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Green Synthesis of Nano Graphite Materials from Lemon and Orange Peel: A Sustainable Approach for Carbon-Based Materials †

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Abstract: This research paper presents a study on the preparation and characterization of nano graphite materials (NGMs) from lemon and orange peel powder using the pyrolysis method. The NGMs were analyzed using X-ray Diffractometer (XRD) and Fourier transform infrared spectroscopy (FTIR) for structural and compositional properties. The XRD analysis confirmed the crystalline nature of the NGMs, while the FTIR analysis provided information about the functional groups present in the materials. Our results suggest that NGMs fabricated from lemon and orange peel powder have potential for applications in various fields, including energy storage and catalysis.

Keywords: nano graphite materials (NGMs); lemon peel; orange peel; pyrolysis; characterization; X-ray diffractometer; Fourier transform infrared spectroscopy; structural properties; compositional properties; energy storage; catalysis

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1. Introduction

Nano graphite materials (NGM) have received a lot of interest lately because of their distinctive qualities, including chemical stability, high water solubility, affordability, and fluorescent traits (Wang, (2014)). It is possible to roughly divide the synthesis of NGM into "top-down" and "bottom-up" methods [1,2]. By dissolving bigger carbon materials using techniques including arc discharge, laser ablation, and chemical oxidation, NGMs are created in the top-down process [3–5]. On the other hand, the bottom-up strategy uses processes including hydrothermal, thermal-decomposition, and microwave approaches to create NGMs from molecular carbon precursors [5–11]. Many of these synthesis procedures, however, involve numerous steps and are laborious; they frequently need pricey carbon sources and follow-up surface passivation [12–15].

Numerous green synthesis methods have been studied to address these issues. These methods make use of low-cost and organic carbon sources such chitosan, egg yolk oil, juice from oranges, lemon peel, bee pollen, collagen, humic substances, the hair, nut shells, milk from soybeans, cashew gum, and garlic [6,13,15–21]. The seasonal variation and foreign contaminants present in natural carbon sources, which might influence the repeatability, shape, and size distribution of NGMs [12], provide difficulties with their utilization. It is still very difficult to achieve uniformity and essential purity in NGMs made from natural carbon sources [6,13,15–20]. Additionally, conventional analytical techniques that concentrate on pH-dependent photoluminescence (PL) spectra of NGMs sometimes miss important data from various excitation wavelengths and pH ranges [6,8,9,13,16–20,22].

As a natural carbon source, lemon and orange peels were used in this work to create nano graphite materials (NGMs) by the pyrolysis method. This method makes it possible to create NGMs with a limited size distribution, a feat that has never been accomplished

utilizing the pyrolysis of natural carbon sources [7,23]. We investigate how reaction time and temperature affect the pyrolysis procedure, offering information on how to create NGMs with useful features. Notably, the created NGMs show outstanding colloidal solubility, photo-stability, and environmental stability without the need for further surface passivation procedures to improve their fluorescence capabilities [24].

The effective synthesis of NGMs from lemon and orange peels offers up new opportunities for their use in a variety of industries, including sensors, solar cells, supercapacitors, LED technology, printing, and bio-sensing [13,25–29]. The objective of this study is to enhance our understanding of the potential applications of nano graphite materials (NGMs) as humidity sensors by utilizing a sustainable and cost-effective carbon source and applying machine learning analysis techniques. Humidity sensors play a crucial role in various fields, including environmental monitoring, agriculture, and industrial processes. However, the development of high-performance humidity sensors with improved sensitivity, stability, and cost-effectiveness remains a challenge.

In this research, NGMs were synthesized from lemon and orange peel powder using the pyrolysis method. The use of these natural carbon sources provides a sustainable and affordable alternative for the fabrication of NGMs. The synthesis process involved grading, sorting, and washing the peel, followed by crushing/grinding and pyrolysis at 500 °C for 3 h. After synthesis, the NGMs were subjected to sonication, centrifugation, and drying processes to obtain the final material.

To evaluate the suitability of NGMs as humidity sensors, their properties were characterized using various techniques. X-ray diffraction analysis (XRD) was used for phase identification and characterization of crystalline materials based on their diffraction patterns. Fourier transform infrared spectroscopy (FTIR) provided insights into the functional groups present in the NGM experimental methods.

The following steps are for the synthesis of NGMs by orange and lemon peel.

