Engineering high-defect densities across vertically-aligned graphene nanosheets to induce photocatalytic reactivity

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Abstract

The fabrication of graphene nanostructures, with a variety of morphologies and densities of defective sites, can be a promising tool to tune their characteristics towards photocatalytic applications, without the need for external dopants. In this study, the impact of morphological properties in terms of the orientation and defect concentrations of graphene nanostructures is demonstrated to support the development of active photocatalytic sites across graphitic structures. Vertically-aligned graphene nanosheets were grown across carbon fibres via electron cyclotron resonance microwave plasma chemical vapour deposition, to yield a range of different wall densities and edge functionalities. The variation of growth conditions was correlated to the photocatalytic activity for the degradation of methylene blue dye under ultra-violet and visible light. The chemical state of oxygen content hybridized with nanosheets was studied by X-ray photoelectron spectroscopy and correlated to the growth conditions and photocatalytic performance. The fastest degradation rate of dye was found on the graphene samples which were grown at 800 °C for 240 min, with a kinetic constant of $46.6 \times 10^{-4}$ min$^{-1}$. Such performance has not been observed to date for any graphitic materials and is shown to be on the same order of performance as the conventional photocatalytic materials.

Keywords

Graphene morphology, vertically-aligned graphene, photocatalysis, defect engineering.
Graphical abstract

VGN/CF structure

Plasma radicals

VGN forest

Carbon fibre (CF)

Defective graphene sheet

Atomic defective sites

Oxygen-related functional groups

C  O  H
1. Introduction

Two-dimensional (2D) graphene nanomaterials have been considered in various applications such as sensors [1], piezoelectric [2], photovoltaics [3] because of their fast carrier mobility [4] and excellent electrical [5] and thermal conductivities [6]. Nevertheless, the zero-bandgap of mono-layer graphene has exhibited no semiconducting properties [7]. Also, the interlayer Van der Waals attractions between graphene sheets during the processing of 2D nanomaterial-based bulk assemblies is likely to cause restacking issues. This restacking, likely inhomogeneous across long-range order materials, maybe resulting in the reduction of the accessible surface area as well as mass transport rates across such graphene-based assemblies [8, 9]. Consequently, such limitations of graphene materials may restrict reaction kinetics during catalytic reactions [10].

Heteroatom doping has been considered to improve the catalytic activity of graphene materials via incorporating heteroatoms such as fluorine, boron, or nitrogen into their graphitic lattices, which exhibited promising catalytic properties in various applications [11, 12]. However, the sustainability of catalytic performance and the cost-effective of large-scale production remain challenges against using doped graphene materials as catalysts in various applications [13, 14]. Engineering the reactivity of the graphene is therefore a prerequisite to utilize them in catalytic applications without the need for external dopants.

The morphological properties of graphene materials play a significant role in the control of their local optical and electrical properties [15, 16] and can either be altered by varying the synthesis conditions [17] or by further treatments that may include the perforation [18], twisting [19], coalescing or overlapping [20] of sheets. Such processes can lead to various forms of defective sites across graphene structures, which can be customized into pores and wrinkles between grain boundaries or near edges of graphene sheets [21-23]. The presence of
such imperfections has the ability to modify the properties of graphene structure [24], making them useful in catalytic applications [10] such as the water-splitting [25] and hydrogen storage [26].

Nanopores across the basal plane of graphene materials, for example, can modify the electronic band structure locally due to a slight electron-hole asymmetry of the ideal graphene materials [27]. This phenomenon is well-known as self-doping [28] and can lead to the injection of charges into the whole electron system of the graphene structure [16, 29]. In addition, defective sites are often decorated with carboxylic acid groups and unpaired electrons around the edges, which can enrich the catalytic properties of graphene materials [30]. Not only the defects but also the number of graphitic layers into the graphene structure could influence the bandgap structures by tuning the interlayer spacing [31] between these layers, which may lead to the generation of a non-zero bandgap similar to the graphite material [32, 33]. This self-modulation of the graphene’s bandgap was also observed in other carbon-based nanostructures such as carbon nanotubes [34, 35], nanoribbons [36, 37] and perforated graphene sheets [38, 39] that demonstrated semiconducting properties in different optoelectronics applications under suitable stimulus conditions. Accordingly, a new class of graphene materials with tunable bandgaps and semiconducting properties can be engineered by fine-tuning of such morphological properties in terms of the density of defective sites and the number of layers of graphene sheets [40].

