm$ 0.04
9.3	284.5 $\pm$ 0.2	292.1 $\pm$ 0.3	5.16 $\pm$ 0.21	8.64 $\pm$ 0.26	0.37 $\pm$ 0.03
9.4	284.5 $\pm$ 0.2	291.6 $\pm$ 0.3	2.53 $\pm$ 0.10	3.87 $\pm$ 0.14	0.39 $\pm$ 0.03
9.4	284.5 $\pm$ 0.2	291.6 $\pm$ 0.3	6.60 $\pm$ 0.23	11.08 $\pm$ 0.34	0.38 $\pm$ 0.03
9.4	284.5 $\pm$ 0.2	291.6 $\pm$ 0.3	9.77 $\pm$ 0.28	15.30 $\pm$ 0.46	0.39 $\pm$ 0.03
9.5	284.5 $\pm$ 0.2	291.8 $\pm$ 0.3	3.92 $\pm$ 0.14	5.96 $\pm$ 0.20	0.40 $\pm$ 0.03
9.5	284.5 $\pm$ 0.2	291.8 $\pm$ 0.3	4.42 $\pm$ 0.15	6.07 $\pm$ 0.20	0.42 $\pm$ 0.04
9.5	284.5 $\pm$ 0.2	291.8 $\pm$ 0.3	7.97 $\pm$ 0.25	12.81 $\pm$ 0.38	0.38 $\pm$ 0.03
9.5	284.5 $\pm$ 0.2	291.8 $\pm$ 0.3	8.67 $\pm$ 0.27	14.16 $\pm$ 0.42	0.38 $\pm$ 0.03
10.4	284.5 $\pm$ 0.2	292.3 $\pm$ 0.3	1.67 $\pm$ 0.08	2.64 $\pm$ 0.11	0.39 $\pm$ 0.04
10.4	284.5 $\pm$ 0.2	292.3 $\pm$ 0.3	3.92 $\pm$ 0.14	5.48 $\pm$ 0.17	0.42 $\pm$ 0.04
10.4	284.5 $\pm$ 0.2	292.3 $\pm$ 0.3	2.04 $\pm$ 0.09	3.18 $\pm$ 0.12	0.39 $\pm$ 0.04
11.4	284.5 $\pm$ 0.2	292.3 $\pm$ 0.3	4.68 $\pm$ 0.17	7.27 $\pm$ 0.22	0.39 $\pm$ 0.03
11.4	284.5 $\pm$ 0.2	292.3 $\pm$ 0.3	3.25 $\pm$ 0.13	4.62 $\pm$ 0.16	0.41 $\pm$ 0.04
11.4	284.5 $\pm$ 0.2	292.3 $\pm$ 0.3	1.80 $\pm$ 0.08	2.93 $\pm$ 0.11	0.38 $\pm$ 0.03
11.5	284.5 $\pm$ 0.2	292.1 $\pm$ 0.3	3.34 $\pm$ 0.12	4.47 $\pm$ 0.15	0.43 $\pm$ 0.04
11.5	284.5 $\pm$ 0.2	292.1 $\pm$ 0.3	2.34 $\pm$ 0.10	3.66 $\pm$ 0.13	0.39 $\pm$ 0.04
11.5	284.5 $\pm$ 0.2	292.1 $\pm$ 0.3	2.46 $\pm$ 0.10	3.51 $\pm$ 0.13	0.42 $\pm$ 0.04

Raman spectroscopy was employed to investigate the vibrational properties of the carbon matrices. The spectra acquired from carbon matrices grown on FLBN exhibit characteristic D and G bands centred at

1333 cm^{-1} (D_1) and 1588 cm^{-1} (G_2), respectively (Supplementary Fig. S8a). The D_1 band is assigned to the in-plane breathing (A_{1g}) mode associated with sp^2 carbon domains, whereas the G_2 band corresponds to the stretching vibration of sp^2 -hybridised carbon (Supplementary Fig. S8a). The D and G bands are characteristic of an sp^2 -rich carbon framework with a significant degree of structural disorder. Such disorder may arise from the coexistence of different carbon hybridisation states, lattice defects, or the incorporation of heteroatoms [15–16, 22].

In addition to the conventional D and G bands, the Raman spectra consistently exhibit a broad band centred at approximately 1770–1780 cm^{-1} (Supplementary Fig. S8c–d), which is reproducibly observed under different excitation wavelengths (532 and 633 nm). The reproducibility of this feature across excitation wavelengths supports its assignment as a characteristic vibrational feature of carbon matrices. Similar Raman features in the 1700–1800 cm^{-1} region have been reported for long linear carbon chains and other carbon systems containing mixed sp^1/sp^2 bonding, where reduced bond-length alternation and local structural strain may shift the characteristic sp^1 -rich carbon stretching mode to lower wavenumbers [20, 36]. For the CNC2 spectrum, an additional distinct Raman feature is observed at 1884 cm^{-1} (Fig. 4b), further extending the high-frequency vibrational response of the carbon matrices. Taken together, the Raman features and the complementary EELS observations are consistent with a carbon framework containing mixed sp^1/sp^2 carbon configurations.

Deconvolution of the Raman spectra using Gaussian functions also reveals additional bands at 1593 cm^{-1} , attributed to the stretching vibration of phenyl-ring-like structures, and at 1165 cm^{-1} , tentatively associated with vibrations of cumulene-like carbon configurations (Supplementary Fig. S8b) [15–16, 22]. Furthermore, several Raman features are observed in the 100–320 cm^{-1} spectral region. These bands may be associated with collective vibrational modes involving sp^1 -hybridised C–C bonds, consistent with theoretical and experimental studies presented in Supplementary Fig. S10 [15–16, 22, 37]. Their observation under different excitation wavelengths further supports their intrinsic origin in the carbon matrices and warrants further investigation. Overall, the Raman measurements reveal a vibrational response distinct from that of conventional sp^2 carbon materials, in agreement with the complementary EELS and XPS analyses.

The optical properties of the carbon matrices were investigated by photoluminescence (PL) spectroscopy using 532 nm and 633 nm excitation lasers for the CNC1 and CNC2 samples grown on FLBN. Both types of carbon matrices exhibit photoactivated emission spanning the visible and near-infrared spectral regions. The FLBN@CNC1 sample displays a maximum emission at 774 nm, corresponding to an emission energy of approximately 1.6 eV, whereas the FLBN@CNC2 sample exhibits a maximum emission at 953 nm, corresponding to an emission energy of approximately 1.3 eV (Figs. 5a and Supplementary Fig. S15–S18). The systematic red shift in the emission wavelengths correlates with the increase in the average diameter of the carbon matrices (8.7 ± 1.0 nm for FLBN@CNC1 and 12.4 ± 1.3 nm for FLBN@CNC2; Supplementary Fig. S3), suggesting that the optical response is strongly influenced by the dimensions of the carbon matrices.

In addition to the principal near-infrared emission, the CNC2 spectra acquired under 532 nm excitation exhibit additional higher-energy emission features (Fig. 5c). A pronounced feature is observed at approximately 2.13 eV, accompanied by a lower-energy feature centred at approximately 1.99 eV. The occurrence of these features in independent measurements suggests that they are not associated with a single spectral acquisition artefact, although their microscopic origin cannot be established from the present measurements alone.

