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Carbon Nanostructure: Innovations and Challenges in Improving Nutrient Delivery to Plants

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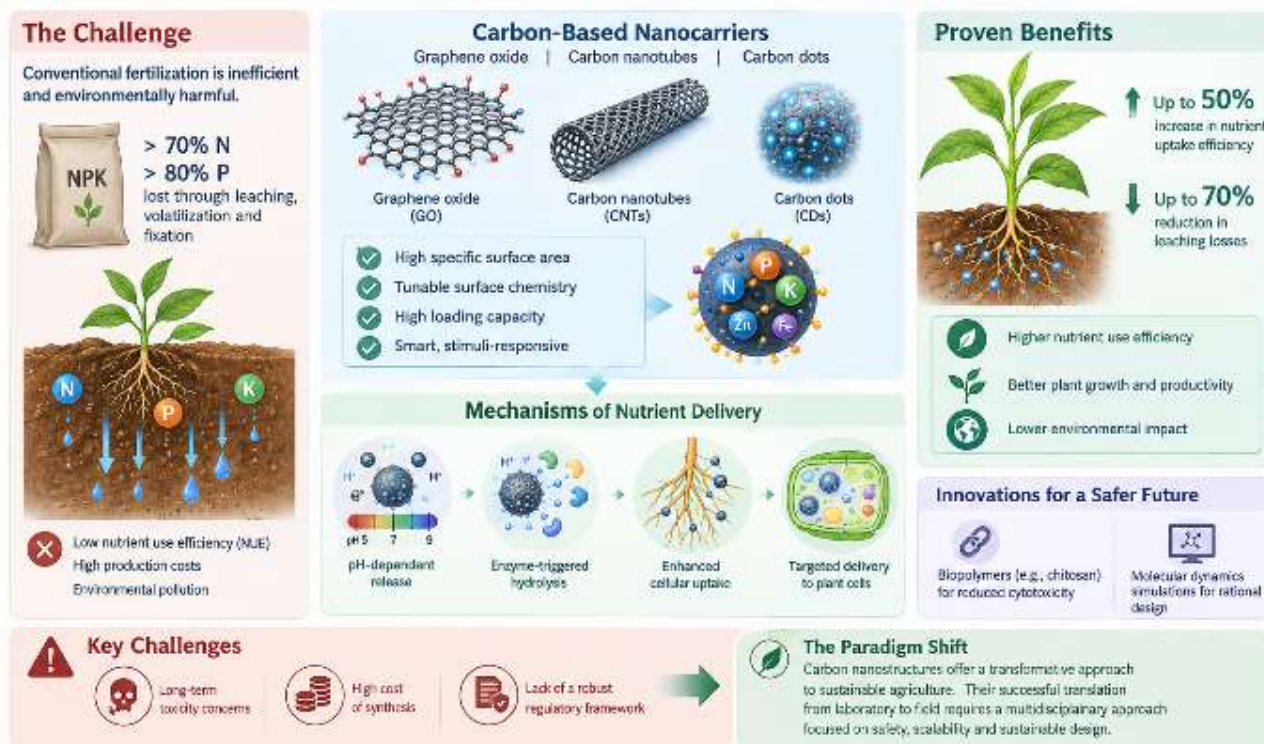
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Abstract

The imperative to enhance nutrient use efficiency (NUE) and mitigate the severe environmental impact of conventional fertilization is driving innovation in sustainable agriculture. This review comprehensively examines the burgeoning field of carbon-based nanocarriers-including graphene oxide, carbon nanotubes, and carbon dots as advanced delivery platforms for macro and micronutrients. We delve into the unique physicochemical properties of these materials, such as their high specific surface area, tunable surface chemistry, and exceptional loading capacity, which underpin their function as smart, stimuli-responsive systems. The mechanisms facilitating nutrient delivery, such as pH-dependent release, enzyme-triggered hydrolysis, and enhanced cellular uptake, are analyzed in detail, with documented evidence showing increases in nutrient uptake efficiency by up to 50% and concurrent reductions in leaching losses by up to 70%. Furthermore, we explore cutting-edge innovations, including the integration of nanocarriers with biopolymers like chitosan to reduce cytotoxicity and the application of molecular dynamics simulations for rational nanocarrier design. Despite their transformative potential, significant challenges impede commercialization, namely concerns regarding long-term toxicity, the high cost of synthesis, and the absence of a robust regulatory framework. This analysis concludes that carbon nanostructures represent a paradigm shift in agrochemistry, yet their successful translation from laboratory research to field application necessitates a multidisciplinary approach focused on safety, scalability, and sustainable design.

