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Heteroatom Modified Carbon Dots (N, P, K): Synthesis, Surface Functionalization, and Prospects for Soil-Fertility Enhancement

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Abstract

Heteroatom-functionalized carbon dots (H-CDs) have emerged as a class of zero-dimensional carbon nanomaterials offering tunable optical, electronic, and catalytic properties through controlled nitrogen, phosphorus, and potassium doping. This review highlights the chemistry and chemical-technology dimensions of N-, P-, and K-doped carbon dots (N-CDs, P-CDs, K-CDs), focusing on their synthesis strategies, surface functionalization, and structure–property relationships. Conventional routes such as microwave-assisted pyrolysis, hydrothermal carbonization, and one-pot solvothermal methods are discussed, with particular attention to precursor selection, reaction conditions, and the resulting nanoscale morphology and surface terminations. The incorporation of heteroatoms modifies the electronic density, surface charge, and fluorescence behavior of CDs, enabling their use in sensing, catalysis, and delivery systems. In parallel, these features open opportunities for agricultural applications, especially in nutrient-efficient soil-fertility management. The article critically evaluates reported effects of N- and P-CDs on seed germination, root growth, biomass accumulation, and chlorophyll content, emphasizing dose-dependent responses and mechanistic insights at the nanomaterial–plant interface. By contrast, K-CDs remain underexplored, and their potential as K-rich nanofertilizers derived from potash-rich biomass waste is presented as a forward-looking prospect. The review also addresses key challenges related to reproducibility, characterization standardization, and scalability of heteroatom-doped CDs, underscoring the need for cross-disciplinary collaboration between materials chemists, agronomists, and environmental scientists. By integrating fundamental chemistry with applied chemical-technology perspectives, this work aims to stimulate further research on heteroatom-doped carbon dots as functional materials for sustainable soil-fertility enhancement.

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INTRODUCTION

According to the Food and Agriculture Organization of the United Nations (FAO, UN), demand for food is predicted to increase by 70% between now and 2050 as a result of the rising global population, rising incomes, and changing eating habits [1]. Traditional fertilizers have been used to boost agricultural productivity, but their effectiveness has significantly decreased since the "Green Revolution," and the overuse of chemical fertilizers has had detrimental effects on soil health, resulting in inefficient nutrient uptake and environmental pollution. The search for innovative materials and methods has become increasingly critical in contemporary agriculture due to the challenges posed by climate change, land degradation, and urbanization. Excessive fertilizer usage has a detrimental impact on soil health, lowers plants' ability to utilize nutrients efficiently, and pollutes the environment. To overcome this predicament, the use of controlled release of fertilizer is increasing [2]. Carbon dots (CDs), a type of zero-dimensional carbonaceous nanomaterial, are composed of sp2- and/or sp3-hybridized carbon domains and are embellished with surface functions.

Green chemical technologies, environmental remediation, and sustainable agriculture have all benefited from the interdisciplinary and promising applications of nanotechnology. Nanomaterials are important components of various biotic and abiotic remediation systems and significantly influence the fate, mobility, transformation, and toxicity of soil contaminants. Owing to their unique physicochemical characteristics, surface chemistry, stability, and possible biological interactions, carbon-based nanomaterials, particularly nitrogen-functionalized carbon nanostructures (N-FCNs), have garnered considerable interest. These nanomaterials have demonstrated favorable eurytopic effects on a wide range of plant species by promoting seed germination, root elongation, biomass accumulation, root cell development, chlorophyll content, and transpiration efficiency during the early seedling growth stages [3]. Additionally, their applications are particularly significant for current chemical and technological research because they are intimately related to the development of surface chemistry, bioremediation, biomaterials, electrochemical interactions, and environmentally sustainable nanotechnology.

In this review, we offer a chemistry and chemical technology-focused perspective on heteroatom-doped carbon dots (N-, P-, and K-CDs), emphasizing their synthesis methods, surface functionalization, and structure–property correlations. We analyzed the reported effects of N- and P-CDs on seed germination, root growth, biomass accumulation, and chlorophyll content, as well as microwave-assisted, hydrothermal, and solvothermal methods for the scalable synthesis of these CDs. Additionally, we provide K-enriched carbon nanodots as a promising future for biomass-derived sustainable nanofertilizers to improve soil fertility. The goal of this effort is to promote interdisciplinary research on heteroatom-doped carbon dots for sustainable agriculture and soil health management by fusing basic nanomaterial chemistry with applied chemical technology, as shown in Figure 1.