Our low-loss EELS measurements, which reveal a localised electronic excitation in the 0.9–1.1 eV, 5.0–5.4 eV and 7.3–8.3 eV regions, spatially confined to the central region of the FLBN@CNC (Fig. 5b and Supplementary Fig. S6). In addition, a broad maximum centred at approximately 7.8 eV, consistent with an inter-band electronic transition, is observed (Fig. 5b and Supplementary Fig. S6) [15–16, 34]. They do not directly reproduce the 1.99 eV and 2.13 PL peaks. These observations are complementary to the low-loss EELS measurements, which independently establish low-energy electronic excitations. Together with the structural, vibrational and spectroscopic analyses presented above, these results establish a consistent relationship between the atomic structure, electronic structure and optical response of the carbon matrices.

Discussion

Structural basis for mixed sp^1/sp^2 carbon

Recent theoretical studies have predicted the existence of sp^1 -hybridised carbon in the form of one-dimensional atomic chains possessing a tensile strength exceeding that of graphene, carbon nanotubes and diamond [14]. In addition, mechanical deformation, such as stretching or twisting, has been predicted to significantly modify their electronic band gap, while a 90° end-to-end twist may induce a transition to a magnetic semiconducting state [14]. Consequently, one-dimensional carbon chains have attracted considerable interest as potential building blocks for future nanoelectronic and spintronic devices, as well as atomically thin interconnects for electromechanical systems [14, 18–19]. Similar to graphene, monoatomic carbon chains possess an exceptionally high surface-to-mass ratio, making them attractive for electrochemical energy storage technologies and hydrogen storage applications, particularly when functionalised with calcium atoms [14].

Despite these promising theoretical predictions, the existence of extended sp^1 carbon as a stable bulk phase has remained a subject of considerable debate. The principal limitation arises from the tendency of neighbouring carbon chains to undergo exothermic cross-linking reactions, which substantially reduce their thermodynamic stability, thereby hindering the formation of extended sp^1 -rich carbon nanostructures

As previously reported by Casari et al. [37], silver nanoparticles exhibit a strong affinity for the formation of carbon structures containing hydrogen-terminated polyynes chains. Similarly, Okada et al. demonstrated the synthesis of polymeric composites containing polyyne chains stabilised by silver nanoparticles [38]. These studies demonstrate that noble-metal assisted stabilization is an effective

strategy for producing sp^1 -carbon motifs. Owing to these advances, short polyyynes with well-defined terminal groups can now be synthesised in solution with controlled chain length, while solid-state samples have also been prepared in powder form. Chalifoux and Tykwinski reported the synthesis of linear carbon chains containing up to 44 carbon atoms, stabilised by bulky end groups that suppress cross-linking reactions [39]. Nevertheless, it has been argued that carbon chains terminated by large molecular end groups should not be regarded as true carbyne [21]. In contrast, both polyyne and cumulene chains, which constitute the fundamental structural motifs of the carbyne allotrope, have been directly observed under the electron beam inside the column of a transmission electron microscope [18–19]. Previous experimental studies have also demonstrated measurable electrical transport through individual carbon chains, including asymmetric current–voltage characteristics [18–19]. Such observations provide experimental evidence for the electronic functionality of one-dimensional carbon structures and are consistent with theoretical predictions that their electronic properties are highly sensitive to atomic configuration and bonding. To date, experimental realizations of extended sp^1 -rich carbon have remained limited, primarily involving isolated atomic chains observed either as free-standing structures under transmission electron microscope or confined within narrow carbon nanotubes [18–20, 40]. La Torre et al. previously demonstrated that transition and noble metals could promote the formation of carbon chains. In particular, Ag nanoparticles were shown to catalyse the cutting and restructuring of carbon nanotubes under both oxidative and electron-beam irradiation conditions [41–42]. These studies established that Ag is not merely a passive support, but can actively interact with the carbon framework and facilitate carbon–carbon bond rearrangement. The catalytic activity of Ag nanoparticles was attributed to interactions between Ag atoms and the carbon networks, which can lower the activation energy, required for carbon bond breaking and promote subsequent carbon reorganization [41–42]. In the present work, this previously established reactivity of Ag provides an important scientific basis for interpreting the observed restructuring of the carbon precursor and the formation of carbon matrices.

Formation mechanism

Our approach employs sp^3 -hybridised carbon contained within the alkyl chains of dodecanethiol as a precursor for the formation of sp^1 -hybridised carbon, through a process of progressive dehydrogenation (Fig. 1b). The spontaneous assembly of dodecanethiol into well-ordered self-assembled monolayers (SAMs) on metallic surfaces provides a defined molecular precursor platform for the formation of carbon rich domains containing sp^2 character. Noble-metal nanoparticles have previously been shown to interact with and stabilise polyyne and related carbon species [40–43] while Ag nanoparticles have also been reported to promote carbon-carbon bond rearrangements in carbon nanostructures [41–42].

During heating under vacuum from RT to 650°C, the dodecanethiol molecules are expected to undergo progressive structural transformation. Around 300°C, C–H bond dissociation is expected to initiate the conversion of alkyl chains into alkene, polyene and eventually polyyne species, providing a plausible pathway for the gradual transformation of sp^3 -hybridised carbon into sp^1 -rich carbon structures (Fig. 1b).

Because isolated carbyne is predicted to undergo spontaneous cross-linking [21], the close proximity of neighbouring molecules within the self-assembled monolayer is expected to favour the formation of sp^1 -hybridised carbon domains interconnected through sp^2 -rich carbon domains, thereby stabilising the developing carbon framework around the silver nanoparticle. The AgNPs may therefore provide both a transient structural template and an active catalytic environment for the thermally induced transformation of the molecular precursor into the observed carbon structure (Supplementary Fig. S2a–d). This interpretation is consistent with our previous studies demonstrating that Ag nanoparticles actively interact with carbon and promote carbon–carbon bond rearrangement during nanotube cutting [18, 41–42]. Although silver is not generally considered a conventional carbonisation catalyst, its strong interaction with low-coordinated carbon species provides a plausible basis for its active role in the carbon restructuring observed during formation of the present carbon matrices.

Simultaneously with these chemical transformations, the silver nanoparticles increase in size through Ostwald ripening, as previously reported for noble-metal nanoparticles supported on carbon nanofibres, flat carbon substrates and quasi-one- and two-dimensional carbon materials [40–43]. The extent of ripening depends on the heating conditions and is therefore expected to influence the final dimension of the carbon matrices. The initial AgNPs had an average diameter of 7.3 ± 0.7 nm, while the resulting carbon matrices exhibited average diameters of 8.7 ± 1.0 nm for FLBN@CNC1 and 12.4 ± 1.3 nm for FLBN@CNC2. The evolution of the nanoparticle size during thermal treatment therefore provides a plausible explanation for the difference in the dimensions of the resulting carbon matrices (Supplementary Figs. S2a–d and S3) [40–43]. Upon reaching 650°C, in situ TEM observations demonstrate the rapid disappearance of the silver cores (Supplementary Videos 1 and 2), while the carbon matrices largely retain their morphology, indicating that the carbon framework remains structurally stable after removal of the metallic template.