2. Synthesis of NGMs

Nano graphite materials were synthesized by the pyrolysis method. Grading, sorting, and washing lemon and orange peel was carried out to obtain fresh lemon and orange peels, which were then carefully sorted to remove any damaged or discolored parts. The peels were then thoroughly washed with deionized water to remove any surface impurities. The washed lemon and orange peels were dried to remove excess moisture, and then they were crushed or ground into fine particles. This step aimed to increase the surface area of the peels for better pyrolysis efficiency. The crushed or ground peels were subjected to pyrolysis in a controlled environment at a temperature of 500 °C for a duration of 3 h. Pyrolysis involves the decomposition of organic materials in the absence of oxygen, resulting in the formation of carbon-based materials such as NGMs. After pyrolysis, the resulting NGMs were subjected to sonication for 10 min. Sonication involves the use of ultrasonic waves to disperse and break down any aggregated particles, ensuring a more uniform dispersion of NGMs. To separate any remaining impurities or larger particles from the NGMs, centrifugation was performed at a speed of 800 rpm for 10 min. Centrifugation causes the NGMs to settle at the bottom, while impurities and larger particles are separated and collected in the supernatant. The purified NGMs were then dried to remove any residual moisture. This step aimed to obtain dry and stable NGMs suitable for further characterization and application.

2.1. Characterization of NGM

2.1.1. X-ray Diffraction Analysis (XRD)

XRD is a quick analytical method for characterizing crystalline materials based on their diffraction patterns and identifying their phases. Constructive interference is created when X-rays make contact with a crystallite NGM sample, and these diffracted X-rays are then detected, processed, and tallied, exposing the outcomes that are depicted in Figure 1. The XRD spectra for NGMs made from powdered lemon peel are displayed in

Figure 1. For NGMs, one sharp peak can be observed at 2θ = 22.8°. With the use of the Scherrer Formula, this peak indicated the presence of a well-ordered layer structure with a 0.365754 nm d-spacing (FWHM = 0.825°) and determined the size of NGM made from lemon peel powder to be 9.818 nm. An as-synthesized NGM sample's purity may also be determined using XRD. The inadequate carbonization of lemon peel powder resulted in many impurity peaks in the XRD pattern of NGM, as shown in Figure 1 above. Although the XRD is a useful tool for characterizing NGM with a crystallite structure, it cannot be used to determine the essential characteristics of amorphous NGM.

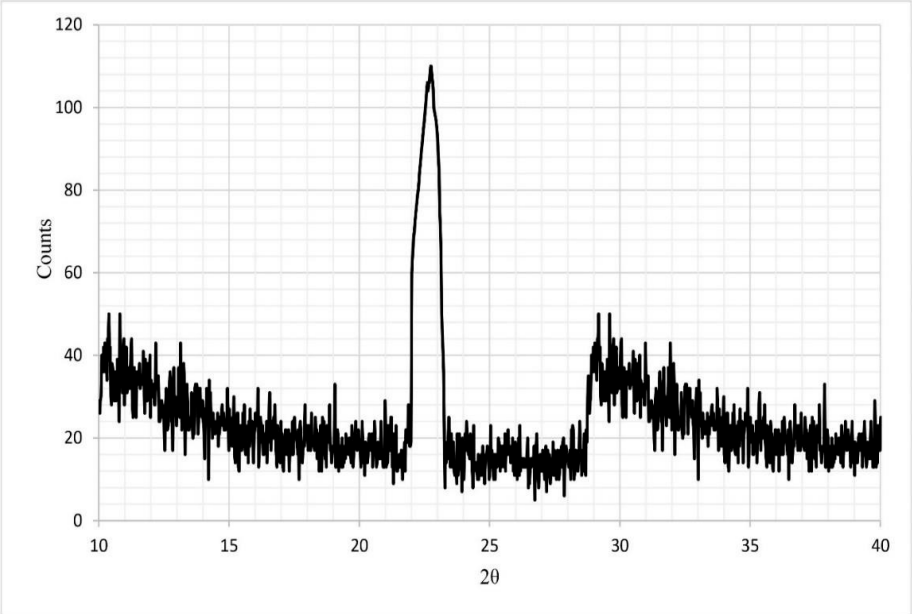

Figure 1. Diffraction pattern of NGMs fabricated from lemon peel powder.