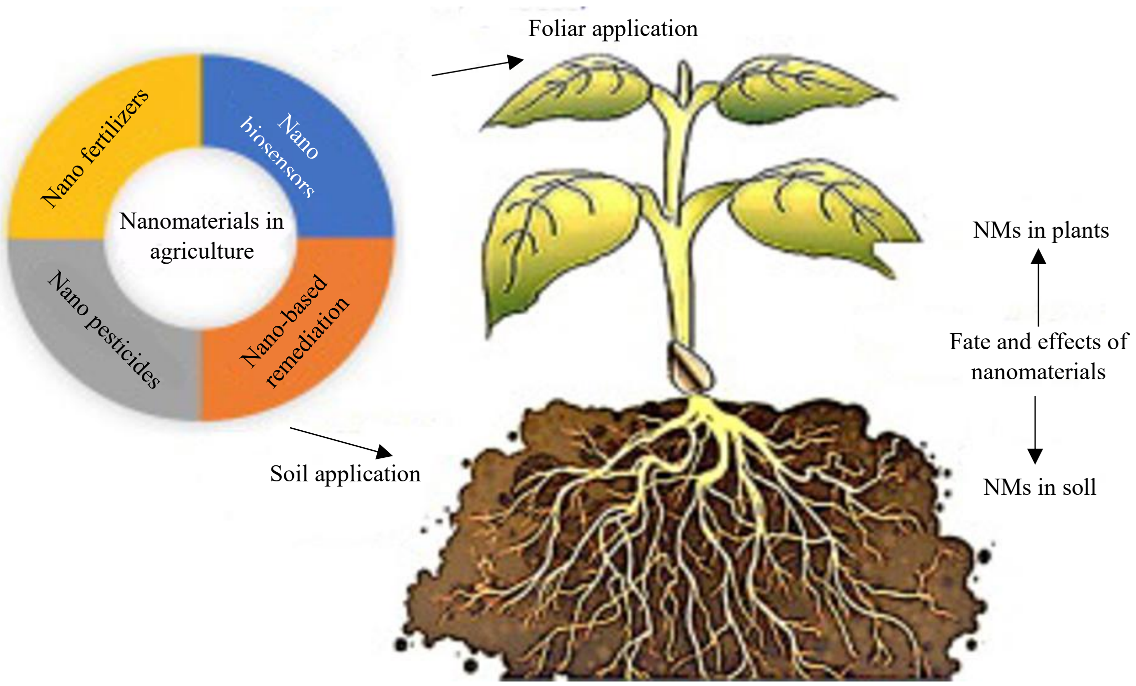

Figure 1. Pictorial representation of the application of nanoparticles for the enhancement of soil fertility.

N-CDs

Nitrogen atoms are integrated into the carbon nanodot structure of nitrogen-doped carbon nanodots (N-CDs), which are a family of carbon-based nanomaterials. Because nitrogen is introduced as a heteroatom within the carbon structure, these materials are also known as heteroatom-functionalized carbon nanodots. The electronic structure, surface chemistry, optical behavior, and physicochemical characteristics of carbon nanodots are all greatly altered by nitrogen doping, which increases their usefulness in fields such as environmental remediation, bioimaging, sensing, catalysis, and sustainable agricultural technologies.

Synthesis of N-CDs

Numerous techniques have been adopted for the synthesis of nitrogen-doped carbon nanodots (N-CDs). To name a few:

1. An innovative, facile, and rapid microwave-assisted pyrolysis procedure was applied for the synthesis of N-CQDs using available and economical starting materials (the carbon source is orange juice, and the nitrogen source is urea) in less than 10 min.
2. One-step hydrothermal method using TIPA as nitrogen and carbon source.
3. Nitrogen-doped carbon dots may be prepared using cellulose and urea.
4. N-doped C-dots by one-pot solvothermal method using CCl_4 and $NaNH_2$ as precursors Figure 2.
5. N-doped carbon dots (N-CDs) were synthesized from the main components of plants, including cellulose (N-cCDs).

In this review, we discuss one-pot solvothermal synthesis using CCl_4 and $NaNH_2$ as precursors.