Structural evidence

High-resolution TEM observations show that the carbon matrices differ qualitatively from previously reported carbon nanostructures, including fullerenes, carbon onions, carbon black and nanohorns, exhibiting a characteristic quasi-hemispherical morphology composed of three to four carbon layers (Supplementary Fig. S5). The measured interlayer spacing is 4–16% larger than that of graphite (Supplementary Fig. S2c–d) [44]. Determining the bonding configuration within the carbon matrices requires consideration of both EELS and Raman spectroscopy. The EELS spectra do not exhibit features characteristic of sp^3 -bonded carbon, consistent with extensive dehydrogenation of the dodecanethiol precursor. Both EELS and Raman spectroscopy provide evidence consistent with the presence of sp^1 -hybridised carbon; however, the spectral signature differs markedly from those expected for well-ordered sp^2 graphitic carbon. Taken together, these spectroscopic observations are consistent with a highly defective carbon framework containing sp^2 -rich carbon domains interspersed with sp^1 -hybridised carbon domains. Such a structural arrangement is consistent with the proposed dehydrogenation and cross-linking mechanism and provides a plausible explanation for the observed quasi-spherical morphology of

the carbon matrices (Figs. 1 and Supplementary Fig. S5a–d). XPS analysis provides complementary evidence for C–N bonding through the chemical-state components resolved in the C 1s and N 1s spectra (Supplementary Fig. S14). This observation is consistent with the localised N K-edge signal observed by EELS (Supplementary Fig. S7).

Unlike freestanding linear carbon chains, the structural model proposed in the present work consists of one-dimensional sp^1 -rich carbon motifs embedded within a continuous sp^2 carbon framework. Although the surrounding sp^2 network is expected to influence their structural stability and electronic structure, these embedded motifs may retain several characteristic electronic, vibrational and optical properties associated with sp^1 -hybridised carbon. This distinction provides a physically plausible interpretation of the experimental observations while remaining consistent with the observed structural stability.

Electronic structure

The low-energy excitations near 1 eV are consistent with electronic transitions involving the π electronic states separated by an energy gap of approximately 1–2 eV. In contrast, the feature centred at 7.8 eV is consistent with transitions from the bonding σ band to the antibonding σ^* band at $k = \pi/a$ [15–16, 34]. These low-energy features have previously been discussed in terms of electronic transitions within one-dimensional carbon systems [15–16].

Photoluminescence measurements performed on the self-assembled carbon matrices reveal emission maxima at approximately 1.3 eV for CNC2 (Fig. 5a and Supplementary Fig. S18) and 1.6 eV for CNC1 (Fig. 5a and Supplementary Figs. S15–S18). These emission energies are consistent with electronic transitions previously reported for carbyne-related structures [15, 26, 45] and are in good agreement with the low-energy electronic excitations observed by EELS. The correspondence between the low-energy EELS excitations and the photoluminescence emission provides complementary evidence for the electronic states associated with the carbon framework. Collectively, the PL and EELS measurements support the presence of sp^1 -rich carbon motifs within the carbon matrices. Together, these observations indicate that the mixed sp^1/sp^2 carbon framework exhibits electronic behaviour distinct from conventional sp^2 carbon materials [15–16, 34, 46]. The low-energy electronic excitations are consistent with an electronic gap associated with Peierls-type bond-alternation in sp^1 -rich carbon segments. In one-dimensional carbon systems, bond-length alternation can lower the total energy by lifting electronic degeneracy, resulting in a semiconducting state. The observed EELS excitation near 1 eV and the corresponding photoluminescence emission therefore support an electronic structure in which sp^1 -rich carbon motifs contribute significantly to the optical band gap within the mixed sp^1/sp^2 carbon framework.

Optical Response

The coexistence of sp^1 and sp^2 carbon is expected to have important consequences for the electronic properties of the carbon matrices. A fully sp^2 -hybridised carbon framework of comparable dimensions would generally be expected to exhibit a substantially different electronic structure and, depending on its degree of disorder and confinement, a relatively small band gap. In contrast, theoretical studies predict that sp^1 -rich carbon motifs linking sp^2 -hybridised carbon domains, as in graphyne-like structures, increase the band gap to approximately 1.3 eV [26]. Consistent with this prediction, EELS measurements reveal a low-energy excitation near 1 eV for an individual carbon matrix (Fig. 5b), while photoluminescence measurements show emission energies of approximately 1.3 eV for FLBN@CNC2 (Figs. 5a and Supplementary Fig. S18) and 1.6 eV for FLBN@CNC1 (Fig. 5a and Supplementary Figs. S15–S17). These observations are consistent with the presence of sp^1 -rich carbon domains and support the proposed electronic structure of the carbon matrices.

These emission energies are consistent with the low-energy electronic response observed by EELS and with electronic transitions previously reported for carbyne-related and one-dimensional carbon structures [15, 26, 32]. The correspondence between the low-energy EELS excitations and the photoluminescence emission provides complementary evidence for electronic states associated with the carbon framework.

The photoluminescence emission shifts from approximately 1.3 eV for FLBN@CNC2 to 1.6 eV for FLBN@CNC1, corresponding to a pronounced blue shift of the optical emission. The shift is likely to arise from the combined influence of several factors rather than a single mechanism. The smaller CNC1 matrices, which exhibit greater curvature, may experience increased structural strain that could influence the electronic structure of the embedded sp^1 -rich carbon motifs and their bond-length alternation [18, 46]. Quantum confinement within the nanoscale carbon domains may also contribute to the observed blue shift. In addition, localised electronic states associated with the residual sulfur present in the carbon matrices cannot be excluded as contributing to the optical response, although their relative contribution cannot be quantitatively separated from the present measurement.

In addition to the principal near-infrared emission, an additional photoluminescence feature centred at approximately 2.13 eV is observed in the carbon matrices (Fig. 5c). This feature shows that the optical response extends beyond the principal size-dependent near-infrared emission. Its microscopic origin cannot be uniquely assigned from the present measurements and may reflect localised electronic states within the heterogeneous sp^1/sp^2 carbon framework. We therefore regard the 2.13 eV feature as an additional component of the optical response rather than assigning it to a specific electronic transition.

Interestingly, the additional higher-energy PL feature of CNC2 at approximately 2.13 eV occurs together with the distinct higher-frequency Raman feature at 1884 cm^{-1} (Fig. 4b). The coexistence of these higher-energy optical and vibrational features is noteworthy; however, the present measurements do not establish a direct microscopic correspondence between them. We therefore regard both features as experimentally observed characteristics of CNC2 whose microscopic relationship requires further investigation. The concurrent higher-energy optical response and higher-frequency vibrational feature

may therefore reflect differences in the extent or confinement of the sp^1 -rich domains within the two carbon matrices. In this context, the 2.13 eV emission and the 1884 cm^{-1} Raman feature provide complementary signatures of the local sp^1 -rich carbon structure in CNC2. While the present measurements do not permit a unique microscopic assignment, their correlation is consistent with a modification of the electronic and vibrational states associated with the smaller sp^1 -rich domain.

