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Faculty of Engineering and Information Technology

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**Optical Properties and Photoactivity of Carbon Nanodots Synthesized from
Olive Solid Wastes at Different Carbonization Temperatures**

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Statement of Originality

We, the undersigned, hereby declare that this work has not previously been submitted for a degree or diploma at any university or insititute. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is indicated in the thesis itself.

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Abstract

Carbon nanodots (CNDs) have many fascinating properties such as optical properties (UV-Visible absorption and fluorescence emission), which nominate them to be good candidates in many applications such as photocatalysts for the degradation of several organic pollutants.

This study aims to synthesize CNDs from olive solid wastes at different carbonization temperatures from 300 to 900 °C and study their effect on the optical properties of CNDs such UV-Vis, fluorescence, quantum yield, and energy bandgap in addition to their influence on the photoactivity of CNDs as photocatalysts for the degradation of methylene blue (M.B). CNDs were prepared from olive solid wastes (OSWs) by pyrolysis at different temperatures (300-900°C) to be converted to carbonized material, then oxidized chemically in the presence of hydrogen peroxide (H₂O₂). It was found that the increase in carbonization temperature of olive solid wastes leads to an increase of product yield with a maximum value at 500 °C and then decreased dramatically. On other hand, a decrease in fluorescence due to the diminishing of oxygen groups and destruction of the surface of CNDs was observed. The higher quantum yield (5.17%) and bandgap (2.77 eV) were achieved for CNDs prepared from OSWs carbonized at 300 °C. The rate and degradation efficiency of M.B were studied with different synthesized CNDs, finding that the increase in carbonization temperature leads to decreases in the rate and degradation efficiency of M.B realizes the highest values at 300 °C with a degradation rate of 0.0575 min⁻¹ and degradation efficiency of 100% after 120 minutes of light irradiation.

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Chapter One: Introduction

In 2004, carbon nano-dots (CNDs) were discovered accidentally during the purification of single-walled carbon nanotubes [1, 2]. These new carbon materials were quasi-spherical nanoparticles with a size of less than 10 nm [3, 4]. The CNDs are rich in functional groups, such as hydroxyl, carboxylates, epoxides groups, etc. [5-7]. These groups may confer the uniform dispersity of CNDs in polar solvents such as water [8] and showing good water solubility [9, 10]. CNDs have many significant properties such as optical quantum [11], small size [12], uniform shape, and composition [13-15], low toxicity and biocompatibility [16, 17], fluorescence emission [18], ease of functionalization [19], good conductivity [20], and low cost in preparation [21].

There are two routes for the synthesis of CNDs: Top-down and Bottom-up [22]. In the first approach, the "Top-down" synthetic route, bulk materials such as graphite are broken down into CNDs. This route includes laser ablation [23, 24], arc discharge [13], and chemical oxidization techniques [25]. The second approach is the "Bottom-up" synthetic route which involves synthesizing CNDs by hydrothermal/solvothermal treatment [26] and microwave pyrolysis [27] from small precursors such as carbohydrates, citrate, and polymer silica nanocomposites [19]. Both methods are carried out using physical, chemical and electrochemical process.

CNDs have been synthesized from a wide range of precursors either man-made (e.g. candle soot [28], graphite [29], fullerene [30], ethanolamine [31], and citric acid [32]) or natural resources (e.g. orange juice [33], lemon juice [34], broccoli [35], milk and milk protein [36, 37], coffee grounds [38], egg white [39], and banana [40]). Moreover, some waste materials have also been well utilized for the synthesis of CNDs such as paper pieces [41], tire soot [42], cigarette butts [43], and olive solid wastes [5]. which not only reduce CNDs production costs but also abate environmental pollution. Properties of CNDs are highly affected by the selected method, precursor, synthesis conditions, pretreatment, and post-treatment, and the intended applications are also influenced. For instance, the carbonization temperature of sago highly affected the fluorescence and sensing parameters of synthesized carbon nanodots [44].

CNDs and due to their peculiar properties have been used in many applications [45]. The most important of which are bioimaging [46], biomedical sensing [45, 47], drug

delivery[48], cancer phototherapy[49], optronic[50], fingerprint recovery[22, 51], and photocatalysis [52] as a photosensitizer in water splitting[53], organic pollutants degradation [54] and degradation of organic dyes (e.g. methylene blue)[55].

CNDs may be one of the best candidates for photocatalytic possibilities for the degradation of organic dyes (M.B)[56]. Photocatalysis is an energy conversion process that can be initiated by light absorption in semiconductor materials. Light exposure can generate electrons and holes during photocatalysis[57]. CNDs with an energy bandgap between 1.5-3.5 eV [58] are considered semiconductors with high visible-light absorption and excellent light-trapping ability generating electron-hole pairs which are needed for photocatalysts and degradation of organic dyes.

In this work, CNDs will be synthesized from olive solid wastes by combined pyrolysis-chemical oxidation methods at different carbonization temperatures from 300 to 900 °C and study their effects on the optical properties of CNDs such UV-Vis, fluorescence, quantum yield, and energy bandgap. The influence of carbonization temperature on the photoactivity of CNDs as photocatalysts for the degradation of methylene blue (M.B) will also be investigated, estimating the degradation efficiency and rate.

Chapter Two: Materials and Methods

2.1 Materials

Olive Solid wastes (OSWs) were obtained from the olive oil extraction plant in Der-Istia (Palestine). All required chemicals and reagents were purchased from Sigma Aldrich, and used without further purification. Milli-Q grade water ($>18.2 \text{ M}\Omega\cdot\text{cm}$ resistivity) was used in the synthesis of carbon nanodots and distilled water was used to prepare methylene blue solutions.

2.2 Characterization Instruments

Beckman Coulter DU 800 Spectrophotometer was used to record UV-Vis spectra from 200 to 800 nm. In the emission range of 320 to 650 nm, steady-state fluorescence spectrum measurements were made using a Perkin Elmer LS50B Fluorescence Spectrophotometer. The spectra were taken at different excitation wavelengths from 320 to 460 nm with an increment of 20 nm. AFM images and profiles were acquired by a Nanosurf CoreAFM microscope and were analyzed by Gwyddion software. AFM samples were prepared by drop-casting of diluted solution of CNDs on mica substrate and then dried under vacuum at 110°C . Thermo Scientific Nicolet IS5 FTIR device equipped with an ATR sampling apparatus was used to record Fourier Transform Infrared spectra of carbonized olive solid wastes and synthesized CNDs in powder in the range of $4000 - 650 \text{ cm}^{-1}$ with 8cm^{-1} resolution and 64 scans. ζ -potential measurements were performed for all samples using NanoBrook Omni instrument.

