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RESEARCH ARTICLE

Synthesis and characterization of amine-functionalized mesoporous carbon nanomaterial from biowaste

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Abstract

Garlic (*Allium sativum*) is widely cultivated and consumed, making it one of the most important crops in the world. India is the second largest producer next to China. The garlic peels from the garlic processing industry are often discarded as agricultural waste. These wastes are rich in carbon precursors, making them an ideal feedstock for mesoporous carbon nanomaterial (MCN) synthesis. Pyrolysis is the top-down approach to synthesizing the nanomaterial, which involves heating organic materials such as garlic peel waste that breaks into smaller compounds, resulting in a mixture of gases and carbon-rich solid residues (bio-char). The amine-functionalization was performed over the mesoporous surface and confirmed by the shifts in zeta potential value from -31.6 mV to + 22 mV to increase the surface charge density. Similarly, the Brunauer Emmett Teller (BET) analyzer confirmed the reduction in the pore diameter from 12.5 nm to 7.41 nm due to amine functionalization. Furthermore, the synthesized MCN were thoroughly characterized using advanced analytical techniques, providing comprehensive insights into their size, shape, surface functional groups, crystallinity and porosity. This study transformed agricultural waste into high-value materials (MCN), reducing environmental impact and promoting resource efficiency.

Keywords

biowaste; garlic peel; HRTEM; mesoporous carbon; pyrolysis

Introduction

Mesoporous carbon nanomaterial refers to the broad or narrow porous structure with diameters ranging from 2 to 50 nanometers (nm). They have a larger surface area, uniform pore size, remarkable functionalization and excellent thermal and chemical stability, which make them versatile materials. Due to supramolecular π-stacking interactions, nanoscale mesoporous carbon has more significant specific surface areas and pore volumes, making it suitable for drug delivery applications and able to house several aromatic medicines (1, 2). Additionally, the superior biocompatibility and stability of these nanoparticles (NPs) in aqueous conditions enhance their biomedical applications (3, 4). The well-ordered mesoporous carbon structures are omnipresent in novel scientific research for their promising applications in diverse fields, including wastewater treatment, catalysis, energy storage, air purification, gas adsorption and separation of large biomolecules, electrical double-layer capacitors and sensing (5-10). These porous nanomaterials are

generally considered non-toxic and biocompatible, inspiring researchers to explore following-generation healthcare diagnostics, bio-imaging, drug delivery, tissue engineering, disease management and antimicrobial treatment (11-16). There has been an alarming rise in the human population with increased agricultural waste production from agro-based industries. Since the early sixth century BC, garlic has been widely utilized as a spice or medicinal herb (17). It was estimated that the present production of garlic is roughly 25 megatons, with an average of 2.3 pounds per person (18). The incineration of such biomass waste poses a significant threat to air pollution by releasing suspended particulate matter, dioxin-like compounds, furans, nitrogen oxides, sulfur dioxide and volatile organic compounds. As a result, it can be identified as a significant part of the vegetable peel trash produced worldwide. Two approaches, top-down and bottom-up, can synthesize the mesoporous carbon nanomaterial. The former is more favorable for sustainable large-scale production and later for tailoring structures and properties (19). Pyrolysis is a thermal decomposition top-down process typically between 300 °C and 900 °C that occurs either in a controlled atmosphere or in anoxic condition. The present work highlights the “waste-to-wealth technology,” which facilitates the conversion of garlic bio-waste into pioneering mesoporous carbon nanomaterials via a one-pot pyrolysis method.

Materials and Methods

Garlic peels (*Allium sativum*) were collected from the local sandy unit at Coimbatore in Tamil Nadu, India. The peels were washed, shade dried and ground to a fine powder using a pulverizer and sieved under British Standard Sieve (BSS) 200 (75-micron mesh) to obtain the uniform-sized particles and stored in airtight plastic bags until use. Ethylenediamine (Mol. Wt. 60.10) was purchased from the Sigma Aldrich. Double-distilled water was used throughout the experiments.