Collectively, the structural, vibrational, electronic and optical characterisation consistently support a model in which the carbon matrices comprise interconnected sp^2 -hybridised carbon domains containing localised sp^1 -rich motifs. Rather than isolated freestanding carbyne chains, the present results indicate a hybrid carbon framework in which the coexistence of sp^1 and sp^2 bonding gives rise to the distinctive electronic and optical properties observed experimentally.

The present results can also be viewed in the broader context of our previous investigations on catalyst-assisted synthesis of low-dimensional nanostructures. We previously demonstrated that few-layer hexagonal boron nitride (FLBN) could undergo catalyst-assisted activation, leading to the formation of half-dome boron nitride nanostructures under in situ transmission electron microscopy conditions [47]. The present work extends this concept to carbon-based materials, where sulfur-containing dodecanethiol molecules surrounding silver nanoparticles act as the carbon precursor while the Ag nanoparticles simultaneously template and stabilize the formation of hybrid sp^1/sp^2 carbon matrices. More recently, we further demonstrated that replacing the sulfur-containing precursor with the nitrogen-containing precursor Tetramethylammonium Hydroxide (TMAH) leads to the formation of carbon nitride nanostructures while preserving the same catalyst-assisted growth strategy [48]. Taken together, these studies suggest that the chemistry of the molecular precursor, together with the catalytic nanoparticle and the supporting substrate, provides a versatile platform for controlling the composition, bonding configuration, and functional properties of low-dimensional carbon nanostructures.

Implications

An important outcome of the present work is that the synthesis of the carbon matrices is not limited to the transmission electron microscope environment. The experimental approach demonstrates that these structures can also be formed under vacuum conditions outside the TEM, indicating that electron irradiation is not a prerequisite for their formation. This finding broadens the applicability of the synthesis route and suggests the possibility of preparing larger quantities of material for further structural, spectroscopic and application-oriented investigations.

Unlike isolated carbyne chains, which are generally expected to be sensitive to oxygen and elevated temperatures, the carbon matrices reported here remain structurally stable under ambient conditions and during heating under vacuum. No measurable structural or optical degradation was observed under the experimental conditions employed in this work, indicating that these carbon matrices combine the structural robustness of an sp^2 -hybridised carbon framework with well-defined low-energy electronic and optical responses.

The carbon matrices described in this work combine structural characteristics associated with both sp^2 -hybridised carbon domains and sp^1 -rich carbon motifs, giving rise to a combination of properties that may be attractive for future technological applications. In particular, the observed low-energy electronic excitations and size- dependent photoluminescence extending into the near-infrared spectral region suggest potential applications in photonic [49] including hybrid organic-inorganic photovoltaic systems [50]. The coexistence of sp^1 and sp^2 carbon domains may also provide favourable electronic properties for charge injection into dielectric materials such as h-BN or SiO_2 , potentially enabling the development of carbon-based electroluminescent devices. Furthermore, the carbon matrices can be synthesised on a variety of substrates, including planar supports such as FLBN and Si_3N_4 , as well as cylindrical carbon nanofibres (Supplementary Fig. S4), which may facilitate their integration into a range of nanoscale device architectures.

Beyond their electronic and optical properties, the present fabrication strategy provides a route for transforming intrinsically two-dimensional carbon networks into three-dimensional hollow nanostructures with diameters of approximately 8.7 ± 1.0 nm (FLBN@CNC1) and 12.4 ± 1.3 nm (FLBN@CNC2). These hollow carbon matrices are structurally related to fullerene-type carbon nanostructures but possess cavities approximately three orders of magnitude larger than those of conventional fullerenes. Consequently, they may provide versatile nanoscale containers for optically [49–50], magnetically [51] or catalytically [52–53] active species. These structural characteristics suggest that the carbon matrices may provide a versatile platform for future studies in catalysis, sensing, energy conversion and data storage, [54–56] although further investigation will be required to establish their functional performance.

Methods

Hollow carbon matrices were synthesised both in situ inside a transmission electron microscope (TEM) and ex situ in evacuated glass ampoules. In situ heating experiments were performed using a JEOL 2100F transmission electron microscope equipped with a Gatan Tridiem imaging filter for electron energy-loss spectroscopy (EELS) and a Gatan 652 double-tilt heating holder at the Nanoscale and Microscale Research Centre, University of Nottingham (UK). Aberration-corrected high-resolution TEM (AC-HRTEM) imaging of carbon matrices supported on few-layer hexagonal boron nitride (FLBN) and carbon nanofibres (CNFs) was performed using a JEOL JEM-ARM200F microscope operated at room temperature.

Commercially available few-layer hexagonal boron nitride (FLBN) dispersed in methanol (Graphene Supermarket) was used as the supporting substrate. Silver nanoparticles (AgNPs) were synthesised by a modified Kang and Kim procedure. Briefly, dodecanethiol (0.4 mmol) was added to a solution of silver nitrate (0.9 mmol) in ethanol (30 mL), and the mixture was stirred vigorously for 10 min at room temperature. A saturated solution of sodium borohydride in ethanol (60 mL) was then added, and the reaction mixture was stirred for 2 h at room temperature. The product was precipitated by adding ethanol (350 mL) and stored at -30°C for 24 h. The resulting precipitate was collected using a $0.45\ \mu\text{m}$

PTFE membrane, washed successively with ethanol (250 mL) and acetone (250 mL), and dried under vacuum to obtain approximately 180 mg of AgNPs.

A suspension containing 1 mg mL⁻¹ of AgNPs in cyclohexane was prepared and mixed with either 1 mg of FLBN or 1 mg of carbon nanofibres (CNFs). The resulting composites were filtered through a 0.45 µm PTFE membrane, washed with ethanol and acetone, and dried under vacuum to produce AgNP@FLBN and AgNP@CNF composites.

For ex situ synthesis, the AgNP@FLBN and AgNP@CNF composites were sealed in evacuated glass ampoules and heated at 650°C, yielding FLBN@CNC and CNF@CNC, respectively. The same thermal treatment was applied to AgNP@FLBN supported directly on TEM grids, producing FLBN@CNC1 and FLBN@CNC2.

High-energy electron energy-loss spectroscopy (EELS) measurements were performed using an aberration-corrected JEOL ARM microscope equipped with double delta correctors and a monochromator operated at 60 kV. The instrument provided a spatial resolution of approximately 1 Å and an energy resolution of 24 meV. High-resolution TEM images were recorded using a Gatan OneView camera operating at 1–3 frames s⁻¹ with a detector resolution of 4k × 4k at the National Institute of Advanced Industrial Science and Technology (AIST), Japan. Although the TEM specimens were exposed to ambient air during transport from the UK to Japan and prior to EELS analysis, no detectable oxygen signal was observed in the carbon matrices by either EELS or EDX, within the detection limits of these techniques.