2.3 Synthesis of CNDs

The first step in the preparation of CNDs was pyrolysis of the olive solid wastes (OSWs) at different temperatures from (300–900) $^\circ\text{C}$ with 100°C increments for 1 hr. OSWs were purified from impurities and remaining oil by washing several times using hot water. The purified OSWs were dried in an oven for 24 hr and then cooled to room temperature. Carbonization (pyrolysis) was performed by inserting a dried weighed OSWs sample in a muffle furnace at different temperatures for 1 hr. After completion of carbonization, samples were cooled to room temperature inside a desiccator. 100 mg of carbonized olive solid wastes (COSWs) were grounded manually using mortar and pestle to a fine powder and then mixed with 10 ml of MilliQ-water and sonicated for 5 min. 200 μl of 30 wt.% H_2O_2 were added into the previous solution and sonicated by using (Elmasonic S 100 H sonicator) for 20 min, and then the solution was refluxed for 90 min. After the completion of the reaction, the resulting solution was centrifuged by

using universal 320 centrifuges at 8000 rpm for 20 min. The resulted supernatant was filtered through a 0.2 μm microfilter. A brown powder of CNDs was obtained after lyophilization of CNDs solution for 36 hr. The as-synthesized CNDs for further characterizations and applications have been named CD300 CD400, ...CD900. The modified synthesis method conducted in this work is based on the protocol followed previously by Sawalha et al.[5]. The synthesis process is installed in (Figure 1)

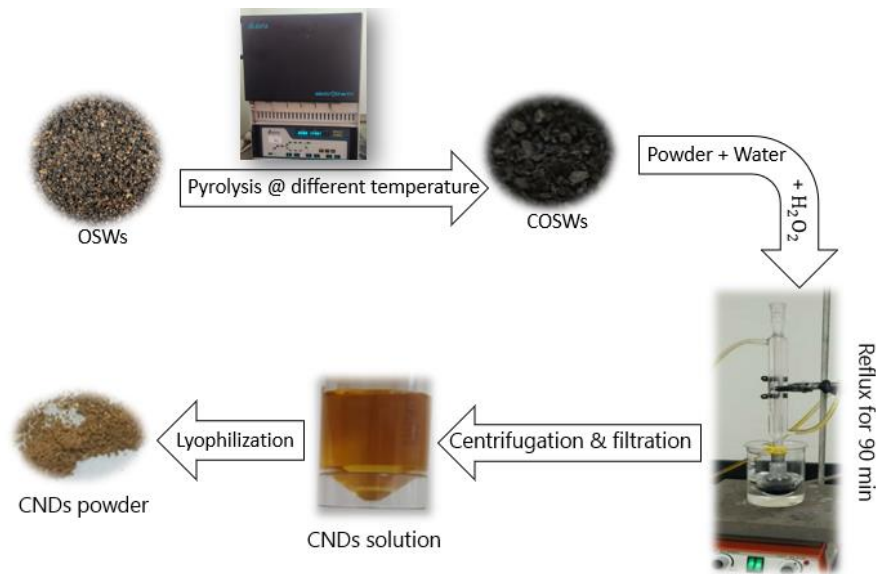


Figure 1: The synthesis process of CNDs.

2.4 Proximate Analysis

Proximate analysis of virgin olive solid wastes and pyrolyzed (carbonized) samples at temperatures from (300-900) $^{\circ}\text{C}$ were performed to determine moisture content, volatile matter, ash content, and fixed carbon. In brief, a moisture content test was performed by insertion of 1 g of sample in a crucible and heated for 1 hr at (107 $\pm$ 3) $^{\circ}\text{C}$, and then cooled inside a desiccator and weighed. On the other hand, volatile matter measurement was conducted after moisture content test by heating the sample inside a lid covered crucible in a muffle furnace at (950 $\pm$ 20) $^{\circ}\text{C}$ for 7 min, and after cooling to ambient temperature the crucible was weighed and the volatile matter has been calculated as:

$$VM\% = \frac{\text{Loss of weight}}{\text{dried sample weight}} * 100\% \quad (1)$$

Moreover, the ash content was obtained after burning the sample in an open-lid crucible in a furnace operated at (700-750) $^{\circ}\text{C}$ for 4 hr. The remaining material was weighed

after cooling to room temperature[59]. Finally, the fixed carbon could be estimated directly from the following formula:

$$\%FC = 100 - (\%Moisture + \%VM + \%Ash) \quad (2)$$

2.5 Quantum Yield Estimation

The following equation was used to determine the fluorescence quantum yield (%QY) of CNDs:

$$QY = Q_R \frac{I}{I_R} \frac{A_R}{A} \frac{n^2}{n_R^2} \quad (3)$$

QY is the quantum yield, **I** is the measured integrated emission intensity, **n** is the refractive index, and **A** is the absorption of the sample. The subscript **R** refers to the reference fluorophore of known quantum yield. for water **n** is equal to 1.33. Quinine sulfate in 0.1 M H₂SO₄ (**Q_R** = 0.54 at 360 nm) was chosen as a reference. To minimize re-absorption effects, absorbencies in the 10 mm cuvette were kept under 0.1 at the excitation wavelength[60, 61]

2.6 Photodegradation of Methylene Blue (M.B)

Methylene blue (M.B) was prepared at a concentration of 35 µM by weighted 0.011 g of M.B powder and dissolved in 1 L of deionized water. To determine the wavelength of maximum absorption, a UV-Vis spectrum scan was done for the M.B solution.

M.B solution in the absence of CNDs was irradiated for 120 min by a tungsten visible light source of 50 W, and the UV-Vis absorption was recorded at 664 nm (maximum absorption peak) of M.B with 10 min interval.

500 µL of 0.27 mg/ ml CNDs were spiked to 3 ml of M.B solution and left first in dark for 10 min to achieve the absorption-desorption between solution moieties. The final obtained concentration of CNDs dose was 45 mg/L. For all photodegradation tests, M.B\CNDs solution was irradiated for 120 min and the U-Vis absorption at 664 nm was also recorded .The same procedure was repeated for CD300, CD400, CD500, and CD600 synthesized CNDs.

Chapter Three: Results and Discussion

3.1 Carbonization of olive solid wastes and CNDs Synthesis

The first step in the synthesis of CNDs was the carbonization of olive solid wastes at different temperatures to produce carbon-based material through a bottom-up approach. During this process, drying occurred at the first stages followed by volatile matters liberation and carbon cores build-up from the conversion of hemicellulose, lignin, and cellulose contents of olive solid wastes[62]. The degree of conversion highly depends on carbonization temperature and time which can be indicated initially from weight loss. The weight loss is affected by carbonization temperature as shown in (Figure 2a). Weight loss is increased dramatically (from 11.3 to 25.9%) when temperature increases from 300 to 500 °C and then remains nearly constant ($\approx 27\%$). The weight loss is related to the drop in moisture and volatile matter and the conversion of organic-based components into fixed carbon. To support the above findings proximate analysis was conducted to find percentages of moisture, volatile, ash, and fixed carbon contents, the proximate analysis at different carbonization temperatures is reported in (Table S1) in the supplementary.