Characterization of synthesized nanoparticles

The synthesized NPs were characterized using High-Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAED), Energy Dispersive X-ray (EDAX), Fourier Transform Infrared (FT-IR), X-ray Diffraction (XRD), Particle Size Analyzer (PSA) and Brunauer Emmett Teller (BET). High Resolution -Transmission Electron Microscope (JEOL Japan, JEM-2100 Plus) was used to measure the sizes of the carbonaceous NPs with 200 kV, which were statistically measured using image J software. For this technique, 1 mg of nanoparticle sample was dispersed in 1 mL of distilled water. Selected area electron diffraction was an experimental technique to determine the crystallographic structures using a High Transmission Electron Microscope (JEOL Japan, JEM-2100 Plus). The obtained diffraction patterns were likely confirmed with the XRD spectral pattern. Energy Dispersive X-ray spectroscopy was an analytical technique usually in conjunction with a Scanning Electron Microscope (Make: FEI, Model: Quenta 250) to determine the elemental/ chemical composition of the sample whose atomic number is greater than 3. Fourier Transform Infrared Spectroscopy utilizing the Jasco Model: R-3000-QE was used to determine the changes in the surface functional group and chemical boning nature of the carbonaceous NPs. Approximately 10000-100 cm^{-1} of radiation was transmitted through 2 mg of finely ground materials placed on the sample injection port. The detector absorbed and recorded some of the radiation in the 4000-400 cm^{-1} range. The results obtained were the sample's molecular fingerprint and the graph was plotted using ORIGIN Ver.8.5.

X-ray diffraction analysis determined the carbonaceous material's crystallographic nature. The Shimadzu XRD 600 model was used to record the diffraction pattern. It used Cu Kα radiation, 40 Kv current and a scan time of 0.5x/min of 50-80°. By utilizing ORIGIN Ver.8.5, the acquired data were plotted in the graph. Using the Nanoparticle Size Analyzer (Model: HORIBA-SZ-100), the surface charge of the electrical double layer of a nanoparticle was determined in between the zeta potential values of -200 mV and +200 mV. The BET Quantachrome TouchWin™ version 1.22 was used to record the nitrogen adsorption-desorption isotherm. After 3 hr of degassing at 300 °C, the samples were placed in the sample port for examination. The interaction between the adsorbent and adsorbate determines the produced materials' characteristic pore size, pore volume and surface area.

Synthesis of mesoporous carbon nanoparticles

A muffle furnace was used to synthesize carbonaceous nanomaterial. The finely sieved garlic peel powder was subjected to the muffle furnace at 500 °C for 2 hr with a ramping heat rate of 10 °C/min. The residues were allowed to cool down to room temperature. The pyrolyzed powder was washed with 1 M hydrochloric acid (HCl) and deionized water to get pristine MCN (16).

Functionalization of mesoporous carbon nanoparticles

Synthesized MCN were functionalized using a colorless organic compound, Ethylenediamine (EDA). For this, 278 µL of EDA was mixed with 500 mg of mesoporous carbon and dissolved in 10 mL of ethanol. The solution was allowed to disperse and stirred for 8 hr to volatilize the ethanol. The dried powder was labeled amine-functionalized mesoporous carbon nanoparticles (A-MCN) (20). The schematic representation of amine-functionalized mesoporous carbon nanoparticle synthesis is shown in Fig. 1.

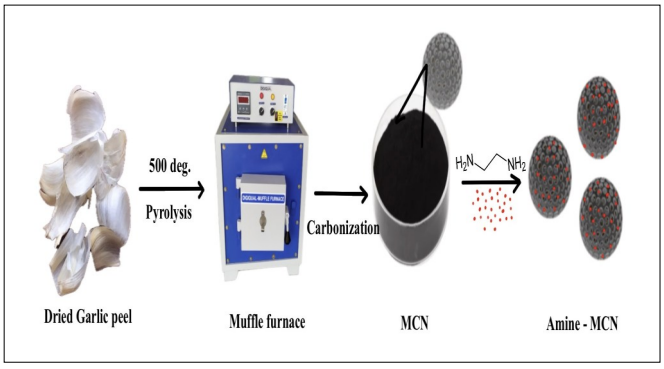

Fig. 1. Schematic illustration of amine-functionalized mesoporous carbon nanoparticles.