Keywords: Carbon Nanotubes, Graphene Oxide, Carbon Dots, Nanofertilizer, Sustainable Agriculture, Stimuli-Responsive

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1. Introduction

The major nutrients nitrogen, phosphorus and potassium, together with micronutrients such as iron, zinc and copper, play a fundamental role in the optimal growth and performance of plants. Nitrogen is known as the most key macroelement in plant metabolism, playing a pivotal role in the formation of amino acids, proteins and nucleic acids. Studies show that this element directly affects the photosynthetic processes by affecting the structure and function of chloroplasts (58). Research shows that nitrogen deficiency can reduce the photosynthetic performance of a plant by up to 70% (39). In addition, nitrogen plays a fundamental role in chlorophyll synthesis and plant biomass development, so that its deficiency leads to yellowing of leaves (chlorosis) and stunted growth.

As a structural component of ATP, NADPH and membrane phospholipids, phosphorus plays a decisive role in energy transfer and the integrity of cell membranes. Research shows that adequate phosphorus can increase root growth by up to 40% (37). It also plays a role in enzyme activation and cell signaling, and its deficiency leads to the accumulation of anthocyanin pigments and stunted growth in early stages of plant development. Studies have shown that phosphorus has a direct impact on the quality of agricultural products through its effects on the synthesis of starch and sugars (61). Potassium is known to be a major factor in regulating osmotic pressure, stomatal opening and closing, and enzyme activation. Research shows that this element can increase drought resistance by up to 50% (6). Micronutrients such as iron (in chlorophyll synthesis), zinc (in auxin production), and copper (in the electron transport chain) play specialized roles in plant metabolism. A comprehensive study has shown that micronutrient deficiencies can disrupt the activity of over 300 different enzymes (41). Although these elements are required in small amounts, their effect on plant growth and performance is absolutely vital.

Traditional fertilization methods face serious challenges in nutrient use efficiency. Studies show that in conventional systems, more than 70% of nitrogen and 80% of phosphorus applied to the soil are lost through leaching, volatilization, and chemical fixation (66). This loss not only increases production costs for farmers, but also severely reduces crop yields. Studies in wheat fields have shown that only 20–30% of nitrogen fertilizers are absorbed by plants (11). This inefficiency is a serious threat to global food security in the face of climate change and rising prices of agricultural inputs. Pollution from traditional fertilization is a major environmental concern. Excess nitrates and phosphates entering groundwater resources leads to eutrophication and the creation of dead zones in aquatic ecosystems (57). Also, the emission of greenhouse gases such as nitrous oxide (N₂O), which is 298 times more potent than CO₂, is another negative consequence of these methods (16). These pollutants not only threaten biodiversity, but can also endanger public health by contaminating drinking water sources. In the face of these challenges, the development of novel nutrient delivery systems with high efficiency and low emissions has become a

necessity. Carbon nanocarriers with controlled and targeted nutrient release capabilities can be a suitable solution to these problems (36). These technologies not only reduce nutrient loss by up to 50%, but also minimize environmental pollution by preventing nutrient leaching (30). Given the increasing global population and resource constraints, the transition from traditional methods to smart nutrient delivery systems is a fundamental step towards achieving sustainable agriculture.

Carbon nanocarriers, including graphene, carbon nanotubes, and carbon dots, are a class of advanced materials that have revolutionized plant nutrient delivery systems due to their unique structure and exceptional physicochemical properties. Graphene with its two-dimensional structure and extremely high specific surface area, carbon nanotubes with cylindrical structure and very high aspect ratio, and carbon dots with dimensions of about 10 nm and low toxicity are all ideal candidates for controlled nutrient release (18). Due to the ability to modify the surface with various functional groups, these nanocarriers enable selective binding and intelligent release of nutrients in response to environmental stimuli such as soil pH or plant enzymes (28). Nanotechnology has provided effective solutions to overcome the limitations of traditional fertilization methods by providing novel delivery systems. Studies show that carbon nanocarriers can increase nutrient uptake efficiency by up to 50% while simultaneously reducing nutrient loss through leaching and evaporation by up to 70% (21). This technology works through various mechanisms, including protecting nutrients from chemical fixation in the soil, increasing plant cell wall permeability, and controlled release based on plant needs (53). Furthermore, targeted use of these nanocarriers can significantly reduce the pollution of water and soil resources caused by conventional chemical fertilizers and is an important step towards realizing sustainable agriculture (48). This review article aims to comprehensively review the potential and challenges of carbon nanocarriers in plant nutrient delivery systems. In this study, the functional mechanisms of carbon nanocarriers, including graphene, carbon nanotubes, and carbon dots, in improving nutrient uptake efficiency (up to 50% increase in yield) and reducing losses (up to 70% reduction) are analyzed. Recent innovations in the design of smart nanocarriers with the ability to respond to environmental stimuli (pH), humidity, and enzymes, and controlled release systems are reviewed. Also, key challenges in the path to commercialization of these technologies, including economic (high production cost), technical (stability under field conditions), and regulatory (lack of clear safety standards), are analyzed in detail. This article will play an important role in advancing sustainable agriculture and achieving global food security by providing practical solutions to overcome these challenges.