Furthermore, (Figure 2b) illustrates how volatile matters are lost and fixed carbon increased by increasing temperature. The volatile matter content is high at low carbonization temperature (i.e., 66.7% at 300°C) which then decreased dramatically after raising the temperature to 400 °C (22.8%), on the other hand, fixed carbon increased from 29.3 to 67.63% at the same temperature range. Further increase in pyrolysis temperature would lead to partial combustion, high volatile matter loss, ash formation, and an increase in apparent density [63].

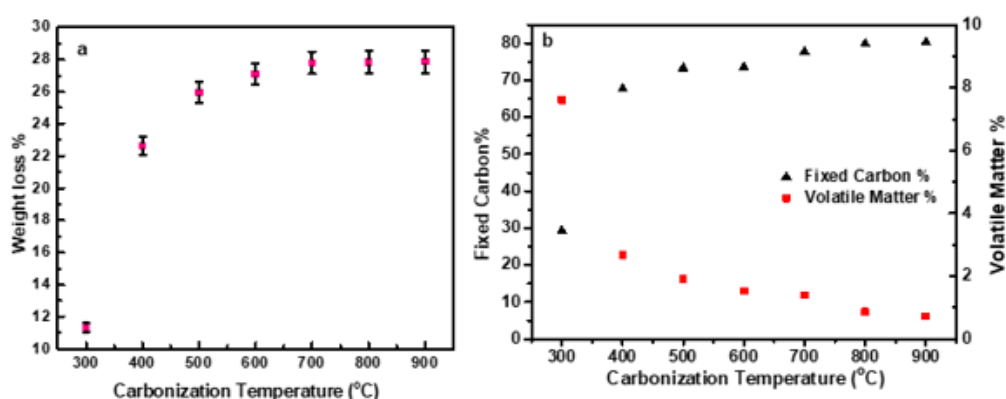


Figure 2:(a) Weight loss at different carbonization temperatures, (b) percent of fixed carbon and volatile matter vs. carbonization temperature.

The conversion of organic matters such as cellulose, lignin, and hemicellulose to carbonaceous materials can be followed up by FTIR acquisition of virgin olive solid wastes and carbonized particles at different temperatures (300, 400, 500, 600, 700, 800, and 900°C) showing a gradual conversion of these organic compound into carbon through the loss of oxygenated groups [64] indicating that the carbonization arrived at completion at 400 or 500°C and further increase of temperature may cause significant damage to the surface functional groups [65] as shown in (Figure 3b).

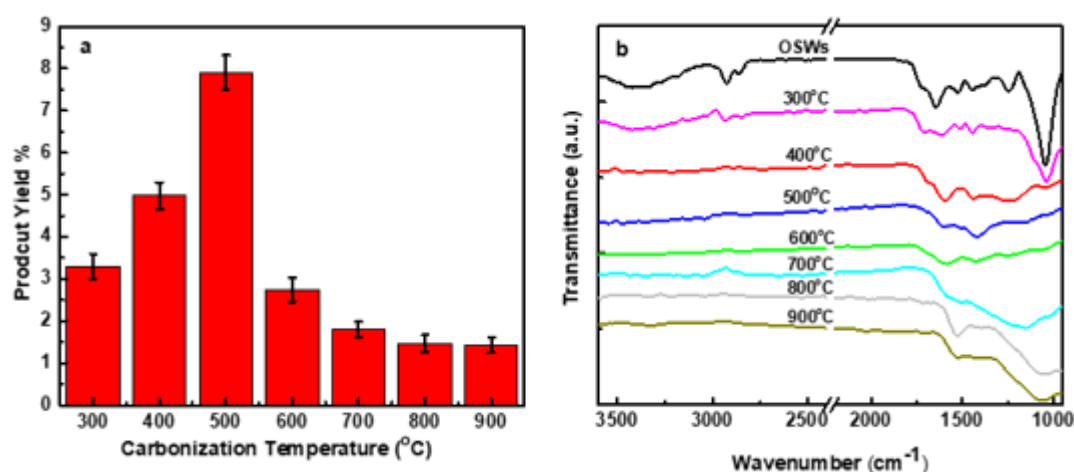


Figure 3:(a) Effect of carbonization temperature on the product yield, (b) FTIR of olive solid wastes.

The carbonized olive solid wastes and through a top-down approach were subjected to chemical oxidation by hydrogen peroxide as an oxidant agent to facilitate the breaking down and extraction of carbon dots from rich carbon particles prepared at different carbonization temperatures. CNDs are successfully obtained for all mentioned

temperatures with varied product yields. The product yield and as shown in (Figure 3a) increases from about 3.3% at 300 °C to 8% at 500 °C then decreased significantly when elevated temperatures are used in the carbonization of olive solid wastes. Firstly, the increase in product yield is related to the increase in the amount of fixed carbon with sufficient content of volatile matters which might facilitate the penetration of hydrogen peroxide into carbon particle and break it into small dots or they may (volatile matters) contribute as a carbon source in producing CNDs. Although carbonization at high temperatures gave high fixed carbon, the product yield was very low because of the high loss of volatile matter and formation of ash which in turn resulted in high compacted rigid carbon particles that hinder the ability of hydrogen peroxide to extract more CNDs.

3.2 Size and surface chemical groups

To study the morphology and size of prepared CNDs at different temperatures, AFM measurements were performed. (Figures 4a, & b) show AFM image and height profile of CD300 showing well dispersed CNDs with a height in the range of 0.3-8.5 nm having an average of 3.27 ± 1.05 nm as illustrated in the size distribution histogram (Figure 4c)

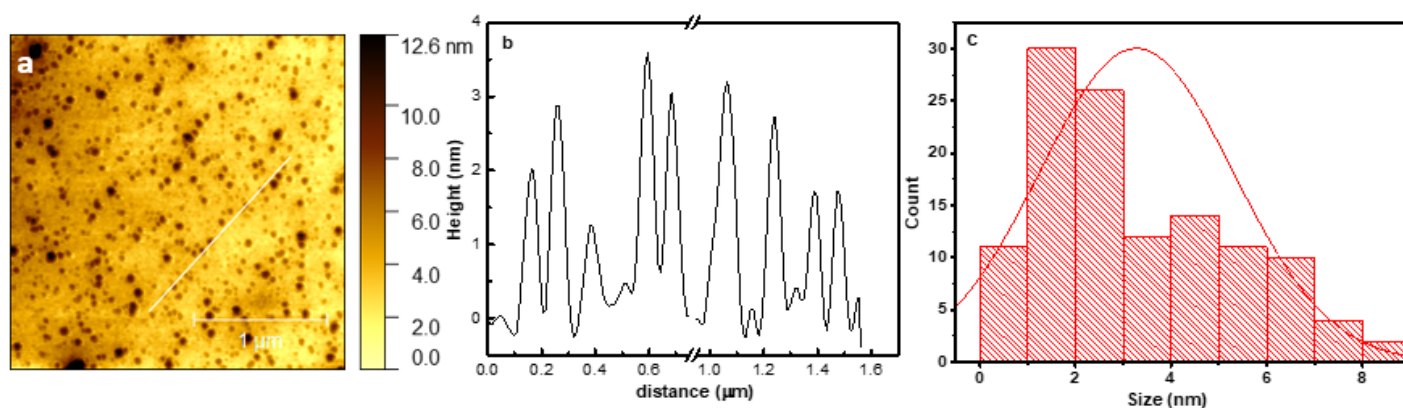


Figure 4: (a) AFM image, (b) Height profile, (c) distribution histogram of prepared CD300.