Results and Discussion

In this present work, the reaction duration of the one-pot pyrolysis process was optimized for 2 hr to produce mesoporous carbon with a yield equal to 92%. The highest yield is mainly due to the pyrolysis process, as it removes all the volatile compounds (16).

Morphology and chemical characterization of mesoporous carbon

The synthesized mesoporous carbon nanomaterials were subjected to characterization. The HRTEM image of the mesoporous carbon nanomaterials showed the particles were spherical in distribution with a size range between 20-50 nm (Fig. 2). These results were in line with the findings (21), who reported the mesoporous carbon nanomaterials synthesized from the self-assembly of resol-F127 composite micelles through hydrothermal route and found that the carbonaceous material was spherical in distribution. The structural property was studied by XRD, showing the amorphous behavior in Fig. 3 and the XRD pattern of mesoporous carbon synthesized by the silica-assisted method showed similar results (22). The SAED pattern from the HRTEM confirmed that the mesoporous carbon nanomaterials were amorphous, as shown in Fig. 4 and the results were in line with the diffraction pattern of XRD. The zeta potential value of mesoporous carbon synthesized at 500 °C for 2 hr showed - 31.6 mV (Fig. 5), indicating their excellent water stability nature and surface hydroxyl groups (20). The amine-functionalized MCNs with the zeta potential value of + 22.2 mV shown in Fig. 6 indicated that the cationic surface charge can be used as a carrier for conjugating the genomic material. The elemental composition shown in Fig. 7 clearly states the highest carbon percentage in EDAX analysis. The Nitrogen adsorption-desorption isotherm of the MCNs exhibited the typical hysteresis type IV isotherm, indicating the mesoporous nature in both MCN and A-MCN shown in Fig. 8 and Table 1. The total surface area, pore size and pore volumes were approximately 432 m^2/g, 12.5 nm and 0.2588 cm^3/g (20).

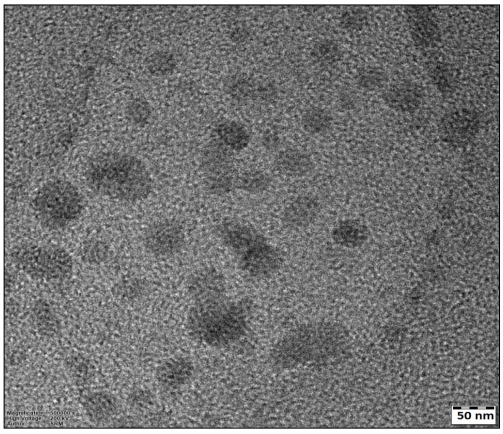

Fig. 2. HR-TEM image of MCN.

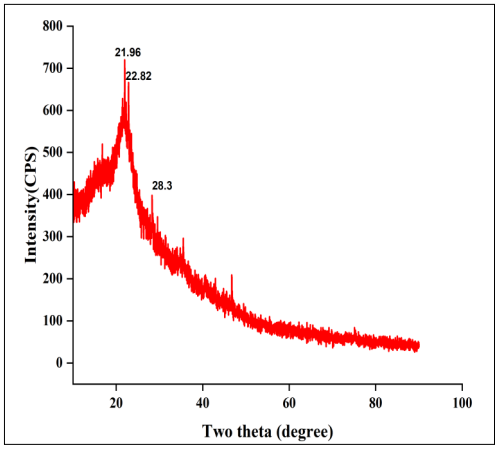

Fig. 3. XRD spectra of MCN.

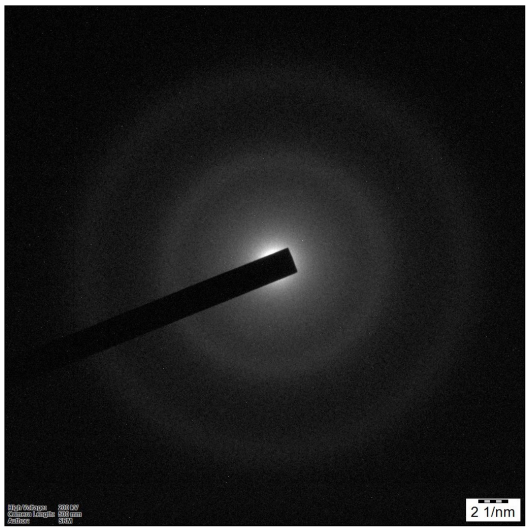

Fig. 4. SAED pattern of MCN.