2. Carbon Nanocarriers and Their Properties in Smart Nutrient Delivery to Plants

Carbon nanocarriers are considered ideal options for nutrient delivery to plants due to their unique structure and exceptional physicochemical properties. Graphene,

with its two-dimensional structure and extremely high specific surface area ($\sim 2630 \text{ m}^2/\text{g}$) and excellent thermal and electrical conductivity, enables the controlled loading and release of significant amounts of nutrients (22). Carbon nanotubes with high aspect ratio (up to 1000) and hollow cylindrical structure are able to penetrate the plant cell wall and can act as smart carriers for nutrients (26). Carbon quantum dots with dimensions of about 10 nm, low toxicity and unique fluorescence properties are a good option for simultaneous detection and delivery of micronutrients (33). These nanocarriers, with the ability to be surface-modified with various functional groups (such as carboxyl, amine, and hydroxyl groups), allow for selective binding and controlled release of nutrients in response to environmental stimuli such as soil pH and plant enzymes (50). The unique properties of these materials increase the efficiency of nutrient uptake by plants by up to 50% and significantly reduce nutrient losses (51).

2.1. Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) are hollow cylindrical structures composed of sp^2 -hybridized carbon atoms arranged in a hexagonal lattice. These nanostructures exist in two main types: single-walled (SWCNTs) and multi-walled (MWCNTs) (26). SWCNTs consist of a single layer of carbon atoms with a diameter of 0.4–2 nm, whereas MWCNTs consist of several concentric layers with an interlayer spacing of about 0.34 nm (59). This unique structure gives these materials extraordinary tensile strength (up to 100 times that of steel) and remarkable flexibility, which are of great importance for agricultural applications.

CNTs have several exceptional properties that make them ideal candidates for nutrient delivery. In terms of electrical conductivity, SWCNTs can exhibit metallic (high conductivity) or semiconducting behavior, depending on their chirality (44). This property is effective in facilitating electron transport in plant metabolic processes. In terms of active surface area, CNTs with high specific surface area (about $50\text{--}1315 \text{ m}^2/\text{g}$) are capable of absorbing and retaining significant amounts of nutrients (65). Studies have shown that this feature can increase nitrogen retention capacity by up to 40%. In agricultural applications, CNTs are used as smart carriers for the delivery of nitrogen and plant hormones. Studies have shown that nanotubes functionalized with carboxyl groups can increase nitrogen uptake efficiency by 30–50% compared to conventional methods (35). These nanostructures are also capable of transporting plant growth hormones such as auxin and gibberellin to target tissues, leading to improved root growth and increased resistance to environmental stresses (31). The mechanism of action involves the penetration through cell wall pores and the gradual release of nutrients in response to physiological conditions of the plant.

2.2. Graphene (G) and Graphene Oxide (GO)

Graphene, the first two-dimensional material discovered, is composed of a single layer of sp^2 -hybridized carbon atoms arranged in a hexagonal lattice. This structure has led to exceptional properties including high mechanical strength (130 GPa), excellent electrical conductivity

($\sim 10^6 \text{ S/m}$), and very high specific surface area ($2630 \text{ m}^2/\text{g}$) (22). Graphene oxide (GO) exhibits improved water solubility and biocompatibility by introducing oxygen-containing functional groups (hydroxyl, epoxy, and carboxyl) into the graphene structure (20). These properties make GO an ideal choice for agricultural applications. Graphene and GO have high loading capacities for nutrients due to their sheet structure and surface functional groups. Studies show that GO can retain up to 15 wt% nitrogen and 12 wt% phosphorus (29). The release of these nutrients is pH-dependent; So that at acidic pH (rhizosphere conditions), carboxyl groups are protonated and nutrients are released. Also, increasing the temperature to 35°C can increase the release rate by 30%, which is compatible with the metabolic needs of plants under different conditions (63).