Other synthesized CNDs; CD400, CD500, and CD600 also show well size distribution with an average of 3.33 ± 1.3 , 3.74 ± 1.2 , and 3.37 ± 1.1 nm respectively. AFM images, profiles, and histograms are presented in (Figure S1, S2, and S3).

The chemical functional groups on the surface of synthesized CNDs were investigated by FTIR spectroscopy, the acquisition was done for powder CNDs obtained after lyophilization as shown in (Figure 5). The FTIR spectrum of CNDs prepared from precursor carbonized at 300 °C (named CD300) shows different peaks at 3256, 2820,

1711, 1600, 1397, 1326, 1230, and 1066/1038 cm^{-1} which could be assigned to -OH (hydroxyl)/N-H, C-H, C=O (carbonyl), COO^- (carboxylates), C-N, C-O-C (Epoxides) and hydroxyl groups respectively[5-7]. Some of these groups are originated from the used precursors and others are formed during the oxidation step by hydrogen peroxide. The presence of acidic and oxygenated groups on the surface was also confirmed by ζ -potential measurements with a strong negative charge of -33.6 ± 0.25 eV, such value manifests that the synthesized CNDs are well-dispersed in water[66-69]. Other synthesized C-dots; CD400, CD500, and CD600 show nearly similar spectra of CD300 spectrum with lack of some functional groups as C=O, C-N, and C-O-C in addition to the reduction in the intensity of C-OH peaks at 3256 and 1066 cm^{-1} and also the formation of intense C=C band. These differences are attributed to the original precursor which lacks these oxygenated groups because of carbonization at elevated temperatures[59]. The lack or decay of oxygenated groups was also confirmed by ζ -potential showing a drop in negativity when carbonization temperature increased, -33.6 for CD300 to -22.4 ± 0.23 for CD600. The negativity of CD400 and CD500 were -27.4 ± 0.85 and -23.01 ± 0.15 respectively.

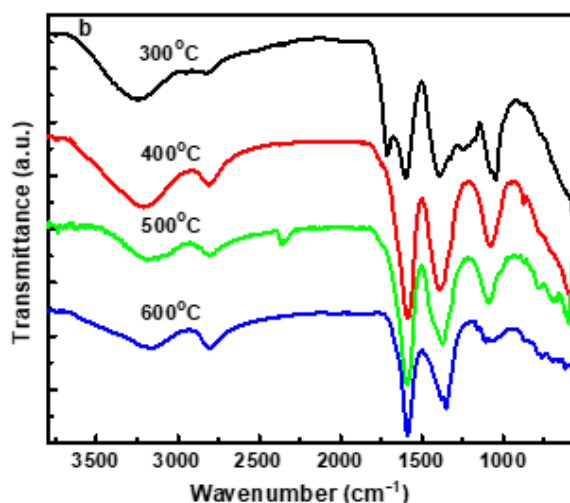


Figure 5: FTIR spectra of synthesised CNDs.

3.3 Optical properties

The optical properties of the synthesized CNDs were explored by conducting the UV-Vis and photoluminescence spectral acquisition. All synthesized CNDs (CD300 – CD600) are pale yellow colored and transparent under daylight while they emit bright blue fluorescence under UV light. The absorption spectrum of prepared CNDs as

illustrated in (Figure 6a) appears generally in the UV region with a tail extending towards the visible region which is considered usually the fingerprint of most CNDs[70]. No significant differences in formed peaks have been observed between different synthesized CNDs. The only difference which could be noticed is the value of the wavelength where CNDs start to absorb energy in the visible region, this discrepancy leads to different values of energy band gaps. The energy bandgap (optical) could be estimated using indirect bandgap calculations based on UV-Vis absorption spectra calculations and by plotting $(\alpha h\nu)^{0.5}$ versus $h\nu$ where h is plank constant, A is the measured absorption, ν is the frequency and $h\nu$ is equal to $1240/\text{wavelength}$ [71]. This plot (Tauc plot) includes a region with a linear relationship that is extrapolated to the x -axis to give the value of the energy bandgap in eV as presented in (Figure 6b). The bandgap for synthesized CNDs (CD300-CD600) has been estimated as in (Figure S4) and the results are 2.77, 2.65, 2.51, and 2.46 eV respectively. The values of the energy bandgap for synthesized CNDs 2.46 to 2.77 eV are in the visible region and still consistent with other studies showing C-dots with values range of 1.5-3.5 eV[4, 58]. Carbon dots synthesized from carbonized olive solid wastes at 300 °C (named CD300) show the highest energy bandgap of 2.77 eV, this high value compared to other CNDs (CD400, CD500, and CD600) could be attributed to the existence of oxygenated groups such as (C=O, C-O-C, and C-OH) on the surface and due to the highest withdraw electron charge capacity[72].

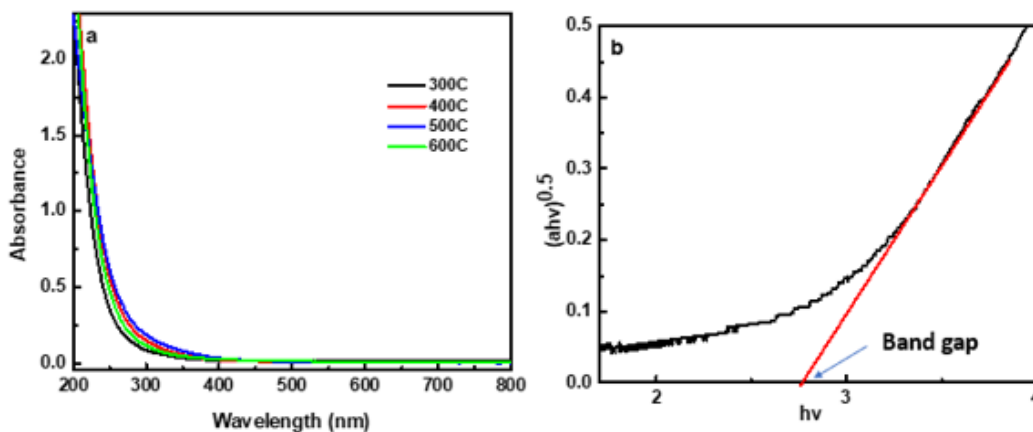


Figure 6: (a) The absorption spectra of prepared CNDs, (b) Tauc plot of CD300.