The three-dimensional interconnected graphitic network is known either by the vertically-aligned graphene nanosheets (VGN), or open-ended multi-walled carbon nanotubes [41]. VGN forests can be grown vertically to the substrate surface and each forest may consist of a few petals, which can be composed of double or multi-layers of graphene sheets [42]. The vertical orientation of VGN nanostructures can reduce the probability of the aggregation of graphene sheets to have occurred due to the high mechanical stability of VGN sheets after the
growth process, in contrast to the horizontally-aligned graphene sheets [43]. Besides, it can increase the specific surface area and the accessibility to active defective sites and unsaturated carbon edges for graphene sheets into the VGN walls, leading to a boosting in the catalytic activity as compared to horizontally-aligned graphene nanostructures [44].

This work focuses on evaluating the impact of the morphological properties of VGN in terms of the orientation of the graphene sheets and densities of defects across VGN matrices on their photocatalytic responses. The morphology of VGN was controlled by varying the temperatures and durations during the growth process, via the electron cyclotron resonance microwave plasma chemical vapour deposition (ECR-MPCVD) on commercial carbon fibres (CF) substrates. X-ray photoelectron spectroscopy (XPS) spectra of the carbon and oxygen species chemical states were evaluated across the pristine and post-catalysis samples to give more insights into the chemical stability and oxidation resistance during the photocatalytic reaction. The impact of growth conditions on the morphological properties of VGN samples was investigated and correlated to their catalytic activity towards the degradation of methylene blue (MB), as a representative model of organic dyes, under the ultra-violet (UV) and visible stimuli. This work demonstrated the catalytic response of a pure VGN/CF material without any catalysts and the effective role of custom-designed graphene materials, to tailoring their electronic and physiochemical properties that can be utilized in applications such as environmental remediation, energy generation or storage.
2. Experimental details

2.1. Growth VGN/CF by ECR-MPCVD technique

Graphene sheets were grown vertically on carbon fibres (CF) of commercially available carbon paper substrate (Avcarb® MGL370) via the ECR-MPCVD facility as mentioned in our previous studies [45-47]. Briefly, a mixture of methane (CH₄) and Argon (Ar) gases with a 1:5 concentration ratio was used as a carbon source and carrier gas, respectively during the growth process. The space between the substrate holder and the plasma source was fixed to be 15 cm. The chamber was vacuumed by using a turbo molecular pump down to 5×10⁻⁶ torr of pressure. The carbon paper substrate was initially annealed at 800 ºC for 30 min of duration, prior to being cleaned with a 200 W Ar-plasma (flow rate 20 sccm) for 10 min. The CH₄ gas was pumped into the chamber for growth with a constant flow rate of 4 sccm at 350 W microwave power and operating pressure of 2×10⁻³ torr. After the growth was completed, all samples were thermally treated at 800 ºC for 30 min to improve the crystallinity of the samples. Finally, samples were cooled down to room temperature at 10 ºC/min rate. The temperatures and growth durations varied during the growth process to generate VGN sheets with different morphological properties across CF substrates.
2.2. Characterization techniques

2.2.1. Microstructure morphology

Scanning electron microscope (SEM, Zeiss Supra 55VP FEG) was used to investigate the morphology of VGN walls over CF substrate at a 10 kV of acceleration voltage and a working distance of 8 mm. All VGN/CF samples were mounted on aluminium holders with carbon tape. No coating was applied prior to the imaging to avoid any variation of the morphological properties of samples. The density of VGN walls value for all samples was estimated by processing SEM micrographs with the ImageJ software over 1 µm × 1 µm scanning area for three locations. The surface roughness characteristics of VGN/CF samples were evaluated by a 3D microscopic laser (Olympus LEXT 4100) over a 3 µm × 3 µm analysis area with a cut-off roughness of 80 µm for considering the waviness parameters of VGN/CF nanostructure in the roughness calculation [48]. The root-mean-square, $S_q$ and arithmetical mean, $S_a$ of roughness values were computed and averaged over twenty points of VGN/CF samples.