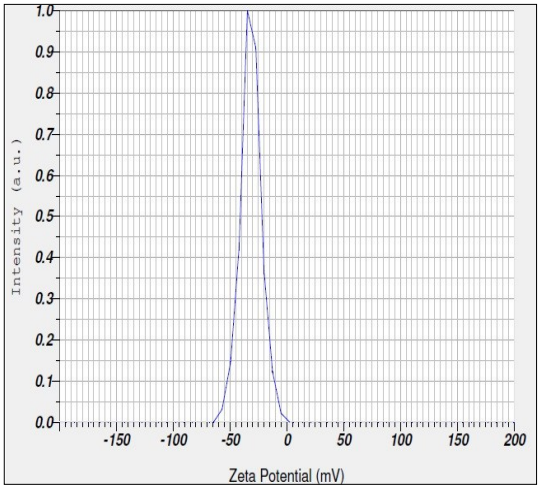

Fig. 5. Zeta potential (MCN) – 31.6 mV.

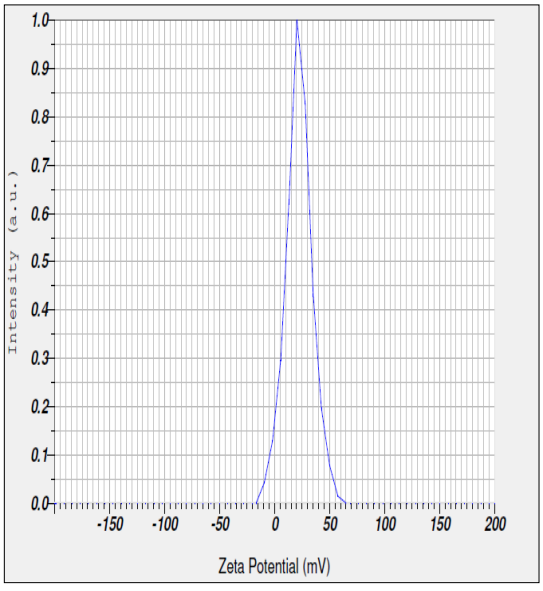

Fig. 6. Zeta potential (A-MCN) +22.2 mV.

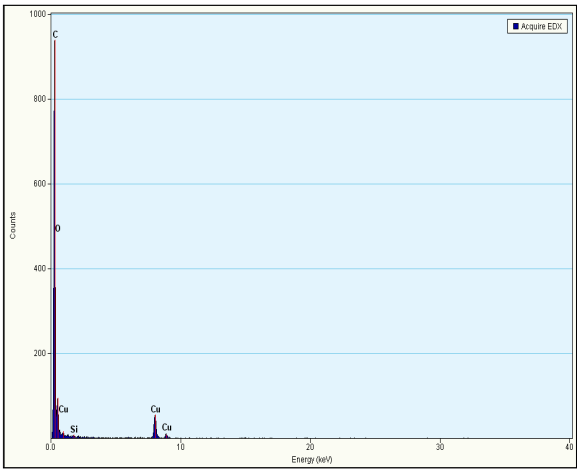

Fig. 7. EDAX of MCN.

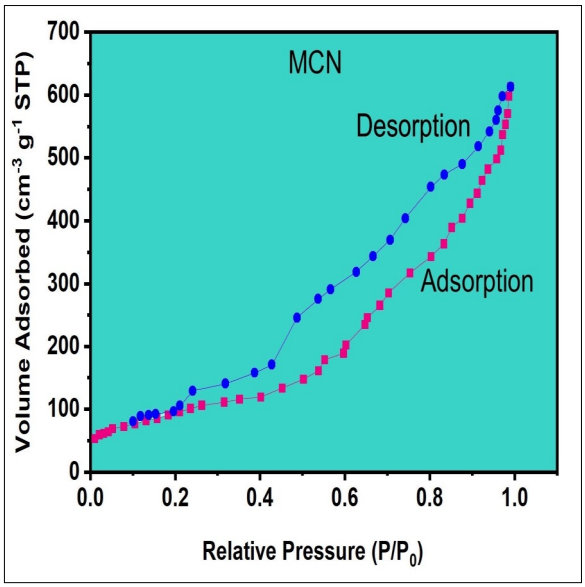

Fig. 8. BET surface area of MCN.