Because nitrogen has five valence electrons and an atomic size similar to that of carbon, it is one of the most widely employed heteroatom dopants in carbon nanomaterials. When integrated into the carbon framework, nitrogen atoms can act as n-type impurities and replace carbon at lattice sites, adding more electrons to the electrical system. The band structure changes and the Fermi level shifts as a result of this electron donation, which also increases the electron density and modifies the electronic distribution. As a result, nitrogen doping significantly affects the optical, electrical, and physicochemical characteristics of carbon nanodots, improving their performance in various environmental and technological applications [4–8].

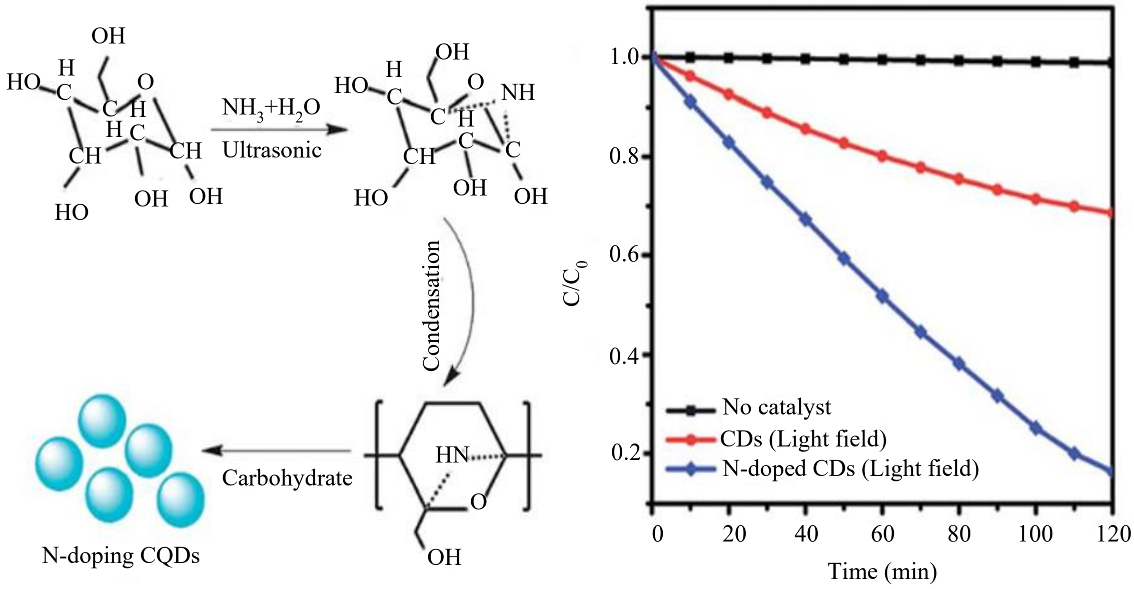

Figure 2. (a) The scheme for the formation process of the N-doped C-dots (represented as N-doped CQDs in the Figure). (b) Relationship between methyl orange concentration and reaction time for different catalysts (C-dots are represented as CDs in the Figure).

In addition, FCNs can change the physiological response of plants. After 17 days of growth under 4 mg kg−1 N-FCNs treatment, the seedlings developed longer roots, larger rosettes, and higher fresh biomass with increasing N content in N-FCNs.

At the beginning of the culture period, N-Functionalized carbon nanomaterials-treated plants had larger rosettes and richer, longer roots than the FCNs-treated and control groups.

Properties of N-CDs

The experimental results showed that the emission wavelength of C-dots could be efficiently tuned by adjusting the nitrogen doping concentration, and nitrogen doping dominates the optical properties of the C-dots rather than the size effect.

Applications of N-CDs

Some researchers have studied the availability of nitrogen-doped C-dots for a wide range of applications, such as photocatalysis, biochemical sensing, bioprocesses, bioimaging, and optoelectronic devices. Utilization as delivery agents for plant and soil fertility.

These nanoarchitectures possess advantages such as facile and economic synthesis, water solubility, negligible toxicity, good biocompatibility, marked electron-donating and accepting capabilities, and increased selectivity and sensitivity.

P-CDs

Carbon nanodots doped with phosphorus are called phosphorus-doped carbon nanodots (P-CDs).