2.2.2. Surface wettability

The wettability properties of VGN/CF samples were evaluated prior and post the photocatalytic experiments through measuring the water contact angle using sessile drop method technique with the assistance of a CCD camera and a fitting method supported by Apex tool. A water droplet with a 1-µL volume was maintained for all measurements. The contact angle value was measured over five points over each sample.
2.2.3. Raman analysis

Intrinsic crystallinity and defect density of VGN/CF samples were assessed by micro-Raman spectroscopy technique (Renishaw inVia) with an excitation laser of 514 nm and a 20 × objective lens. A grating filter with 2400 grooves/mm was employed for the monochromatization of the signals. The power was kept to 50% of the total power (12 mW without the objective lens) to prevent damage to the graphitic planes. The integral time for a single acquisition was fixed at 10 s for all measurements. All Raman spectra are evaluated in the wavenumber range between 1000 and 3200 cm\(^{-1}\) and interpreted with Wire 3.2 platform. The Raman spectra were evaluated over several five points over VGN/CF samples, and then averaged to maintain the statistical aspect in our reported values.

2.2.4. Surface chemistry analysis

The variation of oxygen-related functional groups across VGN/CF nanostructures was revealed by the X-ray photoelectron spectroscopy (XPS) analysis. Data were collected via K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific) using a monochromatized Al Kα X-ray source, with excitation source 250 W and anode current of 27 mA with a constant pressure inside the chamber of 5×10\(^{-8}\) ± 0.1 Pa. All surveys and high-resolution spectra were measured at 100 and 20 eV pass energies with 10 and 20 scans, respectively. A selected area using a 400 μm × 400 μm aperture was analysed on each sample. Each sample was measured over four different spots for statistical relevance. Peak analyses were performed with the CasaXPS software, using a weighted sum of Gaussian and Lorentzian component curves GL\((p)\), where \((p)\) parameter is equal to 50. The asymmetry in the C1s \(sp^2\) and \(sp^3\) peaks were fitted by Gaussian/Lorentzian product modified by an asymmetric form A(a,b,n)GL(p) after Shirley background subtraction. The a and b fitting parameters were fixed at 0.1 to determine the shape
of the asymmetric portion of the curve and \( n \) was kept at 80 for defining the optimal convolution width of the modelled line-shapes [49].
2.3. Catalytic degradation of MB organic dye

The photocatalytic activity of the pure VGN/CF samples was evaluated with an OmniCure S2000 as a UV radiation source with two light filters over a range of wavelength of either 320-480 nm or 400-500 nm. The irradiance of UV radiation was measured by a radiometer (OmniCure R2000) and maintained nearly 180 mW/cm², which is carefully adjusted to reduce the photolysis rate of MB dye [50]. The working distance between the sample holder and the UV lamp was fixed at 7 cm during all experiments. A 2 cm × 2 cm of VGN/CF sample area was immersed into a quartz baker with a 3 mL of MB aqueous solution at a 5-ppm concentration to construct a thin-film of dye over the surface of the sample. Prior to testing, the immersed VGN/CF sample in MB dye was kept in the dark environment for 30 min to reach the adsorption-desorption equilibrium. Furthermore, the adsorption rate of the MB dye on the VGN/CF nanostructure was studied without any light excitation source in a dark environment for 60 min as per previous conditioning experiments to ensure that the solution had reached a steady-state with the surface of the samples [51]. The variation of the UV-Visible absorbance of MB organic dye was collected with an ultraviolet-visible spectrometer (USB-2000) and data was processed by Ocean Optics platform. The maximum value of the absorbance MB dye at the wavelength 665 nm was measured every 10 min and up to 2 h of treatment. For the comparison, the UV irradiation of MB dye was also carried out in the presence of a Buckypaper from reduced-graphene oxide (RGO) as a reference of horizontally-aligned graphene nanostructures, which was prepared as discussed in the Supplementary Materials Section I.
3. Results and discussions

The control of the density distribution of VGN is crucial to engineering active carbon edges and density of defective sites that may increase the specific surface area and enhance the catalytic performance of pure graphene materials [44]. The relationship between the growth parameters of VGN materials, such as temperature and duration on the morphological and physicochemical properties is discussed, and finally linked to the photocatalytic activity of the VGN materials.