The XRD spectra for carbon nano dots made from the powdered orange peel are displayed in Figure 2. At 2θ = 23°, one distinct peak for NGMs can be seen. This peak demonstrated a well-ordered layer structure with a 0.395199 nm d-spacing (FWHM = 0.689°), and the Scherrer formula was used to determine the size of the NGM made from orange peel powder, which was determined to be 11.760 nm. An as-synthesized NGM sample's purity may also be determined using XRD. Figure 2 shows that a number of impurity peaks were seen in the XRD pattern of NGMs as a result of the orange peel powder's inadequate carbonization. The reaction temperature and reaction time are the causes of the as-synthesized NGM's size fluctuation.

2.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were used to corroborate the surface functional groups and chemical makeup of the as-synthesized NGMs from lemon peel powder. According to Figure 3, the NGMs FTIR spectra include prominent peaks at 3250, 2350, 1620, 1380, and 1110 cm^{-1}, which correspond to O-H, C-H, C=O, C=C, and (C-O or C-H) accordingly. While the O-H, C=O, and C-H bending peaks imply that the NGMs contain O-H, C=O, and C-H surface moieties linked to their surfaces, the existence of the C=C peak suggests that the NGMs are formed of graphitic structure. The surface of the as-synthesized NGMs comprises inherent negatively charged moieties, which are necessary for long-term water solubility, according to FTIR analysis. According to Figure 4, the NGMs FTIR spectra include substantial peaks at 3200, 2380, 1595, 1395, and 1105 cm^{-1}, which correspond to O-H, C-H, C=O, C=C, and (C-O or C-H) accordingly. While the O-H, C=O, and C-H bending peaks imply that the NGMs contain O-H, C=O, and C-H surface moieties linked to their surfaces, the existence of the C=C peak indicates that the NGMs are formed of graphitic structure. The surface of

as-synthesized NGMs comprises inherent negatively charged moieties, which are necessary for long-term water solubility, according to FTIR research.

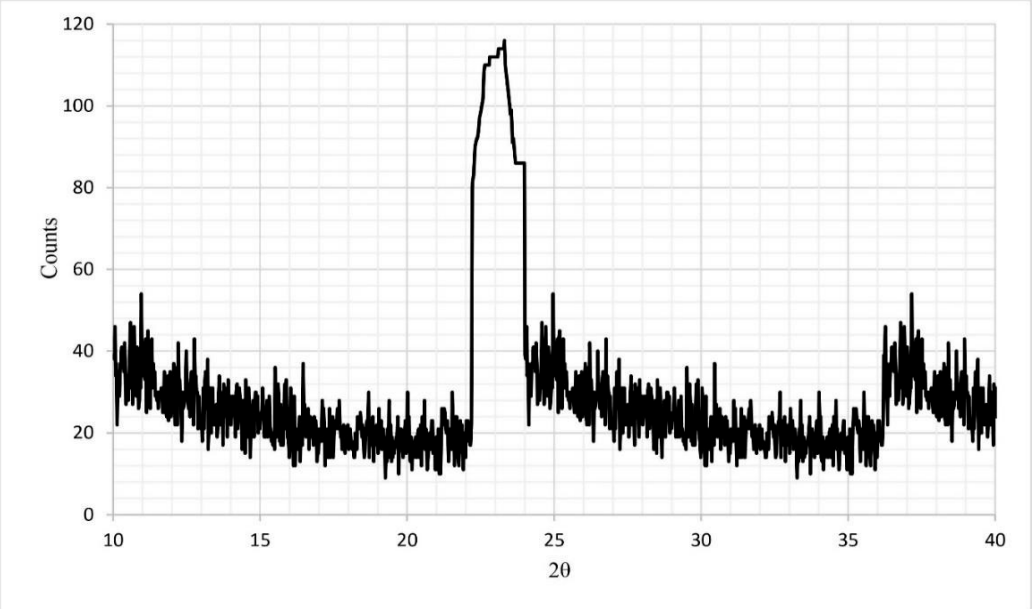

Figure 2. Diffraction pattern of NGMs fabricated from orange peel powder.