The use of graphene and GO in nutrient delivery systems leads to significant improvements in water and nutrient uptake. Research has shown that these nanomaterials can:

- Increase water retention capacity by up to 40% (1)
- Improve nitrogen uptake by up to 50% and phosphorus by up to 45% (36)
- Increase the permeability of the cell membrane for ion uptake (12)

These effects are achieved through various mechanisms, including increasing root surface area, improving the activity of uptake enzymes, and changing the physicochemical properties of the soil.

2.3. Carbon Dots (CDs)

Carbon dots (CDs) are carbon nanoparticles with dimensions less than 10 nm, produced through green synthesis methods using plant precursors such as leaf extracts, fruits and agricultural wastes (7). This environmentally friendly method offers several advantages, including low cost, low toxicity and the possibility of controlling the photochemical properties of carbon dots (2). Studies have shown that carbon dots synthesized from plant sources contain various functional groups (amine, carboxyl and hydroxyl), which increase their biocompatibility and solubility in biological systems (54).

These nanoparticles, with enzyme-like functions, reduce oxidative stress and extend the lifespan of chloroplasts, which has led to improved plant growth by up to 40% *in vitro* (13).

Carbon dots are ideal carriers for micronutrients due to their small size and high active surface area:

- Capable of simultaneous loading of iron, zinc, and copper with 85–95% efficiency (25)
- Increased micronutrient uptake by up to 50% compared to conventional methods (45)

These features, together with low toxicity, make carbon dots a prime option for addressing nutritional deficiencies in plants.

3. Smart Carbon Nanocarriers: A New Evolution in Plant Nutritional Stress Management

In the last five years, significant progress has been made in the development of plant stress-responsive carbon nanocarriers. The most notable of these innovations include the design of smart nanostructured systems based on graphene and functionalized carbon nanotubes that are capable of detecting and responding to biomarkers associated with iron deficiency and other nutritional stresses (55). These advanced nanocarriers utilize multiple mechanisms: (a) nanoscale sensors that detect the concentration of iron ions in the rhizosphere with a sensitivity of 0.1 μM (46), (b) controlled-release systems that release up to 90% of chelated iron in response to a decrease in pH caused by iron deficiency (34), and (c) nanoporous structures that increase the iron loading capacity by up to 25 mmol/g (47). Field studies in wheat fields have shown that the use of these technologies can improve iron uptake efficiency under stress conditions by up to 75% and simultaneously increase crop yield by up to 40% (3). Also, the integration of these nanocarriers with machine learning technologies to optimize the timing and dose of nutrient release is a revolutionary step towards precision agriculture (17).

4. Combining Carbon Nanocarriers with Biopolymers: Reduce Toxicity and Increase Efficiency

In recent years (2020-2025), combining carbon nanocarriers with natural biopolymers such as chitosan has been considered as an innovative strategy to reduce toxicity and improve the performance of these nanocarriers. Chitosan is considered an ideal option for coating carbon nanocarriers due to its unique properties, including high biocompatibility, biodegradability, antimicrobial properties, and ability to bind to various functional groups (14). Studies have shown that coating carbon nanotubes with chitosan can reduce their cytotoxicity by up to 70% and, at the same time, increase the loading capacity of nutrients such as nitrogen and phosphorus by up to 40% (27). The mechanism of this effect is through the formation of hydrogen bonds between the hydroxyl and amine groups of chitosan with the functional groups on the surface of carbon nanocarriers, which leads to the creation of stable structures with reduced toxicity (23). Chitosan also improves plant resistance to environmental stresses by inducing the plant defense system and increasing the production of phytoalexins (10). Recent field experiments have shown that the use of these hybrid nanocarriers can increase crop yields by up to 35% while minimizing negative effects on the soil microbiome (60).

5. Computational Methods and Models in the Design of Carbon Nanocarriers

In recent years, computational models, especially molecular dynamics (MD) simulations, have played a transformative role in the design and optimization of carbon nanocarriers. Studies have shown that multiscale simulations can predict the behavior of nanocarriers in interactions with nutrients and biological systems with

an accuracy of 0.1 nm (38). In particular, MD simulations, using advanced software such as GROMACS and LAMMPS, have enabled the analysis of the dynamics of hydrogen bonds between functional groups of carbon nanocarriers and nutrient ions such as nitrate, phosphate, and iron (64). This computational approach has led to the design of a new generation of smart nanocarriers that can exhibit optimal release behavior under different environmental conditions (such as pH and temperature changes) (8). The results of these simulations show that modifying the surface of nanocarriers with specific functional groups can increase the efficiency of nutrient uptake by up to 40% while simultaneously reducing cytotoxicity by up to 60% (19). Also, molecular dynamics modeling has predicted the ecological effects of these nanocarriers on the soil microbiome and plant root systems with high accuracy (52). These computational advances pave the way for the development of fourth-generation nanocarriers with self-learning capabilities and dynamic adaptation to environmental conditions (62).