3.1. The evaluation of the density distribution and surface roughness of VGN/CF samples based on growth conditions.

The VGN/CF samples were investigated by SEM analysis to estimate the density distribution of VGN walls across carbon fibres in term of the number of walls per surface area. This is typically correlated to the density of defective sites and the concentration of unsaturated carbon edges, as well as the specific surface areas across VGN materials, as illustrated in Figure 1A.

The density of VGN forests across the carbon fibres (CF) substrate was found to gradually increase with respect to the growth temperature at a fixed duration (120 min) as shown in Figure 1B. The VGN sample prepared at 650 °C exhibited a density of 291 ± 188 walls/μm², while those prepared at 725 °C and 800 °C exhibited density values of 465 ± 150 and 678 ± 36 walls/μm², respectively. Figure 1C presents the influence of growth duration on the density distribution of VGN walls that can also be observed by comparing SEM scans in Figure 1A for samples grown for either 120 or 240 min at a fixed temperature of 800 °C. When the growth duration was doubled, the density distribution of walls increased from 678 ± 36 to
1,178 ± 12 walls/μm², in agreement with our previous findings [52]. Height and curling degree between interconnected VGN forests were found to vary based on the growth conditions. Samples that were grown for longer durations exhibited a high tendency to curl as compared to the samples grown over short durations. No significant change in the height of VGN forests was observed across prepared samples at different temperatures, whereas other samples that were grown for different durations exhibited an increase in the height values of VGN/CF samples. For instance, samples grown for a 240 min duration demonstrated a wall height of almost 240 nm, which was two times higher than other prepared samples for 120 min at the same temperature of 800 °C, as illustrated in the 3D representation of SEM micrographs in Figure S1.

The surface roughness was assessed for carbon fibres prior and post to the ECR-MPCVD growth of VGN by processing the 3D microscopic profiles that are illustrated in Figure S2. The results of this roughness analysis are summarized for the series of samples in Table S1. At 120 min growth duration, the roughness of the sample that was grown at 650 °C was 177 ± 53 nm, which was 1.5 times compared to the commercial CF substrates. Other samples exhibited a roughness of 126 ± 12 nm and 153 ± 18 nm for VGN sheets that were grown at temperatures of 725 °C and 800 °C, respectively, as shown in Figure 1B. Therefore, the surface roughness of the VGN nanostructures was not found to be significantly affected by an increase in the growth temperature from 650 °C to 800 °C. The roughest surface was ascribed to the sample that was grown for 240 min at 800 °C, with a roughness of 171 ± 21 nm, compared to other VGN/CF samples as presented in Figure 1C. The primary reason for the development of the surface roughness can be assigned to the orientation of graphene sheets and the density distribution of walls across carbon fibres in contrast of horizontally aligned graphene sheets, with a surface roughness, which typically is less than 1 nm as reported in the literature [53].
Figure 1 (A) Morphological structures analysis of VGN across carbon fibres (CF) substrates at different nucleation conditions. (A) SEM micrographs of VGN samples at two scanning resolution (1 μm and 100 nm) and (B, C) assessment of surface roughness and density distribution of VGN walls across CF based on the growth conditions in terms of the temperatures and durations, respectively.
3.2. Investigation of the surface energy of VGN/CF samples

The wettability properties of VGN sheets on CF substrates were assessed by evaluating contact angle values between the water molecules and pristine samples that were grown at different conditions and the result is summarized in Table S2. VGN/CF nanostructures demonstrated ultra-hydrophobic properties toward the water molecules with no much difference in the contact angle values across the series of samples. VGN/CF samples that were grown for 120 and 240 min at 800 °C exhibited a contact angle of 164 ± 5 and 167 ± 3 degrees, respectively, that was nearly 25% higher compared to the pristine CF substrates at 132 ± 13 degrees. The VGN/CF samples exhibited contact angles, nearly 3-fold higher than that obtained for horizontally-aligned graphene material (RGO) at 75 ± 6 degrees. The ultra-hydrophobic behaviours of the VGN samples were attributed to the poor attraction between non-polar carbon lattices and water molecules, as well as the surface roughness of interconnected VGN sheets over rough carbon fibres substrates [54, 55]. However, this low surface energy of graphene materials can be enhanced by using organic solvents [56], which can be considered in applications such as enzymatic catalysis [57]. Samples, which had been tested for the photocatalytic experiments, exhibited a slight decrease in contact angle by about 5 degrees as compared to the pristine samples. This result suggests that VGN nanostructures were stable in this range of conditions.
3.3. Evaluation of crystallinity and defect density across the VGN materials

The crystallinity of graphene nanostructures in terms of the number of layers and density of defective sites across VGN lattices were investigated by Raman analysis by evaluating the ratio of intensities of 2D-to-G bands and D-to-G bands, respectively [58, 59]. The variation of such crystallographic properties across VGN sheets was also assessed for the pristine and samples that had been used in the photocatalytic experiments and then correlated to the growth conditions.