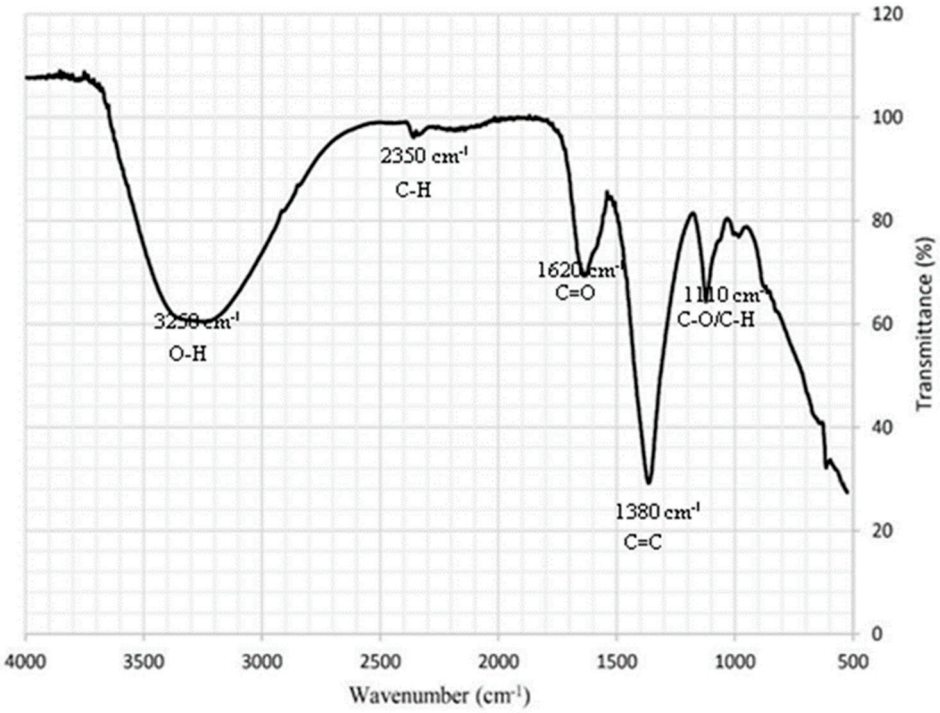

Figure 3. FTIR spectra of NGMs fabricated from lemon peel powder.

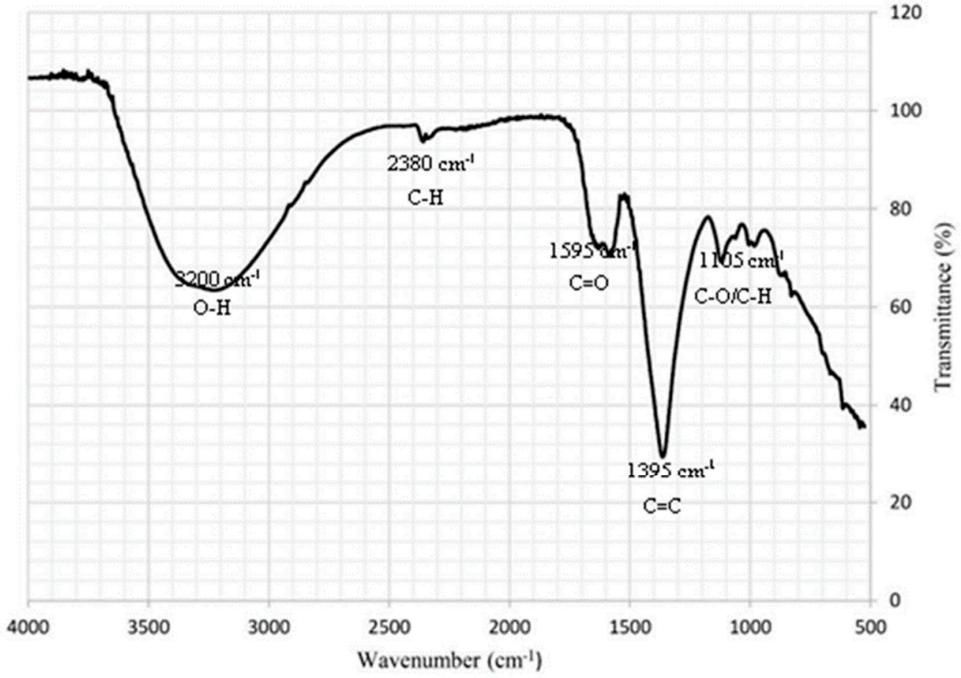

Figure 4. FTIR spectra of fabricated from orange peel powder.

3. Results and Analysis

In this section, we will discuss the results obtained from the X-ray diffraction (XRD) analysis and Fourier-transform infrared spectroscopy (FTIR) experiments. The detailed XRD patterns of the nano-materials (NGMs) can be found in Appendix A, which reveal critical insights into their crystalline nature, crystal structure, and crystallite size. Similarly, the FTIR spectra, along with the identified functional groups, are also presented in Appendix A, offering valuable information about the NGMs' chemical composition and potential applications.