Photoluminescence (PL) measurements for CD300 solution, were carried out at different excitation wavelengths. The fluorescence spectra of CNDs in (Figure 7a) show a maximum emission at 440 nm and at an excitation of 360 nm wavelength. By exciting

from 300 to 360 nm, the CNDs emission intensity increased. At Excitation higher than 360 nm, the maximum emission wavelength shifted to lower energy values with a simultaneous decrease of the fluorescence intensity, this emission excitation dependence is a well-known phenomenon of CNDs [73-75] and could be ascribed to surface defects, different functional groups and emissive surface energy traps[76-78]. The fluorescence of other synthesized CNDs (CD300-CD800) was measured at an excitation wavelength of 360 nm (maximum intensity) as illustrated in (Figure 7b). The fluorescence intensity is decreased when the carbonization temperature increases from 300 to 800°C. Furthermore, fluorescence quantum yield was measured with quinine sulfate (%QY =54%) as a standard reference. (Figure 8) shows QY % for all samples. It is obvious that the QY decreases when carbonization temperature was altered, with a drop of about 2 folds when temperature increased from 300 to 800 °C, this decay could be attributed to the loss of surface defects and diminish of some PL emission responsible oxygenated groups (as carbonyl, carboxyl, epoxides and hydroxyl groups[79]) during carbonization at elevated temperatures [63] and the partial disability of reforming these groups during chemical oxidation step of CNDs synthesis. This was clear from the FTIR acquisition for both raw carbons and synthesized CNDs, (Figure 3b and 5). Detailed calculation of quantum yield is reported in (Table S2).

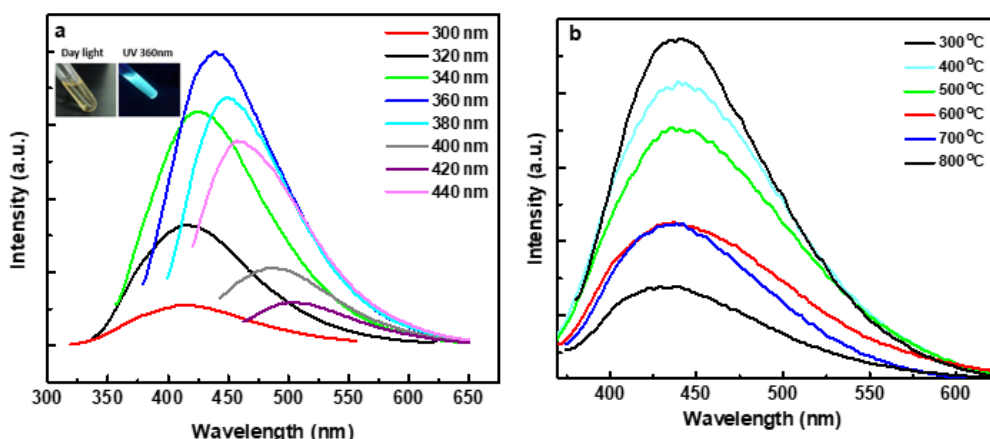


Figure 7: (a) Photoluminescence (PL) intensity at different excitations wavelengths for CD300, (b) PL intensity for 360 nm at different carbonization temperature.

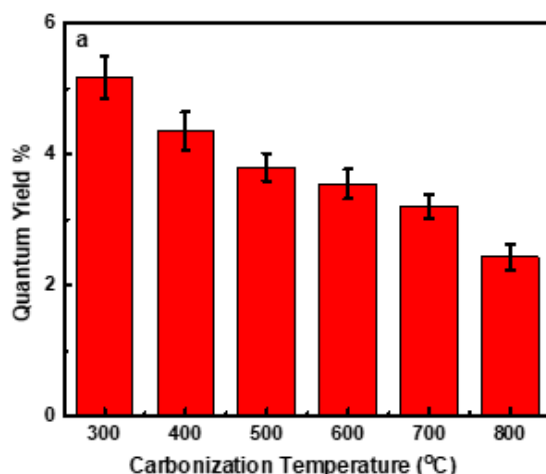


Figure 8: Quantum Yield of synthesised CNDs.

3.4 Photodegradation Methylene Blue (M.B)

The degradation of M.B by CNDs synthesized at different carbonization temperatures was investigated. 500 µl of 0.27mg/ml CNDs were added to M.B solution to obtain a final CNDs dose of 45 mg/L and then irradiated for 120 minutes by a visible tungsten light of 50W. Every 10 minutes, the UV-Vis absorptions were recorded at 664 nm as in (Figure 9a), and the degradation efficiency was evaluated and plotted versus time.

For prepared CNDs (CD300 – CD600) and as shown in (Figures 9b and c), the degradation efficiency at 120 min is increased from 27.4% in the absence of the photocatalyst up to 100% in the presence of CD300. The degradation efficiency was estimated by the following equation:

$$\text{Degradation Efficiency (\%D)} = \frac{A_o - A}{A_o} \times 100\% \quad (5)$$