Low-loss EELS data were processed using custom Python routines. Individual spectra were energy calibrated with respect to the zero-loss peak (ZLP), and the integrated zero-loss peak (IZLP) intensity was used for normalization to compensate for variations in sample thickness and acquisition conditions. Energy-filtered intensity maps were generated by integrating the normalized spectra over selected energy-loss windows (0.9–1.1 eV, 5.0–5.4 eV and 7.3–8.3 eV). The resulting maps were displayed using identical processing parameters to enable direct comparison between the different energy-loss regions.

For the quantitative comparison of the carbon K-edge ELNES, spectra were extracted from several independent regions of each sample. The π* and σ* peak positions were determined after background subtraction using identical fitting procedures for all spectra. The reported energies correspond to the average values obtained from the independently analysed spectra, and the reproducibility of the measurements was used to assess the experimental uncertainty.

Spectra were extracted from multiple regions of interest within individual carbon matrices and processed using identical calibration, background subtraction and normalization procedures. The resulting energy-filtered maps enabled direct visualization of the spatial distribution of the low-energy electronic excitation near 1 eV and the higher-energy inter-band transitions.

Electron Energy-Loss Spectroscopy (EELS) Data Analysis

Low-loss EELS spectra were processed using custom Python routines. Individual spectra were energy calibrated with respect to the zero-loss peak (ZLP), followed by background subtraction and normalization to the integrated ZLP intensity to compensate for variations in specimen thickness and acquisition conditions. Integrating the normalized spectra over selected energy-loss windows using identical processing parameters for all datasets generated energy-filtered intensity maps.

For quantitative analysis of the carbon K-edge ELNES, spectra were extracted from multiple independent regions of each carbon matrix. After background subtraction, the π^* and σ^* components were fitted using an identical fitting procedure for all spectra, and the integrated peak areas were used to calculate the $\pi^*/(\pi^* + \sigma^*)$ ratio. The fitting procedure followed the methodology developed by K. Suenaga for quantitative ELNES analysis. Measurements from six independent carbon matrices were analysed to evaluate reproducibility, and the reported values correspond to the average of the independently analysed spectra. The structural interpretation presented in this work is based on the combined analysis of ELNES, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and photoluminescence measurements rather than on ELNES alone.

Spectral Fitting and Statistical Analysis

Raman spectra were analysed after baseline subtraction using identical fitting parameters for all samples. Peak positions, line widths and integrated intensities were obtained using the same fitting procedure for spectra acquired under both 532 nm and 633 nm excitation wavelengths. XPS spectra were energy calibrated with respect to the C 1s reference peak prior to fitting, and peak deconvolution was performed using identical fitting constraints for all samples.

To assess experimental reproducibility, multiple independent measurements were acquired from each sample. The reported peak positions and characteristic energies correspond to the average values obtained from the independent measurements, while the experimental variability was used to estimate the associated uncertainty. All spectral analyses were performed using identical processing parameters to ensure consistency between different samples and experimental datasets.

Raman and Photoluminescence Measurements

Raman spectra were acquired using a Horiba Jobin–Yvon LabRAM Raman microscope equipped with a 532 nm excitation laser operating at low power (approximately 4 mW) and a 600 lines mm⁻¹ diffraction grating. The spectra were recorded using a Synapse CCD detector. For each spectral window, 64 accumulations of 5 s were collected. Three spectra were acquired from each sample to account for sample inhomogeneity. The Raman shift was calibrated using the 520.7 cm⁻¹ Si peak obtained from a Si (100) reference sample.

Additional Raman spectra were acquired using a 150 grooves mm⁻¹ diffraction grating, providing a broad spectral window that enabled simultaneous acquisition of the first-order Raman bands together with the

high-wavenumber region around 1770–1780 cm^{-1} . This configuration allowed reproducible observation of the broad Raman feature centred at approximately 1780 cm^{-1} under identical acquisition conditions.

Photoluminescence (PL) measurements were performed on FLBN@CNC1 and FLBN@CNC2 samples deposited on TEM grids and subsequently mounted on quartz substrates. Excitation was provided by the 532 nm and 633 nm lines of a pulsed Nd:YAG laser (pulse duration approximately 8 ns). Short-pass and long-pass interference filters were used to suppress higher-order harmonics of the excitation source. The emitted PL signal was collected and focused into a monochromator using a long-pass interference filter (FEL700, Thorlabs). A 600 grooves mm^{-1} grating blazed at 1 μm was used for spectral dispersion. The PL signal was detected using a liquid nitrogen-cooled near-infrared photomultiplier tube (Hamamatsu C5594), and the transient decay was recorded with a 1 GHz Agilent Infinium oscilloscope. The overall temporal response of the system was approximately 20 ns.

Additional Raman measurements were performed on carbon matrix samples supported on TEM grids and mounted on quartz slides. Spectra were acquired at 300 K using excitation wavelengths of 532 nm and 633 nm, with a laser power density of approximately 100 W cm^{-2} .

Abbreviations

FLBN

Few-layer hexagonal boron nitrides

AgNPs

Silver nanoparticles

h

BN–Hexagonal boron nitride

EELS

Electron energy-loss spectroscopy

EDX

Energy-dispersive X-ray spectroscopy

PL

Photoluminescence

TEM

Transmission electron microscopy

STEM

Scanning transmission electron microscopy

HRTEM

High-resolution transmission electron microscopy

AC

HRTEM–Aberration-corrected high-resolution transmission electron microscopy

CNF

Carbon nanofibres containing residual nitrogen

CNC

Carbon matrix

CNF@CNC

Carbon matrices grown on carbon nanofibres

FLBN@CNC

Carbon matrices grown on few-layer hexagonal boron nitride

FLBN@CNC1

Carbon matrices grown on few-layer hexagonal boron nitride on gold TEM grid

FLBN@CNC2

Carbon matrices grown on few-layer hexagonal boron nitride copper TEM grid

PTFE

Polytetrafluoroethylene

STEM

EELS–Scanning transmission electron microscopy–electron energy–loss spectroscopy

ELNES

electron energy–loss near–edge structure

AgNP@FLBN

Silver nanoparticles deposited on few layers boron nitride sheets

AgNP@CNF

Silver nanoparticles deposited on carbon nanofibres

TMAH

Tetramethylammonium Hydroxide

SAM

Self-assembled monolayer

ZLP

Zero–loss peak

iZPL

Integrated zero loss peak

Declarations

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Author Contribution

A.L.T. conceived and designed the study, performed and/or coordinated the experiments, analysed and interpreted the data, prepared the figures, and wrote and revised the manuscript. A.L.T. approved the final version of the manuscript and is responsible for all aspects of the work.

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Data Availability

All data generated or analysed during this study are included in this manuscript and its Supplementary Information. Additional data supporting the findings of this study are available from the corresponding author upon reasonable request.