4. Conclusions

In conclusion, the utilization of waste and by-products in the synthesis of nanomaterials (NGMs) represents a significant advancement, driven by the diverse range of applications associated with these materials. Notably, the composition of the raw materials obtained from waste sources, such as lemon (9.818 nm) and orange (11.760 nm) peel powders, results in varying quantum yields, highlighting the influence of their heterogeneous nature (see Table 1). Furthermore, the adoption of different reaction conditions and synthesis methods introduces further complexities regarding the chosen route. Even when starting from identical raw materials and employing the same synthesis method, the variation in synthesis parameters leads to distinct effects on the characteristics and properties of the resulting NGMs. This underscores the importance of understanding and optimizing the synthesis process for the desired application of these environmentally friendly nanomaterials.

Table 1. Size of NGMs fabricated from fruit peel powder.

Fruit	Size of (NGM) (nm)
Lemon	9.818
Orange	11.760

Author Contributions: M.F.W.B. conducted the synthesis of lemon and orange peel-based nanomaterials (NGMs), performed X-ray diffraction (XRD) analysis, and conducted Fourier-transform infrared spectroscopy (FTIR) experiments. Additionally, M.F.W.B. contributed to the manuscript preparation and research design under the supervision of S.F.H., the second author. S.F.H., the second author supervised and guided the first author in the synthesis of NGMs, provided expertise in experimental techniques, and contributed to the research design. Additionally, S.F.H. assisted in data analysis and manuscript preparation. M.F.S., the third author provided valuable guidance and insights throughout the research project, and contributed to the research design, experimental planning, and manuscript revision. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement: As this research primarily involved laboratory-based experiments using fruit peel powder for nanomaterial synthesis and characterization, it did not require approval from an Institutional Review Board (IRB). However, the utilization of NED University's Chemical Department laboratories and instruments adhered to all institutional safety and ethical guidelines.

Informed Consent Statement: Given the nature of this research, which focused on materials synthesis and characterization, no informed consent from human participants or animals was necessary. All experiments were conducted in compliance with NED University's safety and ethical protocols.

Data Availability Statement: The data generated and analyzed during this study are available upon request from the author Farrukh Waheed for the purpose of academic transparency and scientific inquiry. Additionally, the XRD and FTIR data were obtained using the facilities at NED University, and access to these data can be facilitated through the university's research department.

Conflicts of Interest: The authors declare no conflict of interest regarding the publication of this research. Furthermore, the collaboration with NED University for laboratory facilities and instrumentation usage was conducted in accordance with mutually agreed terms and academic objectives, without any conflict of interest.

Appendix A

The XRD patterns of the NGMs revealed diffraction peaks at specific angles, indicating the presence of crystalline phases. The peak positions and intensities were analyzed to determine the crystal structure of the NGMs. By comparing the obtained diffraction pattern with standard reference patterns, the crystal structure of the NGMs could be identified. The crystallinity of the NGMs was evaluated by calculating the crystallite size using the Scherrer equation.

The XRD analysis provided valuable insights into the structural properties of the NGMs, confirming their crystalline nature and providing information about the crystal structure and crystallite size.

The FTIR spectra of the NGMs exhibited characteristic absorption bands that corresponded to specific functional groups present in the materials. The peaks observed in the spectra were assigned to different vibrations and modes associated with chemical bonds. By comparing the obtained spectra with reference spectra and databases, the functional groups present in the NGMs were identified. The intensity and position of the absorption peaks were analyzed to gain insights into the chemical composition and bonding characteristics of the NGMs.

The FTIR analysis provided valuable information about the functional groups present in the NGMs, allowing for a better understanding of their compositional properties and potential applications in various fields.