Where A_o the absorbance of M.B at $t=0$, A absorbance at different time

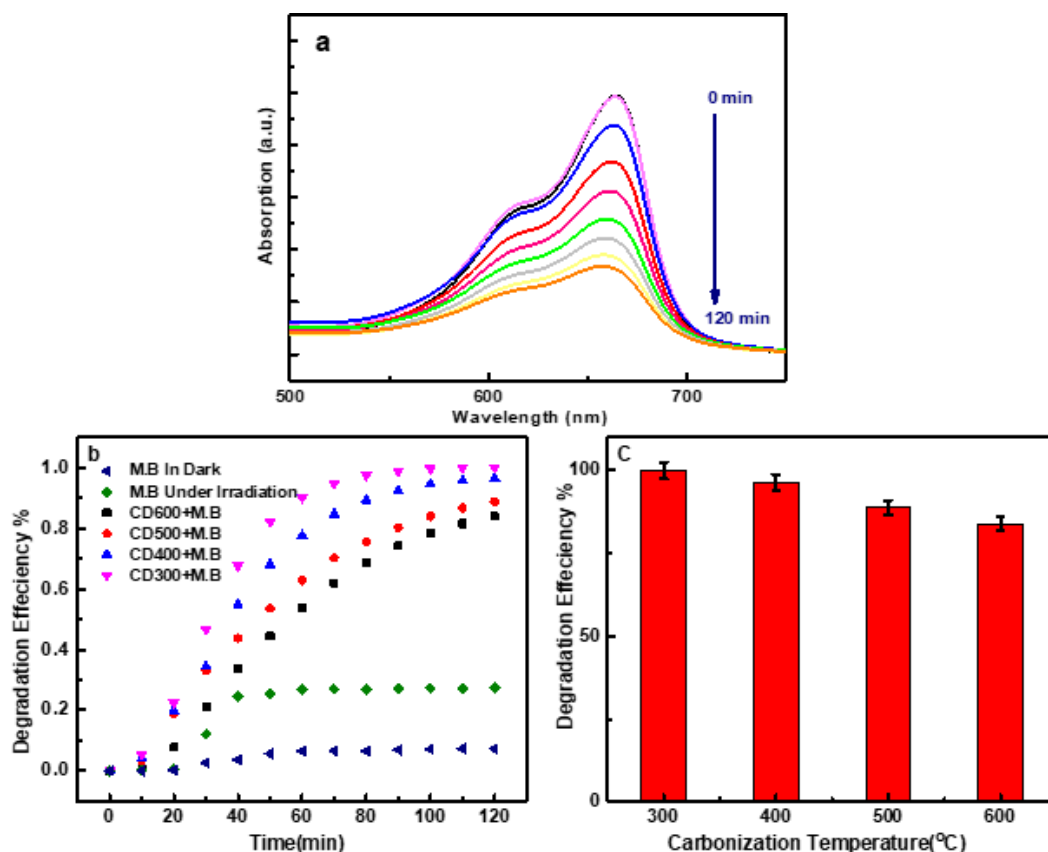


Figure 9:(a) UV-Vis spectrum of M.B solution spiked with 500 μ l of CNDs and irradiated by 50 W visible light for 120 minutes, (b) Degradation efficiency of CNDs at different times (C) Degradation efficiency of M.B spiked with CNDs under light irradiation.

Because the M.B dye is a heterocyclic aromatic chemical compound with three- coupled aromatic rings and functional groups (C–S), (CN), and (C=N), there was no degradation in the dark. Because of the complicated carbon-bonding in the M.B structure, the adsorption reaction between CNDs and M.B molecules was difficult[6]. While the poor degradation of methylene blue in the absence of a photocatalyst (27%) can be attributed to the lone pairs present at the nitrogen and sulfur atoms in M.B. After being exposed to light, these electron-rich areas become active. They possessed repulsive forces between bond pair electrons, which created instability, therefore they attacked the water molecules in their environment to form a stable bond[7]. The photodegradation of the M.B solution was also examined by the use of other prepared CNDs (CD400, CD500, and CD600) with the same dose and previously followed procedure. The degradation efficiency decreased slightly with increasing the carbonization temperature of the olive solid wastes as illustrated in (Figures 9b, c).

The degradation rate is another important degradation parameter that should be considered. In this work, the Langmuir–Hinshelwood dynamic model was

suggested[80], where the degradation kinetics of M.B can be simplified using the pseudo-first-order kinetic as indicated in equation (6)

$$\ln\left(\frac{A_0}{A}\right) = k \times t \quad (6)$$

Where A_0 and A should be the equilibrium absorbance and the absorbance of M.B after irradiation time t , respectively, and k represents the dye degradation rate constant. For example, a fitted plot of $\ln(A_0/A)$ vs time, as shown in (Figure 10a), gives a straight line with a slope representing the rate of degradation of CD300. The degradation rates of M.B in the presence of other CNDs are shown in (Figure 10b).

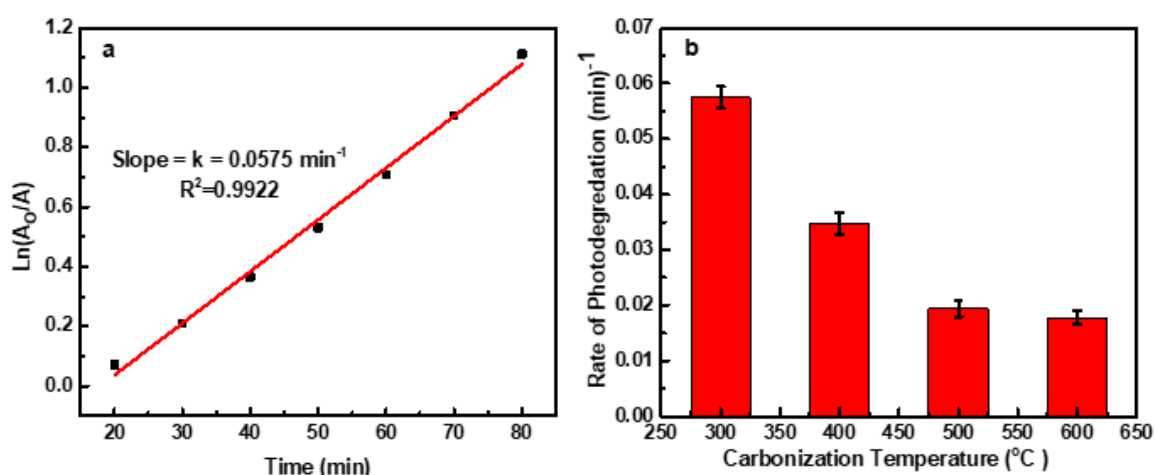


Figure 10: (a) Fitting of Langmuir–Hinshelwood dynamic model at 45 mg/L CD300, (b) Degradation rate of M.B at different temperatures of CNDs.

CD300 gives the highest degradation rate of the M.B solution with 0.0575 min^{-1} , in addition to degradation efficiency of 100% after 120 min. The degradation rate is gradually decreased when carbonization temperature increases by -3.25-fold when the temperature raised from 300 to 600 $^{\circ}\text{C}$. The high degradation efficiency and the rate at 300 $^{\circ}\text{C}$ are ascribed to a wide bandgap compared to other synthesized CNDs, because an increase in bandgap energy in the visible region 2.46 to 2.77 eV can increase separation of holes (h^+) and electrons (e^-) and hinder and delay the rapid recombination process of charge carriers h^+ and e^- [81].

When high-energy photons excite CNDs, electrons are excited from the ground state (valence band) to the excitation state (conduction band), resulting in excess electrons (e^-) and holes (h^+). Because of the abundance of surface defects on CNDs, some excited carriers are trapped, preventing e^- and h^+ recombination. As a result, the methylene

blue might be immediately oxidized by h^+ , resulting in degradation[62]. Meanwhile, part of the e^- may be caught by oxygen dissolved in the solution, resulting in superoxide radicals, while some of the h^+ may interact with surface-adsorbed H_2O , resulting in hydroxyl radicals. Organic dyes are known to be degraded by reactive oxygen species (ROS), superoxide[82], and hydroxyl radicals[62, 83]. The degradation mechanism is summarized in (Figure 11).