Several peaks were observed in the measured Raman spectra at 1351, 1582, 1621, 2704 and 2953 cm\(^{-1}\) corresponding to D-, G-, D’-, G’- and D+D’ band. G- and G’ bands were located at 1582 and 2704 cm\(^{-1}\) as illustrated in the spectra in Figure S3 confirms the graphitic structure. The G-band associates to the E\(_{2g}\), second-order stretching-mode of well-ordered carbon atoms in the graphitic structure [60], while the G’-band, which sometimes is known by 2D-band corresponds to the double- or triple- responses. D- and D’ bands were observed at 1351 and 1621 cm\(^{-1}\), respectively. The D-band attributes to the A\(_{1g}\), first-order breathing-mode of \(sp^2\) bonded carbon in the graphene sheet structure. The observed D-, D’-, D+D’ bands are related to activated defects in the VGN lattices that can be generated due to the plasma radicals during the growth stage [61].

The impact of the growth temperature on VGN lattices was studied based on Raman spectra for pristine VGN/CF samples. After a 120 min growth duration, the VGN sample that was prepared at 650 °C showed an I\(_D\)/I\(_G\) ratio of 1.52, whereas another sample at 800 °C exhibited a ratio of 1.74. This confirms that the development of defective sites in the VGN structure with the increase of growth temperature. The I\(_{2D}\)/I\(_G\) ratio experienced a slight increase in its magnitude with higher growth temperature, which indicates that the growth temperature
may increase the crystallinity nature of VGN structure as shown in Figure 2A, which is in good agreement with the literature [58].

Figure 2B represents the variations of the well-ordered structure and defective properties of prepared VGN sheets based on the development of growth duration. As the growth duration increased to 240 min at 800 °C, the $I_D/I_G$ ratio increased by 25% compared to the VGN samples that were grown for 120 min at the same temperature. Interestingly, the sample that was grown for 60 min demonstrated the highest density of defects, which is indicating a non-linear change of the $I_D/I_G$ ratio with this range of growth durations, as supported by the disorder model of graphitic materials, proposed by Ferrari and Robertson [62, 63]. In this regard, the crystallinity of VGN sheets was found to decrease slightly with the increase of the growth duration. This result may be ascribed to the overlapping between VGN forests, which may be negatively influenced the crystallinity of the two-dimensional graphene nanostructures as observed in Figure 1A. In addition, pristine VGN samples exhibited a crystallinity factor i.e. $I_{2D}/I_G$ ratio from 0.61-0.74, suggesting that VGN walls are composed of more than triple graphene layer in comparison with other findings in the literature [59].

VGN/CF samples that were used as catalysts in the photodegradation experiments i.e. post-catalysis samples demonstrated a decrease in the concentrations of defective sites across their graphitic structures as reported in the Table S3, which may have been experienced a degree of bond repair during the degradation process of organic dye due to the UV light irradiation. This restoration of the graphitic structure by defect reparation may occur upon reaching minimum energy to pass the threshold activation barrier, provided by external energy sources such as irradiation or thermal stress [64]. However, there is no theoretical support for confirming this trend at this point. This may be indicative of the effective role of atomic defective sites across graphene nanostructures during the catalytic reaction. To shed the light of the impact of UV irradiations on the development of defects across the graphitic structure,
the crystallographic results were compared to that obtained for horizontally-aligned graphene materials: graphene oxide (GO) sheets, as tested in another work in the literature [65]. The horizontal GO structures exhibited a sharp increase in the defect density as a function of UV exposure yield, which is not in agreement with our findings. This difference may be attributed to the high intensity of UV radiations used during their photo-reduction experiments, which was almost 15 times higher than the applied intensity in this study.