Table 1. BET Surface properties of mesoporous nanoparticles

Sample	Surface area (m^2/g)	Specific pore volume (cm^3/g)	Pore diameter (nm)
MCN	432	0.2588	12.5
A-MCN	52	0.13	7.41

Furthermore, the A-MCN showed the BET surface area, pore size and pore volume of 52 m^2/g, 7.41 nm and 0.13 cm^3/g, which indicated that the amine groups were successfully grafted on the mesoporous carbon surface shown in Fig. 9. The FTIR spectra revealed the strong absorbance at 3490 cm^{-1} corresponds to -OH stretching of MCN. The peak at 2912 cm^{-1} corresponds to C-H stretching saturated carbons, whereas the peak at 1421 cm^{-1} tends to bend vibrations of the hydroxyl ion group. The bending vibrations of C=C were observed around 865 cm^{-1}. The FTIR spectra revealed the strong absorbance at 3490 cm^{-1}, corresponding to the -OH stretching vibration in MCN. A peak at 2912 cm^{-1} indicates the C-H stretching of saturated carbons, while the peak at 1421 cm^{-1} is attributed to the bending vibrations of hydroxyl groups. Additionally, bending vibrations of C=C bonds were observed around 865 cm^{-1}. The FT-IR datasets generated in this study were shown in Fig. 10 and were in line with the datasets of (16, 23), who synthesized porous carbon NPs from biowaste.

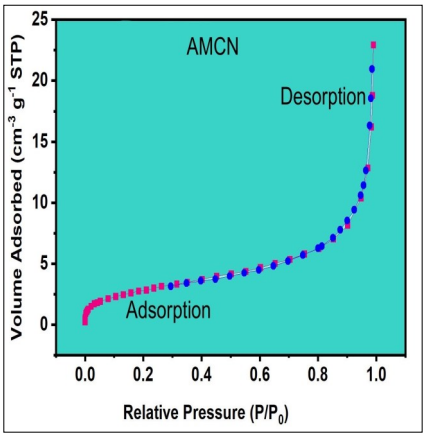

Fig. 9. BET surface area of A-MCN.

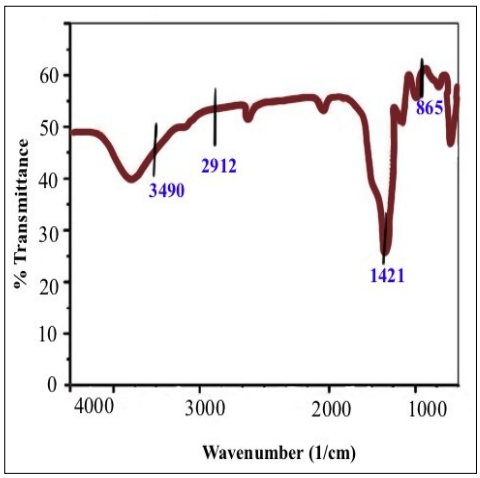

Fig. 10. FT-IR spectra of MCN.

Conclusion

The present study showcases the viable way to utilize garlic peel wastes into valuable mesoporous carbon nanomaterials. The one-pot pyrolysis process and amine surface functionalization make them versatile for specific molecules' adsorption. The synthesized MCN was analyzed using advanced tools like HRTEM, SAED, EDAX, FT-IR, XRD, PSA and BET, revealing their excellent structural and functional properties. These results open up exciting possibilities for creating sustainable solutions that address environmental concerns and advance the field of nanotechnology for various meaningful applications in the future.

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Authors' contributions

MR and JSS provided the conceptualization resources and drafted the manuscript. KA carried out the synthesis, optimization and characterization studies. MP, MS and TK carried out the validation. RRK edited the manuscript. All authors have read and agreed to the published version of the manuscript.

Compliance with ethical standards

Conflict of interest: Authors do not have any conflict of interest to declare.

Ethical issues: None

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