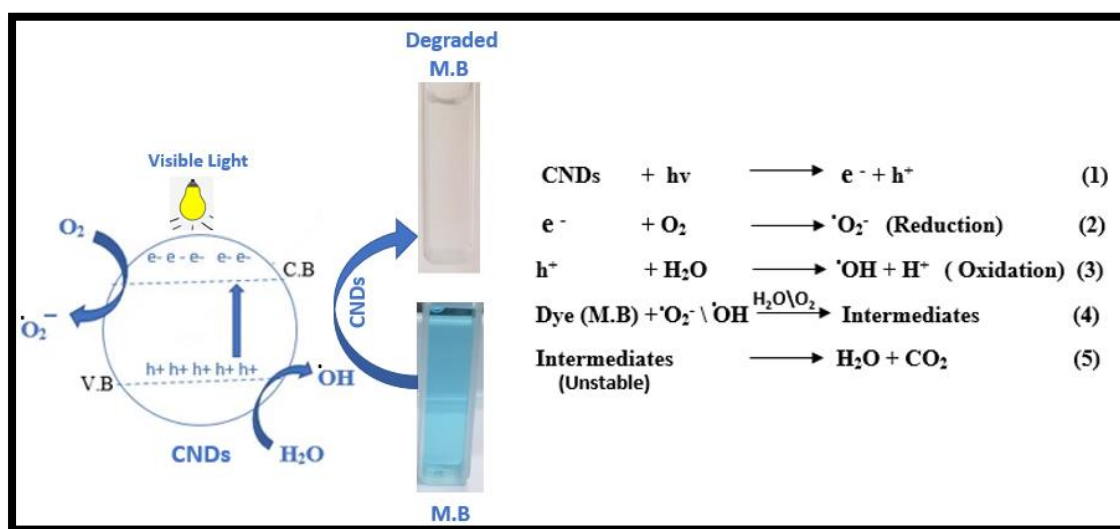


Figure 11: The degradation mechanism of methylene blue.

It is worthy to point that CNDs prepared in this work are shown to be very promising candidates for dye photodegradation, environment protection, and cleanliness. Synthesized CNDs at different carbonization temperatures have been compared with other works in terms of M.B photodegradation efficiency and rate showing excellent results as summarized in (Table 1)

Table 1: Compare CNDs synthesized with other works in terms of M.B photodegradation efficiency and rate.

CNDs precursor	Efficiency (%)	Rate (min ⁻¹)	Dose (mg/L)	Degradation Time (min)	Light source	Photocatalyst	Dye	[Ref]
Graphite rods	94.45	0.0080	1000	120	Tungsten light (400 W)	CQDs/Bi ₂ O ₂ CO ₃	M.B	[84]
ascorbic acid	56.00	0.0284*	500	90	Tungsten light (400 W)	mesoporous hematite + CQD	M.B	[85]
citric acid and O-phosphoryl ethanol amine	91.5*	0.0808*	2000	25	Xenon lamp (300 W)	CQDs/TiO ₂	M.B	[86]
Solid tire wastes	90.00	0.0852*	0.4	1560	UV (10 W high-pressure Hg lamp)	ZnO-P-CNDs	M.B	[87]
Pear juice	99.50	0.03889*	N. R	130	Tungsten lamp(60W)	CQDs	M.B	[62]
Frying oil	88.00	0.0777*	N. R	1800	UV light	CNDs	M.B	[88]
Uric acid, HCL, and glucose	50.00	0.0248*	N. R	1500	Tungsten light (20W)	CNDs	M.B	[89]
Uric acid, HCL, and glucose	95.00*	0.0867*	0.4	1800	Tungsten light (20 W)	ZnO +CNDS	M.B	[89]
Glucose +Sodium hydroxide +acetic acid	29.00*	0.0107*	2000	30	xenon lamp (400 W)	magnetic CNDs	M.B	[90]
Citric acid and urea	99.90	0.0447	1000	90	solar light	CQDs+TiO ₂	M.B	[91]

Citric acid	99.90	0.0240	3000	170	high power mercury-xenon light source set at 310 W	CNDs	M.B	[92]
Olive solid wastes								
CD300	100.00	0.0575	45	120	Tungsten light (50 W)	CNDs	M.B	in this work
CD400	96.50	0.0348	45	120	Tungsten light (50 W)	CNDs	M.B	
CD500	88.80	0.0194	45	120	Tungsten light (50 W)	CNDs	M.B	
CD600	83.80	0.0177	45	120	Tungsten light (50 W)	CNDs	M.B	

*Not reported, calculated from the available data

N.R =Not reported by the author.

Conclusion

In this work, carbon nanodots were synthesized by the combination of pyrolysis (carbonization) of olive solid wastes and chemical oxidation of produced carbonaceous material, clarified that the carbonization temperature had a significant effect on the production yield of CNDs with an increase by increasing the temperature up to 500°C and then decayed to very low values. Furthermore, the carbonization temperature affected strongly the properties and intended applications of synthesized C-dots. Negativity, quantum yield, energy bandgap, and photoactivity are the main affected properties with maximum values obtained for CNDs produced from olive solid wastes at 300 °C due to existing oxygenated functional groups on the surface. The prepared CNDs were efficient visible-light photocatalysts used successfully to photodegrade methylene blue with an efficiency of 100% after 120 minutes and a rate equal to 0.0575 min⁻¹. It was also obvious that an increase in carbonization temperature from 300 to 600 °C resulted in a decrease of the degradation rate of about 3.25 folds which could be ascribed to rapid electron-holes recombination in CNDs produced by carbonization at elevated temperatures.

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Supplementary Information

Table S1: The proximate analysis at different carbonization temperatures .

Carbonation temperature °C	Moisture Content (%)	Volatile Matter (%)	Ash Content (%)	Fixed Carbon (%)
Virgin OSW	4.3	73.7	2.0	20.6
300	0.9	64.7	5.1	29.3
400	2.17	22.8	7.4	67.63
500	0.5	16.2	9.0	73.3
600	0.5	13.0	13.0	73.5
700	0.8	11.9	9.6	77.7
800	1.0	7.4	11.7	79.9
900	4.1	6.2	9.4	80.3

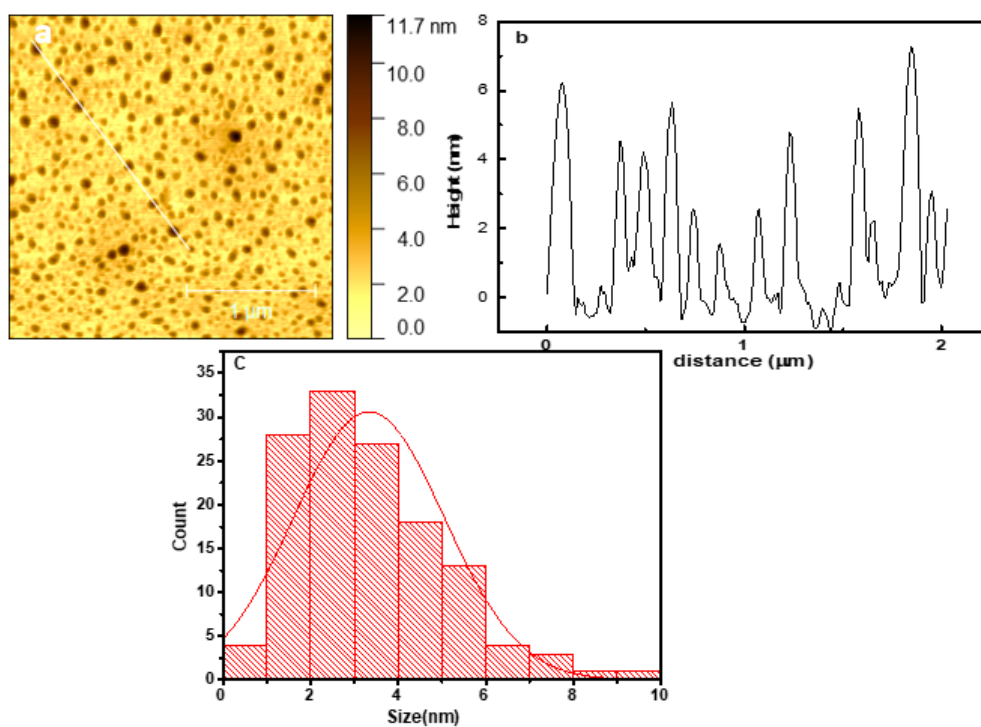


Figure S1: (a) AEM image, (b) Height profile, (c) distribution hisdtogram of prepared CD400.