Figure 2 Raman analysis of well-ordered structure and defect density of pristine and post-catalysis VGN/CF samples, which were grown at different (A) temperatures and (B) durations.
3.4. The chemical stability and oxidation resistance across polycrystalline VGN/CF samples during the photocatalytic reactions

The evaluation of the oxygen atomic concentration across the VGN series was calculated from the XPS surveys as shown in Figure S4. Analogous expanded O at. % spectra were observed for both pristine and treated VGN/CF samples at 532.08 eV, which could be associated with oxygen doubly bound to the aromatic rings of the graphitic structures [66]. Surface oxidation could have occurred in the pristine samples from the saturation process of dangling bonds around the sheet edges and defective sites across VGN nanostructures, whereby oxygen that can be easily bonded to them once the sample is exposed to the oxygen in the surrounding environment after the growth process [67]. The impact of the growth conditions on the variation of the oxygen atomic concentrations across the series of pristine VGN samples was evaluated by analysing the O/C ratio obtained from the XPS surveys, as shown in Figure 3A and B. All pristine VGN samples, regardless of their growth conditions, exhibited non-significant O/C ratios variations. This was attributed to the fact that the growth mechanism by 650 °C in 800 °C conditions is typically considered to lead to high crystallinity graphitic materials and low-oxidation level in ambient air [68].

Furthermore, the chemical stability of the VGN structure was investigated across the whole samples post the photodegradation experiments. The post-catalysis VGN sample, which was grown at 650 °C for 120 min exhibited an increase in the O at. % concentration, raising from 1.6 ± 0.5% of the pristine sample to 2.5 ± 0.11%. The sample was grown at 725 °C for 120 min also showed an increase from 1.2 ± 0.4% for the pristine sample to 2.4 ±0.3 % at the same condition. Similar trends in the atomic oxygen concentration were also noticed in other samples prepared at 800 °C temperature for 60, 120 and 240 min durations, respectively after using them as catalysts under UV radiations as reported in Table S4. In order to emphasize, the role of UV radiations on the variation of oxygen contents across the graphene materials, further
XPS analysis of horizontally aligned graphene materials was considered. It was found that GO sheets showed a dramatic decrease in the concentration of oxygen contents across the graphitic structures of GO sheets [69], suggesting low chemical stability for such oxygenated graphene sheets in contrast to the XPS analysis of treated VGN samples. Therefore, a slight variation in the atomic concentration of oxygen may suggest that VGN/CF samples were chemically much stable during the photodegradation experiments, comparing to other oxygenated graphene nanostructures.

Analysis was carried out on the C$_{1s}$ spectra to quantify the variation of type and contribution of specific functional groups, which were developed across pristine and post-catalysis VGN samples and then associated with the different growth conditions. Figure S5 presents the high-resolution spectra of C$_{1s}$ for each series of pristine and post-catalysis samples, and broadly confirm the surface elemental compositions. Two major peaks were observed at 284.58 and 285.12 eV corresponding to C-C bond with $sp^2$ and $sp^3$ hybridization modes, respectively. The $sp^2$/$sp^3$ ratio was calculated from the XPS data for the series of samples prior and post the photocatalytic experiments. No significant variation was revealed in the $sp^2$/$sp^3$ ratio values across the whole tested VGN/CF series post the photodegradation experiments as illustrated in Figure 3A. Consequently, no significant development of oxygen-related function group’s concentration across VGN sheets during the photocatalytic reaction has occurred, since the change of oxygen-functional group’s concentration across graphitic planes lead to converting the conductive $sp^2$ carbons into nonconductive $sp^3$ bonds across the graphene structure [70, 71]. These findings were found in a good agreement with the obtained results from the quantitative XPS analysis.

Oxygen-related functional groups were detected at 285.7, 287, 288.3 and 290.6 eV and attributed to hydroxyl (C-OH), carbonyl (C=O), carboxylic (COOH) and $\pi$- $\pi^*$, respectively [50, 72]. The presence of hydroxyl groups as a recurring impurity in pure graphitic structures
is in good agreement with previous studies that showed how mild oxidation in the air of graphitic planes could be responsible for the formation of O species [50, 67]. On the other side, it has been reported that epoxy groups could be generated upon exposure of graphene to a fixed dose of atomic oxygen under controlled atmosphere [73, 74]. While the potential formation of epoxy species along with hydroxyl groups cannot be discarded [75], the impact of the oxidation pathway onto the generation of O functionalities plays a critical role. Under mild oxidation conditions, the formation of hydroxyl species can be attributed to the interaction within unstable surface radicals stemmed from the CVD growth and air moisture [50].