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Figures

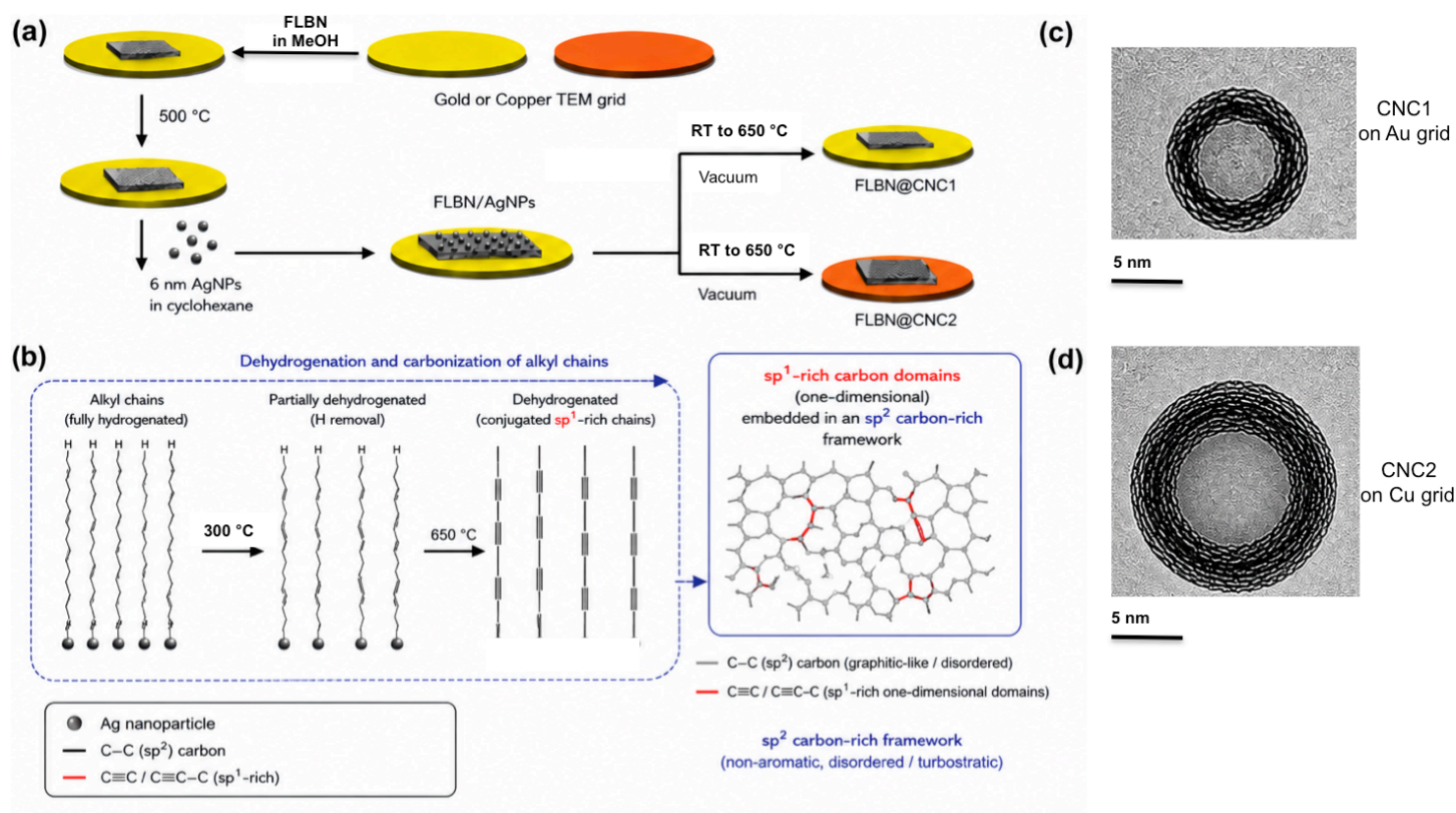


Figure 1

Schematic representation of the proposed formation mechanism of curved hollow carbon matrices. (a) Synthesis of silver nanoparticles (AgNPs) in the presence of dodecanethiol, deposition on FLBN, and subsequent annealing under vacuum (RT–650 °C) on gold or copper TEM grids to obtain FLBN@CNC1 and FLBN@CNC2. (b) Dehydrogenation and carbonisation of alkyl chains: progressive removal of

hydrogen with increasing temperature (300–650 °C), proposed to lead to the formation of conjugated sp^1 -rich one-dimensional carbon domains embedded within an sp^2 -rich carbon framework. Accordingly, the carbon matrices are proposed to comprise a hybrid sp^1/sp^2 carbon framework, with localised sp^1 -rich domains embedded within a sp^2 -bonded carbon framework (c, d) TEM images of the curved hollow carbon matrices (CNC1 and CNC2). The CNC2 matrices are typically larger in diameter than the CNC1.