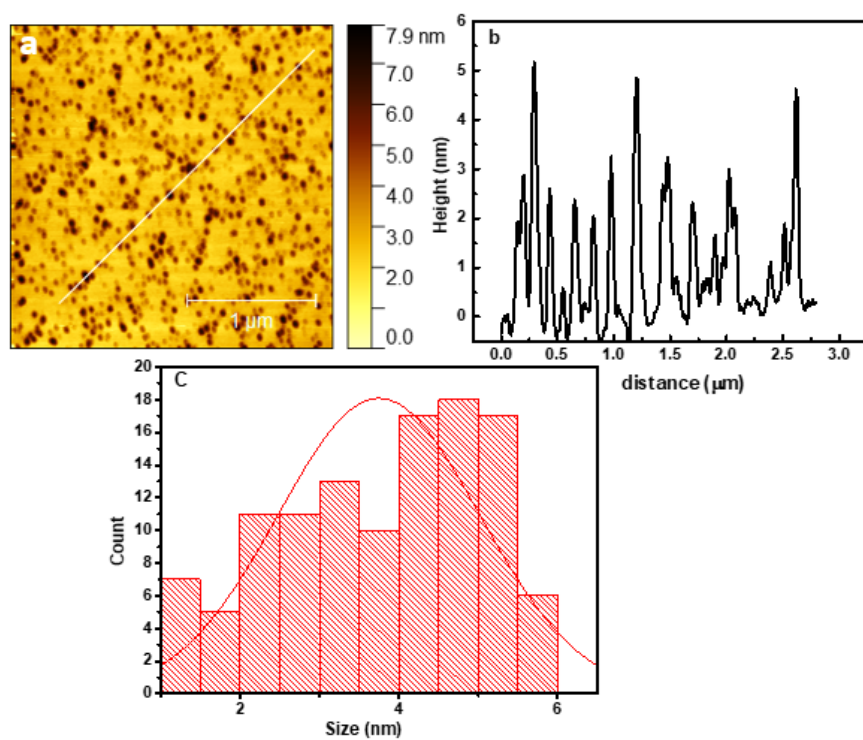


Figure S2: (a) AEM image, (b) Height profile, (c) distribution histogram of prepared CD500.

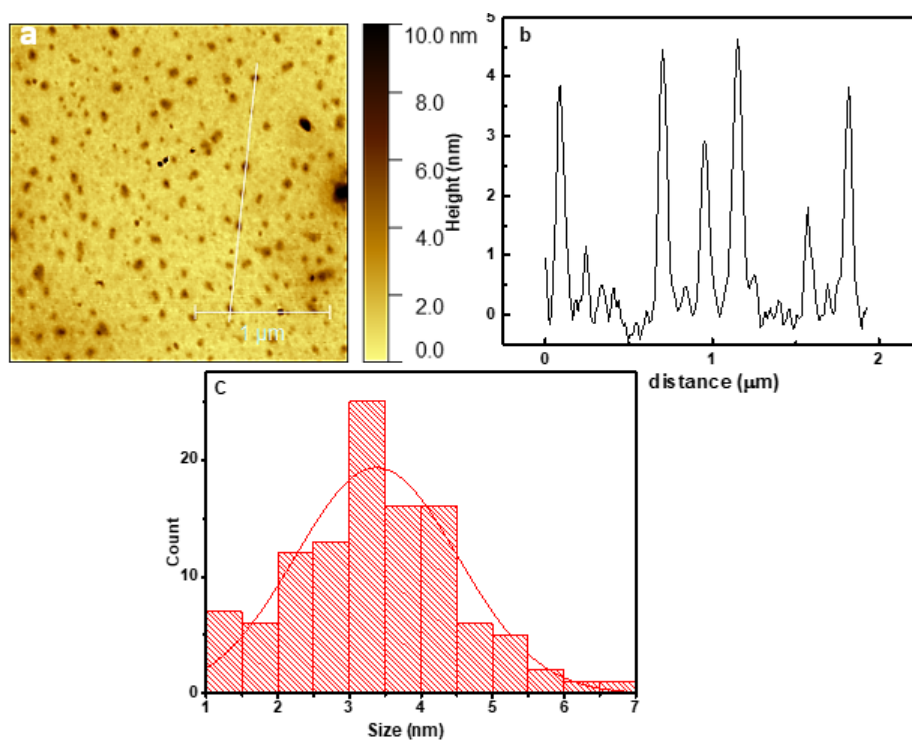


Figure S3: (a) AEM image, (b) Height profile, (c) distribution histogram of prepared CD600.

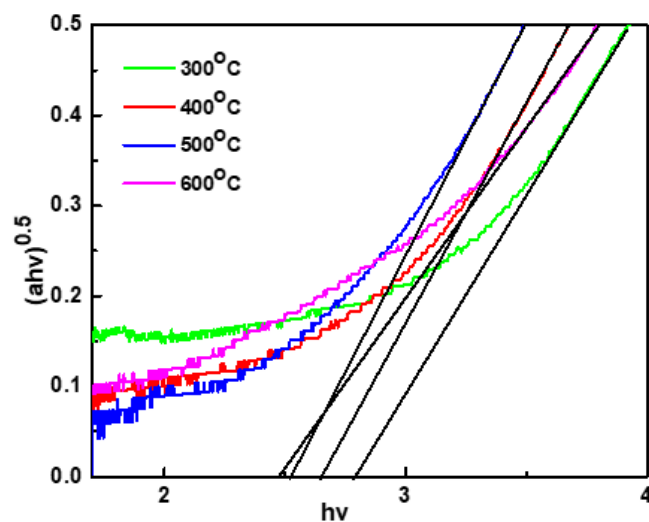


Figure S4: Tauc plot of CD300, CD400, CD500, and CD600.

Table S2: Calculation of Quantum Yield (QY).

Temperature (°C)	Integrated Intensity	Absorbance	Intensity/Absorbance	QY%
300	11.01	0.075	146.83	5.17
400	10.61	0.086	123.37	4.34
500	9.39	0.087	107.98	3.80
600	6.33	0.063	100.59	3.54
700	5.36	0.059	90.85	3.20
800	3.66	0.053	69.06	2.43
Standard (Quinine sulfite)	151.45	0.097	1561.32	55.00