No significant change in the carbonyl and carboxylic groups were seen across the post-catalysis samples, which suggest that VGN samples were very resistive to the oxidation conditions during the photocatalytic process. Interestingly, the VGN sample that was grown at 800 °C for 240 min shows the most significant increase in the carboxylic concentration group across the series, raising from 1.5 ± 0.18% of the pristine sample to 2.4 ± 0.084% after the photocatalytic experiment as shown in Figure 3B. Consequently, this minor increase in the concentration of carboxylic functional groups across the treated samples may be indicative of a substantial role of carboxylic functional groups across the edges of VGN nanostructures in the photodegradation mechanism. Furthermore, the surface atomic percentage for nitrogen (N) was revealed to be 1.3 ± 0.14% in the treated VGN sample, which was originally grown at 800 °C for 240 min. This minor presence of N can be induced by the partial adsorption of the MB dye that may have occurred during the photodegradation process.
Figure 3 XPS analysis of hybridized oxygen-related functional groups across polycrystalline pristine and post-catalysis VGN/CF samples, which were grown at different growth conditions. (A) temperatures and (B) durations.
3.5. Photodegradation of MB organic dye by VGN/CF materials

Pure VGN/CF nanostructures were utilized as photocatalysts to degrade MB dye as a representative model of organic dyes under ultraviolet and visible light irradiations. Figure 4A represents the relative changes in the concentration of aqueous MB (5 ppm) solutions achieved by VGN/CF samples as a function of UV irradiation duration with a light filter of 320-480 nm (Figure S6). Irradiation of a solution of MB with no VGN sample showed a decrease in its concentration, typically 15% over 2 h treatment duration, which can be ascribed to the photolysis process of MB dye [76]. The VGN/CF sample that was prepared at 650 °C for 120 min exhibited degradation of 35%, while other samples that were grown at 725 °C and 800 °C showed a degradation of 30% and 37%, respectively. Other samples that were grown for 60 min and 240 min at 800 °C demonstrated a considerable variation in the degradation values of 28% and 48%, respectively.

The photocatalytic kinetic constants were calculated and are shown in Table S5. The photodegradation of organic compounds in the presence of VGN samples was interpreted according to Langmuir-Hinselwood kinetic theory [77], while the half-life duration (t_{1/2}) also was computed as highlighted in Equations S1 and S2. The degradation of MB dye solutions over VGN/CF substrates was in a good agreement with pseudo-first-order kinetics for all samples. The fastest pseudo-first-order kinetics can be ascribed to the VGN/CF sample that was grown at 800 °C for 240 min, resulting in a kinetic constant, K of 46.6×10^{-4} \text{ min}^{-1}, which is equivalent to 2.6 times higher than the photolysis that achieving of 18.1×10^{-4} \text{ min}^{-1}. This sample demonstrated a t_{1/2} of 148 ± 2 min, whereas the MB photolysis put this value in 383 ± 14 nm.
Figure 4 Photodegradation performance of VGN/CF samples at different growth conditions under UV radiation at 320-480 nm light filter. (A) photodegradation ratio of MB dye, (B) kinetic ratio evaluation of K value and (C-D) kinetic coefficient and half-life time of VGN samples, which were grown at different conditions in terms of the growth temperatures and durations, respectively.

This photocatalytic activity was achieved without any modification with any conventional photocatalyst. The achieved performance was also found to be on the same order of performance as other photocatalytic materials, for instance, titanium dioxide (TiO$_2$) as a common catalyst of semiconducting materials [51]. Figure 4C shows no much variation in achieved kinetic values by the samples, which were grown at different temperatures. However, a noticeable improvement was observed in K values when the growth duration increased as
illustrated in Figure 4D, which may be ascribed to the increase of VGN density across the surface of the fibres. A similar trend of the degradation of organic dyes by the oxygenated graphene materials was reported with no further details on the kinetics of the photodegradation process [78].