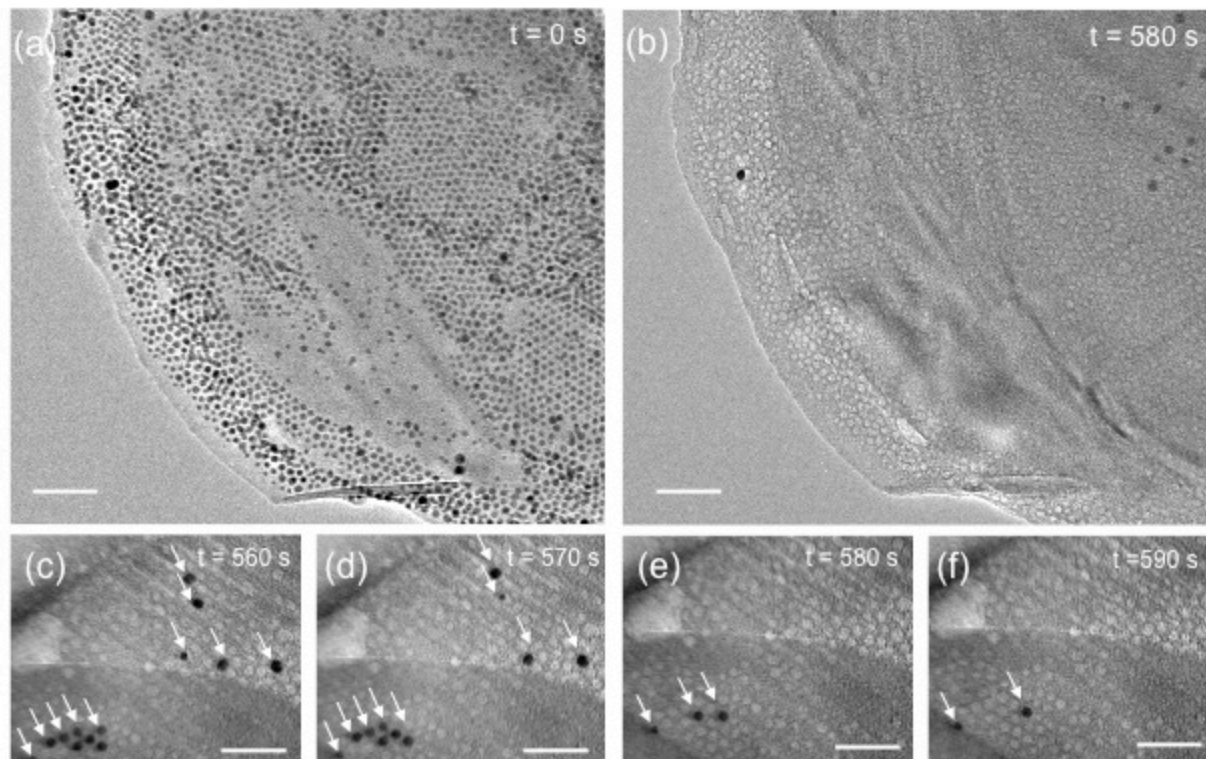


Figure 2

In situ transmission electron microscopy (TEM) images illustrating the formation of carbon matrices. (a) Bright-field TEM image showing a two-dimensional array of silver nanoparticles (AgNPs) supported on a few-layer hexagonal boron nitride (FLBN) sheet before heating. (b) Following heating to 650 °C, the AgNPs are transformed into self-assembled monolayer (SAM)-derived carbon matrices. (c–f) Time-resolved TEM images showing the progressive disappearance of the silver cores (high-contrast features), leaving behind carbon "casts" (low-contrast features) arranged in a hexagonal array on the FLBN substrate. These observations provide direct experimental evidence that the carbon matrices form through thermally induced carbonisation of the organic shell, while the Ag nanoparticles serve as both a transient structural template and catalyst. The time stamps in panel (c–f) indicate the elapsed time from the beginning of the heating experiment. The progressive disappearance of the Ag cores preserves the external morphology, resulting in hollow curved carbon matrices. Scale bars: 100 nm in (a–b) and 50 nm in (c–f).

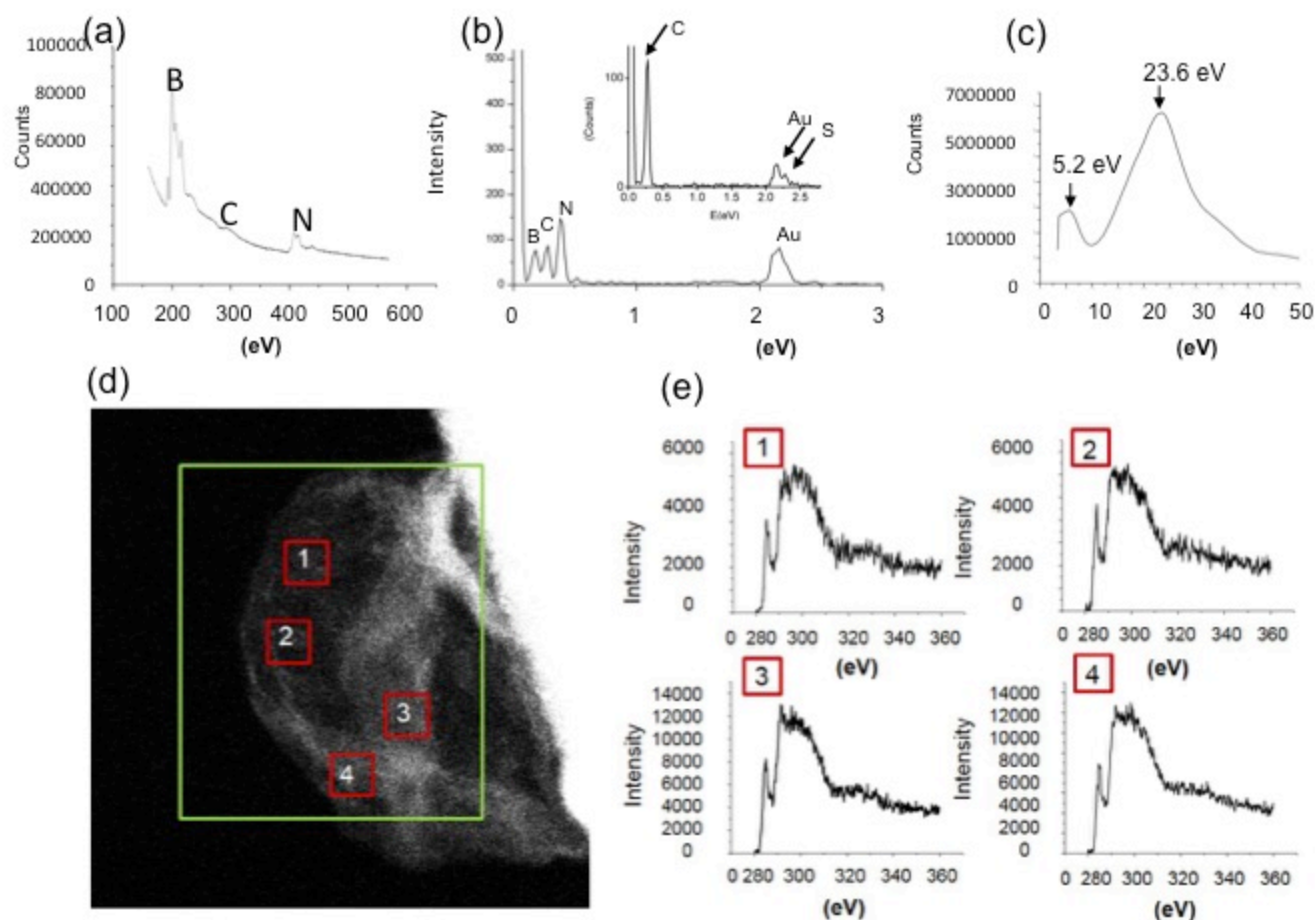


Figure 3

Spectroscopic characterisation of the carbon matrices. (a) Wide-scan electron energy-loss spectroscopy (EELS) spectrum and (b) energy-dispersive X-ray spectroscopy (EDX) spectrum acquired from an ensemble of several thousand carbon matrices (sample FLBN@CNC1) supported on few layers boron nitride sheet. The analyses indicate that the carbon matrices consist predominantly of carbon. The B and N signals originate from the underlying h-BN substrate, whereas the Au signal arises from the TEM support grid. The EDX spectrum acquired from an individual carbon matrix (inset) confirms the presence of residual sulfur. (c) Representative low-loss EELS spectrum showing the principal low-energy electronic excitation centred at approximately 5.2 and 23.6 eV. (d) Aberration-corrected scanning transmission electron microscopy (AC-STEM) image of an individual carbon matrix suspended at the edge of an h-BN sheet. The four-labelled regions were selected for local-probe EELS analysis. (e) Carbon K-edge EELS spectra acquired from the four selected regions shown in (d), demonstrating the reproducibility of the local electronic structure across the carbon matrix.