Synthesis of P-CDs

P-doped CQDs derived from m-aminophenol and phosphoric acid were first prepared using a one-step hydrothermal treatment [9]. m-Aminophenol (≥98%), Britton–Robinson (BR) buffer, and sodium chloride (NaCl) solution were prepared and adjusted to control the acidity and ionic strength. Ultrapure water purified by a Millipore water purification system (Milli-Q, Millipore, Billerica, MA, USA) was used for the preparation of all solutions. All fluorescence spectra were acquired using a Shimadzu RF-5301PC fluorescence spectrophotometer (Shimadzu, Kyoto, Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL 2100F field emission transmission electron microscope (Tokyo, Japan). The thickness of the CQDs was characterized using a Dimension Icon Scan Asyst atomic force microscope (AFM, Bruker Co., Karlsruhe, Germany). Elemental and functional group analyses were performed using an ESCALAB Xi+ X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific Inc., Waltham, MA, USA) and a Nicolet iS5 Fourier Transform Infrared spectrometer (FTIR, Thermo Fisher Scientific Inc., Waltham, MA, USA). The Raman spectrum obtained on the Ag substrate (excited by a 532 nm laser) was recorded using a DXR 2xi Raman microscope (Thermo Fisher Scientific Inc., Waltham, MA, USA). A C9920-02G fluorescence spectrophotometer (Hamamatsu Photonics KK, Tokyo, Japan) was used to measure the fluorescence lifetime. The zeta potentials of the CQDs were obtained using a Zetasizer Nano ZS90 System (Malvern, UK). The bacterial concentration was determined by measuring the optical density at 600 nm (OD600) using UV–vis spectroscopy. The morphology of the bacteria was observed using a Hitachi S-3400N scanning electron microscope (SEM, Tokyo, Japan) [10].

Preparation of the P-Doped CQDs

P-doped CQDs were prepared by one-step hydrothermal treatment using m-aminophenol and phosphoric acid. Briefly, 0.10 g of m-aminophenol and 1 mL of phosphoric acid were first dissolved in 4.0 mL of ultrapure water, and 5.0 mL of the mixture was added to 25 mL Teflon-lined autoclaves and kept at 200 ◦C for 48 h. Once it got cold of course at room temperature, the obtained products were centrifuged at 6000 rpm for 5 minutes, and the supernatant was then filtered to remove it using BIOSHARP membrane filters (0.22 μm). The insoluble impurities and clear solution were subjected to dialysis (Mw = 500 Da) for 48 h to remove unreacted residual material. Finally, the purified CQD was lyophilized to obtain a solid powder. The product was stored at 4 ◦C for future experiments [11].

Properties of P-CDs

The TEM image shows that the size of the P-CQDs was distributed in the range from 2.75 nm to 4.25 nm with an average perimeter of 3.4 nm. The HRTEM image shows a range of 2.75–4.25 nm, with an average periphery of 3.4 nm. The P-doped CQDs exhibited unique absorption and emission properties.

Applications of P-CDs

They are found in various fields, such as fluorometric Probes for Iron Detection, bioimaging, and biosensing. In addition to UV absorption, cell culture, and photostability, these are also important applications. These nanoarchitectures possess advantages such as facile and economic synthesis, water solubility, negligible toxicity, good biocompatibility, marked electron-donating and accepting capabilities, and increased selectivity and sensitivity.

K-CDs

There are very few studies available on potassium-doped carbon nanodots (K-CDs), indicating a promising research opportunity in the area of advanced functional nanomaterials. Potassium-modified carbon dots are expected to demonstrate enhanced performance in agricultural applications because of their ultra-small size, high surface reactivity, and incorporation of potassium within the carbon matrix. These characteristics can enhance soil fertility and enable effective nutrient delivery. Furthermore, potash-rich biomass-derived waste, especially banana peels, can be used as affordable and sustainable precursor materials for the environmentally friendly synthesis of K-doped carbon dots. The utilization of agricultural waste for the development of value-added nanomaterials further supports sustainable chemical processes, eco-friendly material synthesis, and the emerging applications of nanotechnology in agriculture and environmental systems [12].

CONCLUSION

In addition to having a large surface area, carbon-based nanomaterials such as fullerenes, carbon nanotubes (CNTs), graphene, and carbon dots are simple to modify by doping with functional groups or heteroatoms. Owing to their exceptional chemical and physical characteristics, carbon nanomaterials (CNMs) have generated compelling interest in both basic and applied research in the fields of environment and agriculture. Water-soluble carbon nanodots can penetrate plants to increase cereal crop output. A possible smart treatment-delivery system for plants might be created using carbon nanoparticles with the capacity to penetrate and convey various payloads (such as water, ions, fertilizers, and genes) into plant cell organelles. Moreover, CNPs can effectively improve the use efficiency of N, P, and K by enhancing their uptake.

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