To maintain the reproducibility, the photodegradation of MB dye was assessed through three successive cycles, which carried out on the most active sample, the VGN/CF that was grown at 800 °C for 240 min (Figure S7). This sample was annealed at 100 °C temperature for 3 h prior to the repeat experiment to ensure it is completely regenerated. The kinetic constant value remained almost constant upon three cycles, which started by 44×10^{-4}, and ended by 48×10^{-4} min^{-1}, corresponding a t_{1/2} value of 148 ± 26 and 142 ± 9 min, respectively as shown in Figure 5C. The VGN/CF sample that was prepared at 800 °C for 240 min was selected for assessing the degradation performance under visible light with a wavelength range between 400 and 500 nm (Figure S9). Figure 5D demonstrates the photodegradation where 34% of MB was degraded within 2 h treatment duration, with K value of 31×10^{-4} min^{-1}. 
Figure 5 (A) Kinetic ratio evaluation of K value of VGN-800 °C-240 min sample under UV radiation at 320-480 nm filter for three successive cycles, (B) photocatalytic activity of the former under UV-visible radiation at 400-500 nm light filter and (C-D) kinetic coefficients and half-life time value of VGN/CF samples.

To assess the potential adsorption of the MB dye across the VGN sheet during the catalytic reactions, the adsorption rate of the dye on the VGN/CF nanostructure was studied without any excitation source in the dark environment, and the results were illustrated in Figure S8. Only a slight decrease in the dye concentrations, by less than 6%, was observed over the 1 h treatment time. This low adsorption is expected due to weakened electrostatic attraction between the dye and the VGN sheets as discussed earlier in the characterization section.
The photodegradation of MB dye by using the VGN/CF nanostructures is ascribed to the morphological properties of VGN sheets in terms of the orientation of sheets and the high concentration of atomic defective sites. Control experiments were also conducted using other graphene materials, for example, reduced-graphene oxide Buckypaper under the same experimental conditions. The RGO paper showed no degradation of MB dyes and demonstrated a kinetic constant similar to the MB photolysis as demonstrated in Figure S10. This may be attributed to the lower density of defective sites, nearly 1.13 a.u, which is nearly 50% of the highest defective density obtained by VGN materials in this study. Not only this but also the limited specific surface areas of horizontally aligned graphene sheets, which is solely dependent on the restacking between sheets, which can be negatively affected the chemical activity of graphene sheets [79].

The results suggest that the high density of defective sites and unsaturated carbon edges, as well as their associated oxygen-related functional groups in non-aggregated graphitic planes, have enhanced the catalytic activity of graphene nanostructures. One of the possible pathways of MB degradation by VGN samples is the initial one-electron oxidation of MB dye by hydroxyl radicals (•OH) during the photocatalytic water splitting reaction, which is not likely to occur due to instantaneously recombination across ideal graphene nanostructure. However, it was found that oxygenous functional groups across graphene nanostructure can enlarge the zero-bandgap of graphene via converting the conductive \( sp^2 \) carbons into nonconductive \( sp^3 \) bonds, leading to the possibility of tuning the bandgap and giving semiconducting properties for defective graphene nanostructures [71, 80]. Another mechanism may have occurred, is the aerobic oxidation coupling reaction under UV-visible radiations, through the dynamic exchange of oxygen functionalities, around the edges of defective sites, which are decorated by carboxylic acid groups and unpaired electrons [30]. However, further experiments, beyond the scope of the current study, [81] for probing such generated oxygen-
derived radicals during the reaction, would provide a further understanding of the photodegradation mechanism based on VGN materials.
4. Conclusions

In the presented work, the photodegradation of organic dye was demonstrated in the presence of only VGN/CF nanostructures under ultra-violet and visible light without modifications with any conventional catalysts. The engineering of morphological properties of VGN materials, such as highly polycrystalline structures, with enhanced specific surface areas and a high density of atomic defective sites may enhance photocatalytic properties of graphene nanostructures similar to that of semiconducting materials. The synergistic effect of oxygen-related functional groups and unsaturated dangling bonds around the defective sites was found to develop the catalytic activity of graphitic structures for molecular oxygen activation during the UV-visible irradiations. However, at present, the mechanisms of photodegradation with such graphene materials require further mechanistic studies for probing oxygen-derived radicals generated during the photocatalytic process. The highly increased reactivity of VGN compared to horizontal RGO make them extremely promising in environmental remediation and renewable energy, and opens the route for the design of novel photo-electro catalytic reactors.

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