6. Advanced Mechanisms of Nutrient Delivery to Plants Using Carbon Nanocarriers

Carbon nanocarriers have revolutionized nutrient delivery systems by utilizing multiple mechanisms. These nanocarriers mainly operate through three main pathways: (a) penetration through the cell wall and plasma membrane, (b) active transport by membrane proteins, and (c) endocytosis mediated by chelators (49). Studies have shown that carbon nanotubes with a diameter of less than 5 nm can penetrate directly through cell wall pores (approximately 20–50 nm) (35). In contrast, larger particles are taken up by endocytosis mechanisms, in which the nanocarriers, after binding to cell surface receptors, are surrounded by membrane vesicles and transported into the cell (24). After the nanocarriers are delivered into the cell, the release of nutrients depends on the functional groups of the nanocarrier.

Nanocarriers functionalized with carboxyl and amine groups undergo structural changes and release nutrients at the acidic pH of the rhizosphere (5.5–6.5). For example, functionalized graphene oxide at pH=5.5 releases up to 80% of its load (5). Nanocarriers containing azo groups undergo bond breakage upon exposure to visible light (400–700 nm) and release their cargo. These systems have shown up to 70% release efficiency under controlled light conditions (68). Root-secreted enzymes such as phosphatases and esterases can hydrolyze ester bonds in nanocarriers. Designing nanocarriers responsive to specific enzymes allows for selective release of up to 90% (56).

The use of these smart systems results in: a 40–60% increase in nitrogen use efficiency (32), a 50–70% reduction in nutrient leaching (15), a 30–45% improvement in root growth under drought stress conditions (4), and a 25–35% increase in leaf chlorophyll content (9).

To understand the mechanisms of nanocarrier penetration and nutrient release, microscopic and fluorescence techniques and molecular imaging are used.

These techniques allow for direct observation of nanocarriers in the cell wall, investigation of nanocarrier distribution on the cell surface, measurement of interaction forces between nanocarriers and the cell wall, 3D imaging of the distribution of labeled nanocarriers in plant tissues, study of nutrient release dynamics with nanosecond time resolution, and precise identification of nanocarrier binding sites with single-molecule sensitivity (43, 67).

7. Key Challenges and Limitations in the Application of Carbon Nanocarriers in Agriculture

Despite the high potential of carbon nanocarriers in improving nutrient delivery to plants, several major challenges have prevented the widespread commercialization of this technology. The first concern is the potential toxicity of these nanoparticles, as studies have shown that carbon nanotubes with a diameter of less than 10 nm can induce oxidative stress in plants and disrupt the activity of key enzymes such as superoxide dismutase. On the other hand, the high production costs and the need for advanced technologies for the controlled synthesis of these nanocarriers have made industrial scalability difficult. The third challenge is the lack of comprehensive regulatory frameworks to assess the safety of these nanoparticles, as international organizations such as EPA and EFSA have not yet set specific standards for the use of carbon nanocarriers in agriculture. There are also concerns about the cumulative effects of these nanoparticles in the food chain and their long-term effects on soil health. To overcome these challenges, strategies such as surface modification of nanocarriers with biopolymers, development of low-cost synthesis methods, and formulation of standardized risk assessment protocols have been proposed (42). Recent studies show that the use of chitosan coatings can reduce the toxicity of carbon nanocarriers by up to 70%, while maintaining the efficiency of nutrient delivery (40).

8. Conclusion and Future Prospects

Carbon nanocarriers, with their unique capabilities, have revolutionized nutrient delivery systems to plants. Recent studies have shown that this technology can increase fertilizer use efficiency by up to 60% while simultaneously reducing environmental impacts by up to 50%. For the future, the development of multifunctional nanocarriers with the ability to simultaneously release nutrients, growth hormones, and plant protective agents is a research priority. Integrating artificial intelligence and machine learning in the design of customized nanocarriers will allow for the optimization of key parameters such as size, surface charge, and release dynamics. Future research should also focus on better understanding nanocarrier-plant-soil interactions and developing comprehensive safety standards. By addressing existing challenges, carbon nanocarriers have the potential to become a key tool in sustainable agriculture and global food security.

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