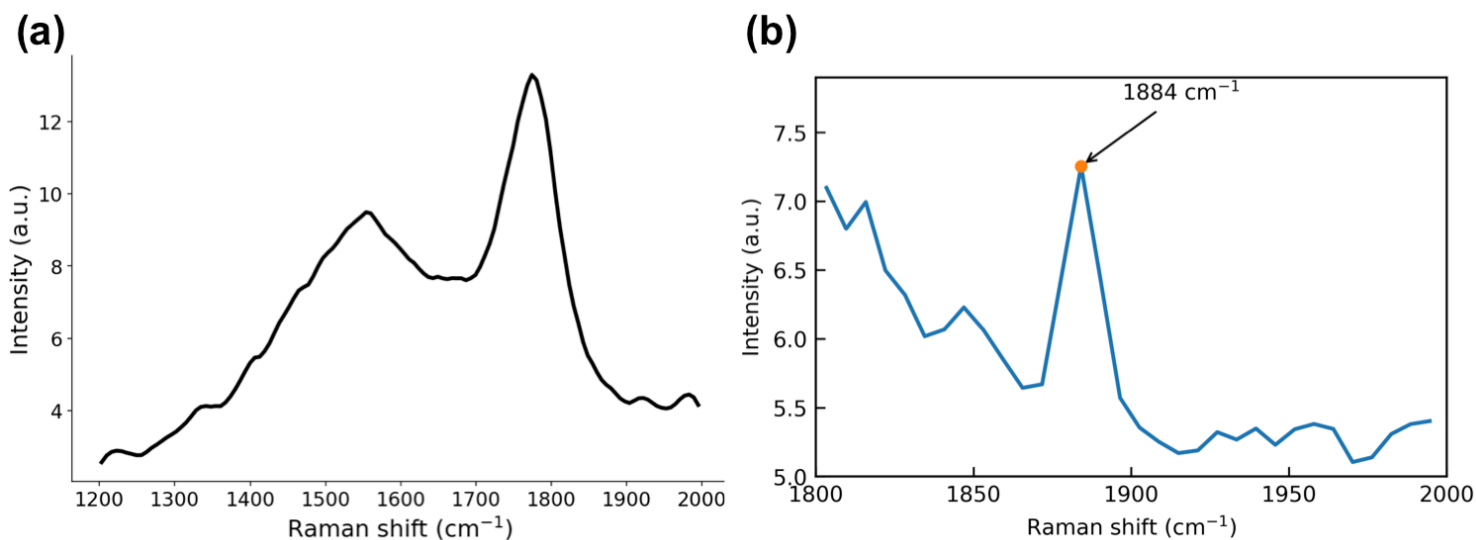


Figure 4

Representative Raman spectrum of the hybrid carbon allotrope (CNC1 and CNC2) acquired on a few layers hexagonal boron nitride substrate. (a) The spectrum exhibits broad vibrational features in the 1200–2000 cm^{-1} region (CNC1), including broad vibrational bands centred at 1550 and 1780 cm^{-1} consistent with the mixed sp^1/sp^2 -bonding configuration discussed in the text. (b) Expanded high-frequency Raman region (CNC2), showing the distinct 1884 cm^{-1} feature.

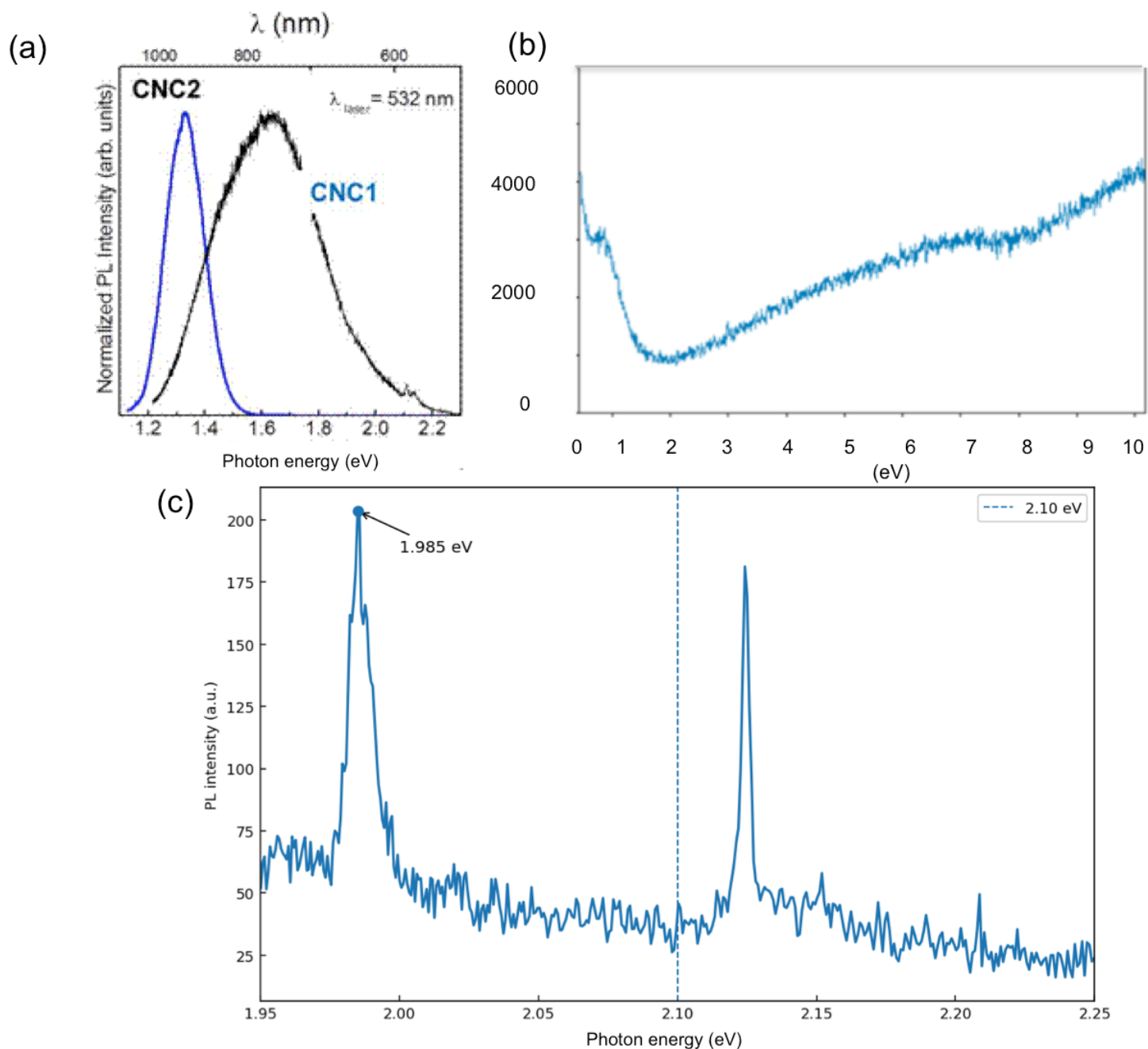


Figure 5

Correlated photoluminescence and low-loss EELS characteristics of the carbon matrices. (a) Comparison of the photoluminescence spectra of carbon matrices with different average diameters, FLBN@CNC1 ($8.7 \pm 1.0 \text{ nm}$) and FLBN@CNC2 ($12.4 \pm 1.3 \text{ nm}$), showing emission maxima corresponding to emission energy of approximately 1.6 and 1.3 eV, respectively. (b) Low-loss EELS spectrum acquired from an individual carbon matrix, showing a low-energy electronic excitation feature at approximately 1 eV (arrow) and a broad maximum centred at approximately 7.8 eV, consistent with an inter-band electronic transition. (c) PL spectrum of CNC2 acquired using 532 nm excitation, showing additional emission features at approximately 1.99 and 2.13 eV.

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