References

1. Wang, Y.; Hu, A. Carbon quantum dots: Synthesis, properties and applications. *J. Mater. Chem. C* **2014**, *2*, 6921–6939. [CrossRef]
2. Liu, H.; Li, Z.; Sun, Y.; Geng, X.; Hu, Y.; Meng, H.; Ge, J.; Qu, L. Synthesis of Luminescent Carbon Dots with Ultrahigh Quantum Yield and Inherent Folate Receptor-Positive Cancer Cell Targetability. *Sci. Rep.* **2018**, *8*, 1086. [CrossRef] [PubMed]
3. Xu, X.; Ray, R.; Gu, Y.; Ploehn, H.J.; Gearheart, L.; Raker, K.; Scrivens, W.A. Electrophoretic Analysis and Purification of Fluorescent Single-Walled Carbon Nanotube Fragments. *J. Am. Chem. Soc.* **2004**, *126*, 12736–12737. [CrossRef] [PubMed]
4. Li, X.; Wang, H.; Shimizu, Y.; Pyatenko, A.; Kawaguchi, K.; Koshizaki, N. Preparation of carbon quantum dots with tunable photoluminescence by rapid laser passivation in ordinary organic solvents. *Chem. Commun.* **2010**, *47*, 932–934. [CrossRef] [PubMed]
5. Wang, J.; Sahu, S.; Sonkar, S.K.; Tackett II, K.N.; Sun, K.W.; Liu, Y.; Maimaiti, H.; Anilkumar, P.; Sun, Y.-P. Versatility with carbon dots–from overcooked BBQ to brightly fluorescent agents and photocatalysts. *RSC Adv.* **2013**, *3*, 15604–15607. [CrossRef]
6. Zhu, C.; Zhai, J.; Dong, S. Bifunctional fluorescent carbon nanodots: Green synthesis via soy milk and application as metal-free electrocatalysts for oxygen reduction. *Chem. Commun.* **2012**, *48*, 9367–9369. [CrossRef]
7. Ma, C.-B.; Zhu, Z.-T.; Wang, H.-X.; Huang, X.; Zhang, X.; Qi, X.; Zhang, H.-L.; Zhu, Y.; Deng, X.; Peng, Y.; et al. A general solid-state synthesis of chemically-doped fluorescent graphene quantum dots for bioimaging and optoelectronic applications. *Nanoscale* **2015**, *7*, 10162–10169. [CrossRef]
8. Suzuki, K.; Malfatti, L.; Takahashi, M.; Carboni, D.; Messina, F.; Tokudome, Y.; Takemoto, M.; Innocenzi, P. Design of Carbon Dots Photoluminescence through Organo-Functional Silane Grafting for Solid-State Emitting Devices. *Sci. Rep.* **2017**, *7*, 5469. [CrossRef]
9. Khan, W.U.; Wang, D.; Zhang, W.; Tang, Z.; Ma, X.; Ding, X.; Du, S.; Wang, Y. High Quantum Yield Green-Emitting Carbon Dots for Fe(III) Detection, Biocompatible Fluorescent Ink and Cellular Imaging. *Sci. Rep.* **2017**, *7*, 1–9. [CrossRef]
10. Bin Chen, B.; Liu, Z.X.; Deng, W.C.; Zhan, L.; Liu, M.L.; Huang, C.Z. A large-scale synthesis of photoluminescent carbon quantum dots: A self-exothermic reaction driving the formation of the nanocrystalline core at room temperature. *Green Chem.* **2016**, *18*, 5127–5132. [CrossRef]
11. So, R.C.; Sanggo, J.E.; Jin, L.; Diaz, J.M.A.; Guerrero, R.A.; He, J. Gram-Scale Synthesis and Kinetic Study of Bright Carbon Dots from Citric Acid and *Citrus japonica* via a Microwave-Assisted Method. *ACS Omega* **2017**, *2*, 5196–5208. [CrossRef] [PubMed]
12. Meiling, T.T.; Cywiński, P.J.; Bald, I. White carbon: Fluorescent carbon nanoparticles with tunable quantum yield in a reproducible green synthesis. *Sci. Rep.* **2016**, *6*, 28557. [CrossRef] [PubMed]
13. Guo, X.; Zhang, H.; Sun, H.; Tade, M.O.; Wang, S. Green Synthesis of Carbon Quantum Dots for Sensitized Solar Cells. *ChemPhotoChem* **2017**, *1*, 116–119. [CrossRef]
14. Chen, Q.-L.; Ji, W.-Q.; Chen, S. Direct Synthesis of Multicolor Fluorescent Hollow Carbon Spheres Encapsulating Enriched Carbon Dots. *Sci. Rep.* **2016**, *6*, 19382. [CrossRef]
15. Zhao, Y.; Zhang, Y.; Liu, X.; Kong, H.; Wang, Y.; Qin, G.; Cao, P.; Song, X.; Yan, X.; Wang, Q.; et al. Novel carbon quantum dots from egg yolk oil and their haemostatic effects. *Sci. Rep.* **2017**, *7*, 4452. [CrossRef]
16. Liu, X.; Pang, J.; Xu, F.; Zhang, X. Simple Approach to Synthesize Amino-Functionalized Carbon Dots by Carbonization of Chitosan. *Sci. Rep.* **2016**, *6*, 31100. [CrossRef]
17. Dong, Y.; Wan, L.; Cai, J.; Fang, Q.; Chi, Y.; Chen, G. Natural carbon-based dots from humic substances. *Sci. Rep.* **2015**, *5*, 10037. [CrossRef]
18. Guo, Y.; Zhang, L.; Cao, F.; Leng, Y. Thermal treatment of hair for the synthesis of sustainable carbon quantum dots and the applications for sensing Hg^{2+}. *Sci. Rep.* **2016**, *6*, 35795. [CrossRef]
19. Xue, M.; Zhan, Z.; Zou, M.; Zhang, L.; Zhao, S. Green synthesis of stable and biocompatible fluorescent carbon dots from peanut shells for multicolor living cell imaging. *New J. Chem.* **2016**, *40*, 1698–1703. [CrossRef]
20. Pires, N.R.; Santos, C.M.W.; Sousa, R.R.; de Paula, R.C.M.; Cunha, P.L.R.; Feitosa, J.P.A. Novel and Fast Microwave-Assisted Synthesis of Carbon Quantum Dots from Raw Cashew Gum. *J. Braz. Chem. Soc.* **2015**, *26*, 1274–1282. [CrossRef]
21. Zhao, S.; Lan, M.; Zhu, X.; Xue, H.; Ng, T.-W.; Meng, X.; Lee, C.-S.; Wang, P.; Zhang, W. Green Synthesis of Bifunctional Fluorescent Carbon Dots from Garlic for Cellular Imaging and Free Radical Scavenging. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17054–17060. [CrossRef] [PubMed]
22. Martindale, B.C.M.; Hutton, G.A.M.; Caputo, C.A.; Reisner, E. Solar Hydrogen Production Using Carbon Quantum Dots and a Molecular Nickel Catalyst. *J. Am. Chem. Soc.* **2015**, *137*, 6018–6025. [CrossRef] [PubMed]
23. Qu, D.; Zheng, M.; Du, P.; Zhou, Y.; Zhang, L.; Li, D.; Tan, H.; Zhao, Z.; Xie, Z.; Sun, Z. Highly luminescent S, N co-doped graphene quantum dots with broad visible absorption bands for visible light photocatalysts. *Nanoscale* **2013**, *5*, 12272–12277. [CrossRef]
24. Zhang, J.; Chen, X.; Li, Y.; Han, S.; Du, Y.; Liu, H. A nitrogen doped carbon quantum dot-enhanced chemiluminescence method for the determination of Mn^{2+}. *Anal. Methods* **2018**, *10*, 541–547. [CrossRef]
25. Parvin, N.; Mandal, T.K. Synthesis of a highly fluorescence nitrogen-doped carbon quantum dots bioimaging probe and its in vivo clearance and printing applications. *RSC Adv.* **2016**, *6*, 18134–18140. [CrossRef]
26. Felten, J.; Hall, H.; Jaumot, J.; Tauler, R.; De Juan, A.; Gorzsás, A. Vibrational spectroscopic image analysis of biological material using multivariate curve resolution–alternating least squares (MCR-ALS). *Nat. Protoc.* **2015**, *10*, 217–240. [CrossRef] [PubMed]

27. Mirtchev, P.; Henderson, E.J.; Soheilnia, N.; Yip, C.M.; Ozin, G.A. Solution phase synthesis of carbon quantum dots as sensitizers for nanocrystalline TiO_2 solar cells. *J. Mater. Chem.* **2012**, *22*, 1265–1269. [CrossRef]
28. Tang, Q.; Zhu, W.; He, B.; Yang, P. Rapid Conversion from Carbohydrates to Large-Scale Carbon Quantum Dots for All-Weather Solar Cells. *ACS Nano* **2017**, *11*, 1540–1547. [CrossRef]
29. Chen, G.; Wu, S.; Hui, L.; Zhao, Y.; Ye, J.; Tan, Z.; Zeng, W.; Tao, Z.; Yang, L.; Zhu, Y. Assembling carbon quantum dots to a layered carbon for high-density supercapacitor electrodes. *Sci. Rep.* **2016**, *6*, 19028. [CrossRef]